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PLENARY LECTURES
Marine mercury cycling in a changing environment
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We are mostly exposed to mercury in the form of methylmercury, when we eat fish from our oceans. The Minamata Convention aims to protect human health from the adverse effects of mercury via the reduction of anthropogenic inorganic mercury releases. To understand the efficacy and time-scales of reduced mercury emissions on fish methylmercury levels, we must precisely quantify the amount of anthropogenic Hg in the ocean and fully understand the drivers controlling methylmercury production. In this talk I will address the two aspects of environmental change likely to impact the marine mercury cycle in the future: reduced anthropogenic inorganic mercury emissions and changing climate. Mercury is one of the least concentrated elements in the ocean and measurements remain a challenge today. This makes it difficult to precisely quantify the amount of mercury in the ocean, and to estimate how much anthropogenic mercury we have added. I will briefly address the technical issues and show perspectives for marine mercury and mercury species measurements. Several lines of independent evidence speak in favor of in situ methylmercury production in oxic seawater: (1) recent large scale oceanographic expeditions find subsurface methylmercury maxima in every ocean basin; (2) incubation experiments with isotopically labeled mercury spikes show significant in situ mercury methylation in oxic seawater; (3) mercury stable isotope signatures of marine fish indicate that 60-80% of the methylmercury is produced in open ocean subsurface waters; (4) carbon stable isotopic signatures of fish methylmercury have a clear marine imprint, suggesting again in situ methylmercury production in the open ocean. A major breakthrough has been made with the discovery of key genes, that control mercury methylation in anaerobic Hg methylators. The hgcAB genes have been found in nearly all anaerobic environments and sea ice, yet only at very low abundances in oxic open ocean waters. The question of “who” methylates mercury in the open ocean remains to be answered. I will review the current state-of-the-art of the marine biogeochemical Hg cycling, and try to give ideas for future research.

Terrestrial mercury cycling in a changing environment
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In this plenary talk, I will discuss recent advances in terrestrial mercury research and provide an outlook on emerging questions associated with terrestrial mercury cycling in a changing environment. Soils contain the largest pool of mercury at the Earth’s surface. With the expected decline in anthropogenic mercury emission under the Minamata convention, the fate of this terrestrial mercury will play a central role in how fast freshwater and marine biota will recover from anthropogenic mercury pollution. The dual role of vegetation and soils in drawing and storing atmospheric mercury and at the same time releasing it to aquatic ecosystems or back to the atmosphere makes it critical to understand how terrestrial ecosystems react to environmental changes. Over the last years increasing evidence, in particular from mercury isotope fingerprints, suggests that terrestrial vegetation acts as a pump for atmospheric mercury. The uptake of atmospheric mercury by vegetation appears to be a major driver of mercury storage in soils, seasonal variations in atmospheric mercury concentrations and mercury transfer to aquatic ecosystems. Climate change has a broad impact on terrestrial ecosystems, which in turn affects terrestrial mercury cycling. Plant growth increased over the last decades driven by CO2 and nitrogen fertilization and may have led to an increase in the plant mercury pump and therefore in deposition to terrestrial surfaces. Other phenomena such as permafrost thaw, drought or deforestation however may release large amounts of mercury into aquatic ecosystems or the atmosphere and thereby counter-act efforts in curbing anthropogenic mercury emissions. Understanding the relative importance of these processes and predicting how they will evolve in the future poses a great challenge for research and policy making.

The microbiome: modulating methylation in the environment and biota
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(1)Johns Hopkins University

Our concepts of mercury as a global pollutant are largely shaped by our knowledge of the complex relationships and transitions of mercury from inorganic to organic species (WHO). These transitions not only condition environmental fate and transport but also ecotoxicity as well as toxicity to humans is also defined in large part by mercury speciation. In addition, research on individual susceptibility has been linked to specific human genes (Basu). Responses to mercury exposures are based on the standard toxicological model of ADME in which the critical stages are arrayed in a process beginning with external exposure, absorption of an internal dose, delivery to target organs, metabolism, excretion. This model was expanded to include external exposure and more defined stages of organ and organism response but the basic ADME model has been maintained with all stages after absorption assumed to take place with the exposed organism (NRC). In 2012, we proposed that this concept requires revision to incorporate the new science of the microbiome. At that time, there was compelling evidence that microbiomes in the environmental and the human gut were capable of methylating and demethylating arsentic and basevi on experimental evidence in vitro and in vivo (Dietert and Silbergeld). Since then, further work has shown that the mammalian gut microbiome can activate procarcinogens, de-activate pharmaceuticals, and alter other substances. It has long been known that environmental microbiomes may possess bacteria that methylate and demethylate mercury. Additional evidence now indicates that as with arsenic, bacteria within the human gut microbiome possess the same metabolic pathways to methylate and demethylate mercury. The implications of these findings are important for several reasons: (1) alter risk assessments for mercury based on specification; (2) explain population or individual differences in outcomes related to mercury based on differences in gut microbiomes in addition to human genomes (Rodriguez); (3) present opportunities for preventing toxicity through regulation of host microbiomes.

Mercury reduction from power and industry – how much is possible?
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Coal combustion is a major source of mercury emissions to the atmosphere globally and this sector is specifically targeted under the Minamata Convention. Unlike sources such as small-scale gold mining, stationary coal combustion sources are easy to identify and quantify. Since that time, further work has shown that the mammalian gut microbiome can activate procarcinogens, de-activate pharmaceuticals, and alter other substances. It has long been known that environmental microbiomes may possess bacteria that methylate and demethylate mercury. Additional evidence now indicates that as with arsenic, bacteria within the human gut microbiome possess the same metabolic pathways to methylate and demethylate mercury. The implications of these findings are important for several reasons: (1) alter risk assessments for mercury based on specification; (2) explain population or individual differences in outcomes related to mercury based on differences in gut microbiomes in addition to human genomes (Rodriguez); (3) present opportunities for preventing toxicity through regulation of host microbiomes.

The challenge of mercury reduction is often more economic or political than technical. Whilst many western economies are starting to turn their back on coal, emerging economies may prioritize energy security over sustainability and see coal as an affordable option for decades to come. It is possible for these regions to minimize emissions of pollutants, including mercury, whilst transitioning to cleaner energy options. For this to happen, countries must work together to share experiences and expertise. Funding will have to be mobilized in regions with financial limitations.
ORAL ABSTRACTS

Monday 9th September 2019
1.1A Atmospheric mercury cycling and transformations: Insights from measurements and models

M.O.1.1A-1

SUBSTANCE FLOW ANALYSIS FOR MERCURY IN POLAND FOR YEAR 2016

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Summary: Substance flow analysis (SFA) is a useful tool for providing environmental policy. It shows main pollutant emissions to air, water and soil, as well as flows between environmental compartments. Due to official national inventory for 2016 coal and lignite combustion in the energy sector is a main source of mercury emission to the atmosphere in Poland (5.1 Mg/year) before other industrial sectors (4.2 Mg) and residential sector and commercial plants (0.9 Mg). Another sources of emission to air was estimated by author; from use of mercury-containing products based on model for distribution and emission (0.8 Mg) and from dental practice and bodies cremation (0.3 Mg). From mercury load 11.5 Mg emitted to air, part (7.8 Mg) is deposited to soil inside Poland. Due to E-PRTR data for 2016, reported mercury releases and transfers to water in Poland was 0.97 Mg, mainly from large and medium industrial facilities (0.91 Mg) and also from urban waste water treatment plants (0.06 Mg). Lack of amalgam separators was important source of mercury in urban waste waters. Sewage sludge from urban WWTPs is later source of mercury emission to soil in agriculture (0.31 Mg). Mercury discharges to water and soil from dental amalgam in buried bodies was estimated on level 0.16 Mg. Significant flow of mercury to municipal wastes is associated with use of mercury-containing products (6.6 Mg mercury in batteries, light sources and other electrical and electronic equipment launched to the market in year). Load of 1.7 Mg of mercury is transferred to municipal landfills, next 3.7 Mg is re-collected and stored safely. Another significant mercury flow in wastes (10.0 Mg annually) originate from dental practice. Majority of mercury contained in dental amalgam is re-collected in dental clinics and stored safely. However load 2.9 Mg is transferred to infectious medical wastes and later incinerated in industrial plants and stored safely.

M.O.1.1A-2

TRACE OF PM2.5 SOURCES BY USING MERCURY ISO-TOPE IN TEN MEGACITIES OF CHINA

LIU, Chen¹; FU, Xuewu¹

Both PM2.5 and total gaseous mercury (TGM) serve as an important atmospheric pollutant in urban areas and pose a health risk to human. Because PM2.5 and PBM are strongly bounded, and different mercury isotope signature could be observed from different source. So mercury isotope can be used as a tracer for PM2.5 sources. TGM and particulate bound mercury (PBM) were collected in summer and winter for ten megacities of China including: Shanghai, Beijing, Wuhan, Chengdu, Guiyang, Shijiazhuang, Lanzhou, Jinan, Guangzhou, Zhengzhou. Two sampling sites were selected including urban and suburban stations for each of the city. Diurnal TGM and PBM concentrations were 2.89±1.28 ng·m⁻³, 270.05±270.52 pg·m⁻³ (1SD) in summer and 2.93±1.52 ng·m⁻³, 123.66±33.67 pg·m⁻³ in winter, respectively. Mass-independence fractionation (MIF) of TGM were Δ199Hg= -0.09±0.07‰ (25D, n = 28) in winter and -0.04±0.05‰ (25D, n = 30) in summer. Only minor seasonal variations were observed asΔ199Hg is 0.05‰ negative than summer. This may cause by different anthropogenic sources as coal heating contribute much mercury in winter which gave much negative Δ199Hg value by fossil fuel burning. Northern cities have significantly higher (t-test, P<0.05) MIF ofΔ199Hg (-0.09±0.06‰, 25D, n = 35) than southern cities (-0.03±0.04‰, 25D, n = 23) due to their difference in energy and industrial structures. Because coal-fired power plants are the major mercury source of northern area whereas more mixed industrial source in the south such as chemical plants and ore mining. Positive matrix factorization (PMF) results, by making use of the combined data sets of total gaseous mercury (TGM), particular bound mercury (PBM), OC, EC, hydrophilic ions, trace elements and meteorological parameters, suggested that atmospheric combustion source, crustal material source, secondary pollution source (>80%) is the most important sources of PM2.5 in these cities. The research could guide the government to take better policies to control urban pollution sources.

M.O.1.1A-3

UPDATED GAS-PARTICLE PARTITIONING MODEL FOR ATMOSPHERIC OXIDIZED MERCURY

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(1) Tsinghua University, China

Gas-particle partitioning of reactive gaseous mercury (RGM) is one significant process impacting mercury transportation in the air. Multi-pollutants observation in three Chinese sites indicated gas-particle partitioning coefficient (Kp) is impacted by surrounding mercury emissions, temperature, relative humidity and particle composition (mainly water content (AWC), Na+, Cl-). By using Generalized Additive Model, functions describing the relationship between Kp and temperature, water content under different relative humidity were developed. When relative humidity is lower than 60%, Kp is mainly dominated by temperature according to the regression analysis, lg(1/Kp)=−3021(1/T)+11 (R²=0.43). Otherwise, Kp is under the joint impact of temperature, particle composition and relative humidity temperature. However, the value of Kp finally relied on temperature and water content based on Akaike’s Information Criterion (AIC) and R² values for each analysis. lg(1/Kp)=−2302(1/T)+300g(AWC)+12 (R²=0.65). In both conditions, R² value of the regression model will be improved by 0.5-1.2 when excluding the point under the impact of emission sources, because the model has not accounted for different mercury speciation profile of the emitted sources. The use of local observation data to parameterize RGM partitioning in the proposed models potentially improves the estimation of mercury cycling in chemical transport models and elsewhere.

M.O.1.1A-4

MERCURY EMISSIONS AND POSSIBLE AIRBORNE PHOTOCHEMICAL REDUCTION OF OXIDIZED MERCURY OBSERVED DURING AIRCRAFT MEASUREMENTS IN THE EMISSIONS PLUMES OF ALBERTA OIL SANDS FACILITIES

MCLAGAN, David¹; STEFFEN, Alexandra²; STUPPLE, Geoffrey W.²; WHEELER, Michael²; LI, Shao-Meng²; WENTZELL, Jeremy J.B.²; LIG-GIO, John²; DARLINGTON, Andrea²; HAYDEN, Katherine²
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(2) Environment and Climate Change Canada

In 2018, Environment and Climate Change Canada (ECCC) conducted an aircraft monitoring campaign of the industrial mining facilities of the Athabasca Oil Sands in Alberta, Canada. The National Research Council of Canada’s Convar-580 was equipped with an array of atmospheric gas and particulate contaminant and meteorological instruments for the characterization of emissions and chemistry processes occurring directly in and around emissions plumes of these facilities. Among these instruments was a Tekran 2537X setup to measure gaseous elemental Hg (GEM). The system was fitted with a 0.45µm Polytetrafluoroethylene (PTFE) filter and a soda-lime trap to remove gaseous oxidized mercury (GOM) and particulate bound mercury (PBM). 30 flights were completed in total and included emissions “box” flights (multi-height, box flight paths circumnavigating an entire facility), used for determining emissions strength, and “transformation” screen flights (a series of
multi-height screens that track the plume at increasing distance from the facilities), used to determine contaminant concentration changes in ageing plumes associated with photochemistry, dilution, and deposition. Significant positive correlations between GEM and primary pollutants (e.g. black carbon, ultra-fine particulate counts, SO2, NOx) observed in box flights showed there were minor, but detectable emissions of GEM being released from the facilities. GEM emissions were strongest at In Situ (steam-assisted gravity drainage) facilities, which is a heat-driven extraction process used for deeper bitumen deposits that may have the tendency to liberate more mercury from bitumen than surface mines. Gaseous oxidized mercury (GOM) or particulate bound mercury (PBM) measurements were not made on these flights, but these species make up a much higher proportion of atmospheric mercury near industrial sources. Thus, considering the observed GEM emissions, we could also expect emissions of GOM and PBM. Transformation flights generally showed increasing GEM concentrations on the edges of emissions plumes and as the plume aged. The positive correlation with ozone, a tropospheric contaminant generated photochemically, was highly significant during these flights, while primary pollutants were significantly, but inversely, correlated. A possible mechanism for the elevated GEM concentrations observed on plumes edges and in aged plumes at greater distance from the facilities is the photochemical reduction of GOM and/or PBM to GEM. This process is an expected reaction mechanism in surface waters, yet until recently it was not thought to occur in the atmosphere. These results add to an emerging body of research that suggest photochemical generation of GEM could also be an important atmospheric process.

M.O.1.1A-6

PHYTOMANAGEMENT OF CHLOR-ALKALI TAILINGS DUMPS USING TREES: TRANSFER OF HG, PLANT PRODUCTIVITY AND IMPACT ON MICROBIAL COMMUNITIES

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Hg is a contaminant classified within the quantitatively most important pollutant groups known as trace elements (TEs). It is highly persistent in the soil environment and is classified as a “priority hazardous substance” by the Agency for Toxic Substances and Disease Registry (ATSDR) due to its toxicity, mobility, and long residence time in the atmosphere. Here we have explored the fate of Hg within tree plantation and its accompanying vegetation, as well impact of Hg on microbial communities at a chlor-alkali tailings dump located in the North East of France. We first demonstrated that most of the Hg detected in the aboveground parts of Salix Aurorea trees collected at that site had entered the poplar leaves through exclusively through an atmospheric pathway. We further characterized aboveground and belowground microbial populations in the environment of planted trees. Aboveground and belowground poplar habitats host completely different fungal communities, as highlighted by the core microbiome of the four habitats that represent only reduced to 5.9% of the total OTUs. Leaf and stem habitats were characterized by few dominant OTUs such as those from the Dothideomycete class producing mutual exclusion with other OTUs. Aureobasidium pullulans, one of the dominating OTUs, was further isolated from the leaf habitat, in addition to Nakazawaea populi species, which were found to be Hg resistant. We also studied the accompanying vegetation under the popular trees that can be valorized within industrial processes and the transfer of Hg into this vegetation, with nettle as the dominant species. The nettle biomass yields are lower than or equal to the lower range of the values obtained when using traditional nettle crop cultivation practices. The properties obtained in this study are equal to or better than those of hemp and flax and make this nettle biomass very promising for composite application. Altogether, these findings provide an improved point of reference for research on vegetation, associated microbes and insects in the phytomanagement of chlor-alkali tailings dumps.

M.O.1.1A-5

MULTI-CENTURY RECONSTRUCTION OF ATMOSPHERIC HG(0) TRENDS IN NORTHERN CANADA USING TREE-RINGS.

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The atmospheric Hg(0) reservoir plays a key role in the global Hg cycle, facilitating long-range transport, and contributing a significant input of Hg to many ecosystems. An improved quantitative understanding of the atmospheric Hg(0) pool and historical anthropogenic emissions is key to be able to predict how regulatory action (i.e., the Minamata Convention on Mercury) will affect Hg concentrations in various environmental compartments and foodwebs, and thus exposure risk in human populations. Due to the limited temporal duration of the instrumental atmospheric Hg record, natural Hg archives such as lake sediments, peat cores and ice cores have been used to infer long term temporal trends in atmospheric Hg(0) concentrations and Hg deposition. Tree-rings have recently been suggested as potential archives of past atmospheric Hg(0). Tree-rings have numerous advantages over other archives, for example, they are annually resolved with excellent dating control, span centuries to millennia, and provide extensive spatial coverage over large areas of Earth’s surface. We present an annually-resolved tree-ring Hg record from the Klondike Goldfields, where the gold-Hg amalgam method was used to recover fine gold from placer ore, to demonstrate that Hg concentrations in white spruce tree rings are consistent with the history of local mining activity. Given that white spruce tree-rings faithfully record atmospheric Hg(0), we use this approach to reconstruct temporal trends in atmospheric Hg(0) spanning from 1600 AD to present-day, from various regions in northern Canada, including continental sites (central Yukon, northern Yukon) and coastal sites (Mackenzie River Delta, Northwest Territories). While regional differences exist in the timing of the initial increase attributed to anthropogenic emissions and the timing of maximum Hg(0), the fastest rate of increase in Hg concentrations occurs between 1850 and the mid 20th century at all sites. Furthermore, the enrichment factor in modern Hg(0) relative to the pre-industrial baseline estimated from tree rings appears to be somewhat lower compared to enrichment factors similarly calculated from sediment and peat cores. Important methodological considerations such as replication and the need to calculate adjusted Hg concentrations to account for systematic inter-tree differences will also be discussed. Overall, tree-rings show tremendous promise for various applications such as validating emission inventories and refining atmospheric Hg models.

M.O.1.3A-1

MERCURY CYCLING IN THE PACIFIC OCEAN AS REVEALED BY MERCURY STABLE ISOTOPES

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1.3A Regional and local scale stable isotope studies in mercury biogeochemical cycling and bioaccumulation
The photochemical decomposition of methylmercury (MeHg) in the surface ocean is an important pathway in the biogeochemical cycle of the global pollutant mercury (Hg), because it limits the amount of Hg available for bioaccumulation in marine organisms. Despite the crucial importance of this pathway there are many unanswered questions about photochemical reaction mechanisms and the relative importance of various MeHg species that lead to Hg incorporation into the food web. Numerous studies have shown that the dominant cause of odd mass independent isotope fractionation (MIF) of Hg in marine foodwebs is due to the partial photochemical decomposition of MeHg, with the residual MeHg containing a distinct MIF fingerprint incorporated into low trophic level organisms and bioaccumulated without additional MIF. Based on this understanding we investigated the photochemical degradation, uptake, and bioaccumulation of MeHg using Hg stable isotope analyses of various components of the marine food web in the Central Pacific Ocean. The isotopic signatures of MeHg from photochemistry experiments, measurements of marine particles, zooplankton, and pelagic fish demonstrate that there are two important photochemical degradation pathways that directly impact the pool of MeHg available for uptake into the marine foodweb. We will discuss the relationship between the isotopic composition of marine MeHg subjected to photochemical decomposition and the Hg stable isotope signatures preserved in marine particles, zooplankton, and fish. These Hg isotopes measurements shed light on abiotic and biotic production and degradation of MeHg throughout the marine water column, and emphasize the importance of marine particles and zooplankton in the vertical transport of Hg.

M.O.1.3A-2

USING MERCURY STABLE ISOTOPES TO UNRAVEL METHYLmerCURY SOURCE ORIGIN AND DISTRIBUTION IN TUNA FROM THE SOUTH WESTERN PACIFIC OCEAN

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In the tropical Pacific Ocean, tuna contribute significantly to the livelihoods, food and economic security of many island nations. Tuna fisheries from the South Western Pacific Ocean (WCPO) account for a significant fraction of the world tuna catches representing a landing value of several billion US$. Mercury concentrations in bigeye (BET), albacore (ALB) and yellowfin tuna (YFT) increase in the following order BET-ALB-YFT. This species-specific pattern is assumed to reflect a relative difference of foraging depth among the three-tuna species, with YFT occupying a more epipelagic habitat compared to mesopelagic BET in the WCPO. At the species level, spatial gradients not explained by fish size have also been observed with increased mercury concentrations at southern latitudes (10S-20S) relative to the equatorial regions (0-10S), with BET exhibiting the strongest latitudinal gradient. To investigate if changes in foraging opportunities and/or differences in marine MeHg biogeochemistry and sources contribute to the geographical trends observed, mercury stable isotopes (d202Hg, D199Hg) and additional trophic tracers (d13C, d15N) were determined at high spatial resolution on YFT, ALB, and BET samples from the WCPO. Complementary samples including pelagic prey items, mollusks from local hydrothermal vents and deep sediments were also considered for analysis. Finally, high resolution MeHg oceanic profiles collected along the OUTPACE cruise will also be shown, providing an oceanographic Hg context to this study. High resolution regional Hg isoscapes (d202Hg and D199Hg) between 20N and 20S will be presented for both YFT and BET. These isoscapes exhibit significant geographical trends, ranging for d202Hg between 0.5 and 1.3 ppm for YFT and between 0.3 to 1 ppm for BET, and for D199Hg between 2.4 to 3.2 ppm for YFT, and between 1.3 to 2.5 ppm for BET, respectively. These results indicate that Hg stable isotopes in tuna vary significantly with geography. Mercury concentrations anomalies not explained by size differences among the different individuals sampled across this large oceanic region are related to spatial changes in the D199Hg/d202Hg ratio, with a stronger latitudinal gradient for BET relative to YFT. These results will be discussed in the context of spatial changes in marine Hg biogeochemistry, and with considering variations in tuna foraging ecology reflecting changes in physical oceanography across this region.

M.O.1.3A-3

ENERGY BUT MERCURY: PINNIPED CONSUMPTION INCREASES MERCURY EXPOSURE FOR THE GREAT WHITE SHARK.

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Methylmercury (MeHg) is known to have deleterious effects on the health of marine organisms. This contaminant is bioaccumulated over time and biomagnified along trophic chains. Because sharks are long-lived species at the top of food webs, they are particularly prone to MeHg contamination, potentially participating to their decline worldwide. The great white shark Carcharodon carcharias is a threatened species with some of the highest mercury (Hg) concentrations within marine top-predators, almost exclusively under the MeHg form. Subadult and adult white sharks aggregate seasonally near coastal pinniped colonies in several parts of the globe, while they spend the rest of the year in oceanic habitats. As predators themselves, pinnipeds have higher MeHg concentrations in muscle than pelagic and mesopelagic prey. However, fat can represent up to 40% of the body weight of pinnipeds and contains low Hg concentrations, mostly in inorganic form and therefore poorly bioavailable. In this context, the aim of this study was to evaluate the contribution of pinnipeds compared to pelagic and mesopelagic prey in trophic mercury exposure for the great white shark. For this purpose, 60 white sharks and 10 northern elephant seal Mirounga angustirostris were sampled in a Northeastern Pacific aggregation site (Guadalupe Island, off the coasts of Mexico). Shark subdermal tissues and seal hairs were analyzed for total mercury concentration (THg) and isotopes of Hg, carbon (δ13C) and nitrogen (δ15N). Our results were compared to the values of pelagic and mesopelagic organisms already published in the same area. White sharks had δ199Hg values similar to both mesopelagic squids and the northern elephant seals, but δ202Hg values closer to the elephant seals. Moreover, a positive correlation was found between THg and δ202Hg values as well as between THg and δ13C or δ15N values, reflecting an increase in mercury contamination with the consumption of elephant seals. Our study thus revealed that (i) white sharks are mainly feeding on pinnipeds near aggregation sites and to a lesser extent on mesopelagic squids, (ii) pinnipeds are the main source of mercury for sharks at the population scale during the coastal season, (iii) pinniped consumption increases mercury exposure for sharks at the individual scale. Overall, this work demonstrates that mercury isotopes are relevant tracers of both diet and mercury source, and provide a better understanding of the trophic exposure to a major contaminant during the migratory life cycle of an iconic marine predator.

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INVESTIGATING ENVIRONMENTAL ORIGINS AND BIOACCUMULATION OF METHYLMERCURY IN A SUB-ARCTIC ESTUARY

LI, Miling; KIRK, Jane; Yin, Runsheng; GLEASON, Amber; KRABBENHOF, David; SCHANTUP, Amina; SUnderLAND, Elsie

Methylmercury (MeHg) is a potent toxicant that can lead to adverse health effects in human and wildlife. The primary route of MeHg exposure for most people is seafood consumption. Northern indigenous populations are particularly at risk of high exposures to MeHg due to their traditional diets primarily composed of fish and marine mammals. To better understand the mercury (Hg) biogeochemical cycling in northern coastal ecosystems that provide important hunting and fishing territory, we measured mercury concentrations, stable isotopes of Hg (δ202Hg, Δ199Hg, Δ200Hg, and Δ201Hg), carbon (δ13C), and nitrogen (δ15N) of a variety environmental samples from a large subarctic estuary (Lake Melville), including plankton, shellfish, fish, seals, and humans. We compare Hg isotopic composition of hair samples from indigenous populations with those of environmental samples to further assess the environmental origins of MeHg for northern communities. Results show methylation varies across seasons and geographic locations. Mammals and humans have enriched δ202Hg values compared to their diet, probably due to the preferential demethylation and elimination of lighter Hg isotopes. The presentation will also discuss how Hg isotopes provide insight into the major environmental origins of MeHg in northern populations.

VARIATIONS OF MERCURY ISOTOPE COMPOSITIONS IN PENGUIN GUANO DEPOSITS DURING THE LITTLE ICE AGE IN ANTARCTICA

ZHENG, Wang; XIE, Zhouqing; GAO, Guang; Wang1

Penguin guano deposits are important records of penguin ecological history, providing valuable information for penguin population, dietary change, migration, and environmental changes in Antarctica. Guano deposits are also excellent proxy of the marine cycling of trace elements, including mercury (Hg). Hg in guano is primarily transferred by penguins from the ocean in Antarctica. Previous studies on guano deposits on Ross Island revealed significant changes in Hg concentration during the Little Ice Age (LIA, ~1500-1850AD), a period characterized by colder climate, stronger katabatic winds, cooler sea surface temperature and larger polynyas (open water surface surrounded by sea ice) than today. However, it is not clear how the climate change during LIA affected the biogeochemical cycle of Hg. Here we studied Hg isotope compositions in two guano sediment cores located at Cape Bird, Ross Island (CB2) and near Zhongshan Station (RNL2), Antarctica, respectively, and investigated the potential link between Hg isotope signals and climate change. Both cores showed significant variations in Δ199Hg only at the onset of the LIA (~1500-1850AD), while different patterns. The RNL2 core showed relatively low Δ199Hg at the onset of LIA and increased gradually during 1500-1650AD, along with increases of Hg concentration and other bio-elements such as C, N, and P. In contrast, the CB2 core showed relatively high Δ199Hg during 1500-1650AD, and then decreased gradually at ~1650AD, and stayed relatively constant afterwards. Such variation of Δ199Hg is unlikely caused by changes in Hg sources because both Hg concentration and %P showed little change during 1500-1650AD, suggesting that the change of Δ199Hg at the onset of LIA was most likely caused by changes in marine photochemistry of Hg, which may have been enhanced due to increased sea surface temperature and larger polynyas.

SEABIRD HG ISOTOPIC SIGNATURES DOCUMENT INTERANNUAL CHANGING DYNAMICS OF THE HG CYCLE IN THE PERUVIAN COAST

RENEDO, Marina; POINT, David; SONKE, Jeroen; GRACO, Michelle; ECHEVIN, Vincent; DEMARCO, Herve; GUTIERREZ, Dimitri; LORRAIN, Anne; BERTRAND, Arnaud; BERTRAND, Sophie

Along the coasts of Peru, the persistent coastal upwelling system, known as the Northern Humboldt Current System, is one of the most productive of the world ocean. Covering 0.1% of the surface of the global ocean it accounts for >10% of global fisheries, with in particular the anchovy (Engraulis ringens) production. This upwelling system off Peru drives one of the most extensive and shallow oxygen minimum zones (OMZ) (upper limit at ~20–100 m). At interannual time scales, this region is mainly affected by the warm phases of the El Niño southern oscillation (ENSO), which result in the reduction of the upwelling efficiency, reducing drastically nutrient inputs to the surface layers. Under these conditions, primary productivity is reduced, impacting the whole ecosystem up to fish and top predators. ENSO is also suspected to influence the Hg cycle, in particular methylmercury production and transformations. The Peruvian coastal region is therefore an interesting case study to explore the potential evolution of the global marine Hg given the predicted expansion of oceanic OMZ in a warming ocean. Because Hg isotopic signatures are a powerful tool to investigate Hg sources and reactivity within marine compartments, we analyzed Hg isotopic composition in time series of seabird blood samples, which are widely used as effective bioindicators of Hg contamination of the marine food webs. Blood samples from two seabird species, the Peruvian boobies (Sula variegata) and the Guanay Cormorants (Leucocaro bougainvillian), were collected in the breeding period from 2009 to 2016. Both seabird species shared similar temporal patterns between mass independent (Δ202Hg) and fractionation (Δ199Hg) signatures, suggesting interannual changes in Hg biogeochemical dynamics rather than strong trophic shifts (that were assessed by simultaneous δ15N analyses). The most significant interannual variations were observed for Δ199Hg values (1.85±0.02 to 2.57±0.04 %), suggesting important interannual differences in the extent of Hg photochemical processes. Variable Δ202Hg values were also observed between years (1.00±0.21 to 1.36±0.11 %), suggesting different extent of methylation/demethylation processes and/or an influence of changing vertical mixing of different Hg sources. Overall, this work demonstrates that Hg isotopic variations recorded in seabird samples help to explore the link between the Hg cycle and climatic factors influencing the ocean dynamics of the Humboldt upwelling system and its impact on the epipelagic communities of the Peruvian coast.
M.0.1.8-1

THIOL FUNCTIONAL GROUPS ASSOCIATED WITH NATURAL ORGANIC MATTER AND BACTERIAL MEMBRANES: CONCENTRATIONS AND THERMODYNAMIC STABILITIES OF COMPLEXES FORMED WITH MERCURY(II)

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Thiol functional groups associated with natural organic matter (NOM-RSH) and bacterial cell membranes (Mem-RSH) play an important role in bioavailability, cellular uptake and biotic transformations of Hg(II). Thermodynamic stability constants (log K) of Hg(II) complexes formed with thiol groups of Suwannee River NOM (2R101N) and membranes of the Hg(II) methylating bacteria Geobacter sulfurreducens PCA and Desulfovibrio desulfuricans ND132 were determined by competitive ligand-exchange. Cysteine (Cys) was used as the competing ligand and the equilibrium concentration of the formed Hg(Cys)2 complex was determined by a mass spectrometry. Side-reactions between Cys and NOM, as well as the potential formation of mixed ligand complexes, Hg(Cys)(NOM-RS)2, were examined by isotope labelled 13C-Cys. To determine concentrations of NOM-RSH and Mem-RSH functional groups, and to characterize structures formed with Hg(II), we used Hg LIII-edge EXAFS. We determined the concentration of thiol groups in Suwannee River NOM and in membranes of G. sulfurreducens and D. desulfuricans to be 7.5 ± 0.4, 121 ± 12 and 144 ± 5 μmol g−1, respectively. The thermodynamic stability constant (log K ± SD) for the formation of Hg(NOM-RS)2 [Hg2+ + 2RS− = Hg(NOM-RS)2] and the mixed complex structure Hg(Cys)(NOM-RS) [Hg2+ + Cys− + RS− = Hg(Cys)(NOM-RS)] was determined to be 40.0 ± 0.2 and 38.5 ± 0.2, respectively. The log K for the structure Hg(Mem-RS)2 [Hg2+ + 2Mem-RS− = Hg(Mem-RS)2] of G. desulfuricans and D. sulfurreducens was 39.1 ± 1.2 and 38.4 ± 0.9, respectively. It should be noticed that log K for Hg(Cys)2 [Hg2+ + 2Cys− = Hg(Cys)2] was set to 37.5 according to previous study; and the pKa values of RSH (here RSH denote any thiol) were set to 37.5. We characterized and quantified microbially produced Hg(LMM-RS)2 complexes (primarily with cysteine) in assays without assay medium. These compounds control the chemical speciation and understanding of the processes of bacterial uptake, reduction/oxidation and methylation of Hg(II).

M.0.1.8-2

FERMENTATIVE BACTERIA DOMINATE MERCURY-METHYLATING COMMUNITY IN THE WATER COLUMN OF A SULFATE-ENRICHED FRESHWATER LAKE

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Methylmercury is produced from inorganic mercury by microorganisms living in anoxic environments. Understanding the timing and location of methylmercury production is crucial to understanding methylmercury uptake into the foodweb. Water column methylation in freshwater lakes is a potentially critical source of methylmercury to food webs in some systems due to the volume of anoxic habitat and proximity to phytoplankton at the base of the food web, but has been studied less than methylmercury production in sediments or periphyton. Known methylating organisms are phylogenetically and metabolically diverse, but in many systems, sulfate-reducing organisms are described as primarily responsible for methylmercury production. In this study, we sought to identify likely hotspots for methylmercury production in a lake with elevated sulfate levels and to identify methylators from samples with different redox conditions using genome-resolved metagenomics.

Lake Mendota is a eutrophic, sulfate-enriched lake with a high methylmercury to total mercury ratio in the anoxic hypolimnion. We collected depth-discrete geochemical and bacterial samples throughout the stratified season. Mercury speciation profiles suggested increased methylation potential near the oxic/anoxic interface during late season stratification. To investigate the methylating community at this time point, we performed shotgun metagenomic sequencing and searched for hgcA homologs (a known marker for methylation capabilities) in the assembled contigs. We identified many hgcA sequences in the assembly that clustered with hgcA sequences from known methylators. However, the hgcA+ population was dominated by non-canonical hgcA sequences. Genomic reconstructions revealed that the hgcA+ genome bins were dominated by fermentative Verrucomicrobia, Bacteroidetes, and Firmicutes in all of our metagenomes. Desulfbacterota, most of them with the capability for sulfate reduction, were also found throughout our metagenomes, albeit at a markedly lower abundance. Methanogenic Archaea and Sulfurobacteria bins were most prevalent in high-sulfide portions of the water column. Metal-reducing Geobacter bins were rare and only identified near the oxic/anoxic interface. Using these bins, we can begin to probe how the ecophysiology of the methylation organisms serve to link biogeochemical cycles to methylmercury production. This study is further evidence that methylmercury production in high sulfate freshwater systems is not driven by sulfate-reducing organisms. Instead, the hgcA+ population is dominated by non-canonical fermentative organisms. This provides support for future studies that will further characterize the links between biogeochemical redox cycling and methylmercury production in freshwater lakes.

M.0.1.8-3

MICROBIAL BIOSYNTHESIS OF THIOL COMPOUNDS: IMPLICATIONS FOR SPECULATION, CELLULAR UPTAKE AND METHYLATION OF Hg(II)

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Cellular uptake of inorganic divalent mercury (Hg(II)) is a key step in the microbial production of neurotoxic methylmercury (MeHg). The uptake mechanisms are not identified but low molecular mass thiol (LMM-RSH) compounds play important roles. Here we show that the iron reducing bacterium Geobacter sulfurreducens produces and exports several LMM-RSH compounds to concentrations exceeding 100 nM in the assay medium. These compounds control the chemical speciation and rates for cellular uptake and methylation of Hg(II) via the formation of Hg(LMM-RS)2 complexes (primarily with cysteine) in assays with either thiol or cysteine binding compounds. It was characterized and quantified microbially produced LMM-RSH compounds during Hg(II) methylating conditions in vivo and in vitro. Our results show that Hg(II) complexes with weaker thermodynamic binding stabilities such as those of mixed ligation with LMM-RS, Cl- and OH- were
methylated at higher rates than the stronger Hg(LMM-RS)2 species. We further demonstrate that moderate differences in chemical structure of LMM-RSH compounds can cause significant differences in methylation rate for the different corresponding Hg(LMM-RS)2 complexes. We also find that high nM concentrations of certain LMM-RSH compounds promote significant increases in Hg(II) methylation via unknown mechanisms which cannot be explained by either thermodynamic modelling or chemical structure alone. Combined, our results form a refined basis for understanding Hg(II) availability for microbial methylation and elaborate on the multiple effects of LMM-RSH compounds for MeHg formation.

M.O.1.8-4

THE ROLES OF MERCURY CHEMICAL SPECIATION AND BIOLOGICAL PRODUCTION OF LOW MOLECULAR MASS THIOLS FOR METHYLMERCURY FORMATION IN BOREAL WETLANDS

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The importance of the chemical speciation of dissolved HgII for MeHg formation has been demonstrated in laboratory experiments on model systems. There is however a lack of studies investigating this relation in natural environments. In this work, we established a comprehensive chemical speciation model for HgII and determined HgII methylation rate constants, kmeth, in boreal wetland soils which have been identified as major sources of MeHg. The speciation model included HgII complexes with inorganic sulfide (S−II), polysulfides (H2Sn), thiols associated with natural organic matter (NOM−RSH) and specific low molecular mass thiols (LMM−RSH). The prediction power of the HgII model was optimized by varying stability constants of Hg−sulfide and Hg−thiol species within their published values. The concentration of NOM−RSH(aq) shows a significant correlation (p < 0.001, R2 = 0.69) with the measured HgII(aq) concentration in porewater for the samples containing low S−II(aq) concentration (<1 μmol L−1), but not for the medium and high S−II(aq) concentration (>1 μmol L−1) (p > 0.05, R2 = 0.13). Thus, it seems NOM−RSH(aq) controls the HgII solubility below, but not above, 1 μmol L−1 of S−II(aq). The modeling results suggest that in these wetland soils Hg(SH)20(aq) is the most important species for cellular uptake and methylation of HgII at sulfidic conditions of >0.4 μM H2S(aq). Eight specific Hg(LMM−RSH)2(aq) complexes were included in the speciation model and these are likely to be more important than Hg(SH)20(aq) for HgII uptake and methylation at ferruginous conditions when H2S(aq) is less than 40 nM. A significant correlation (R2=0.65, p<0.001) was observed between total concentrations of biologically produced LMM thiol compounds and kmeth. We propose that these LMM thiols are produced by anaerobic microbes, and that the correlation with kmeth is reflecting a relation between microbial activity and MeHg formation.

M.O.1.8-5

ROLES OF MICROBIAL COMMUNITIES IN REGULATING MERCURY METHYLATION IN PADDY SOILS

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Rice ingestion has been recognized as an important route of dietary exposure to neurotoxic methylmercury (MeHg) that is usually synthesized in rice paddy soils. Although certain anaerobic microorganisms are known to convert inorganic mercury (Hg) to MeHg and the discovery of a two-gene cluster hgcaAB has linked Hg methylation to several phylogenetically diverse groups of microorganisms, the prevalence and diversity of Hg methylators in microbial communities of rice paddy soils remain unclear; we also lack understanding of the role of non-Hg methylating communities in MeHg accumulation. Here, we collected 141 paddy soil samples from main rice-producing areas across China to identify the diversity of Hg methylators and associations between bacterial community composition (including both Hg and non-Hg methylators), and Hg methylation efficiency (proxy as %MeHg). Results showed that %MeHg in the paddy soils varied from 0.005 to 2.833% at a national spatial scale, which can be explained by the variations of soil microbial community composition across different areas. We show that Hg methylation communities are diverse, with iron-reducing bacteria (i.e., Geobacter) and methanogens as the dominant taxa likely involved in Hg methylation in the soil. Phylogenetic analysis also uncovered some hgcaAB sequences closely related to three novel Hg methylators, Geobacter anodireducens, Desulfuromonas sp. DDH964, and Desulfuovibrio sp. J2 in these paddy soils. Our structure equation modeling suggested a much stronger link between bacterial community composition and %MeHg, compared to the abundance of methylating gene (hgca) and edaphic properties. More importantly, random forest models suggested a more important role of non-Hg methylators in predicting variations of soil %MeHg than Hg methylators. Further analysis of microbial network revealed strong co-occurrence patterns between non-Hg and Hg methylators, suggesting their interactions may affect MeHg production in paddy soils. These findings shed new light on microbial community composition and major clades driving Hg methylation in rice paddy soils. Our work highlight the important role of both Hg and non-Hg methylating communities in predicting MeHg production in paddy fields.

M.O.1.8-6

ASSESSMENT OF MICROBIAL COMMUNITIES AND GEOCHEMICAL PARAMETERS DETERMINING THE MERCURY METHYLATION IN SUBMARINE CANYON SEDIMENTS (ATLANTIC OCEAN, SW FRANCE)

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Microbial mercury (Hg) methylation transforms the inorganic mercury (Hg(II)) to the neurotoxin methylmercury (MeHg) in anoxic marine sediments. Both geochemical parameters and microbial activities constrain the net MeHg production, and were studied in the Capbreton Canyon. Twenty-three deep sea surface sediments were investigated within the first 30 km of this Canyon. A multidisciplinary approach combining geochemical parameters (i.e. organic carbon content (OC) and grain size), Hg(II) and MeHg concentrations (by ID-GC-ICP-MS) with microorganisms' taxonomic diversity (16S DNA by MiSEQ) were investigated in all locations. Strong positive correlations have been found between geochemical parameters (OC and fine grain size) and mercury species concentrations. Both Hg(II) and MeHg levels increased in deep sea sediment, especially in the furthest location reaching 972 ng g−1 dw and 2.1 ng g−1 dw, respectively. Data showed that the MeHg proportion decreased along this canyon suggesting higher methylation production in coastal sediments. Sediment slurry incubations using mercury methylators using HgCA gene (by cloning and SANGER sequencing) were investigated in the sediments. Deltaproteobacteria, notably Desulfobulbaceae and Desulfobacteraceae, suggesting sulfate reducing bacteria were involved in the Hg methylation. The Hg methylators using HgCA gene (by cloning and SANGER sequencing) were investigated in the sediments. Deltaproteobacteria, notably Desulfobulbaceae and Desulfobacteraceae, suggesting sulfate reducing bacteria were involved in the Hg methylation. The Hg methylators using HgCA gene (by cloning and SANGER sequencing) were investigated in the sediments. Deltaproteobacteria, notably Desulfobulbaceae and Desulfobacteraceae, suggesting sulfate reducing bacteria were involved in the Hg methylation.
2.6 Communities affected by Mercury Pollution

M.O.2.6-1

THE RESPONSE OF THE DECHO FIRST NATIONS (CANADA) FOLLOWING FISH CONSUMPTION NOTICES RELEASE AND INCREASED MERCURY LEVELS MEASURED IN ENVIRONMENTAL DATA.

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The Dehcho region in the Northwest Territories, in subarctic Canada, is the land of over 3000 Dene members. Under the Dehcho First Nations (DFN) organization, Dene people aim to self-govern their region to increase the sustainability of their lifestyle so the next generations can benefit from the wealth and health of people and Lands. This objective was sought through local initiatives including the implementation of the first Indigenous protected area in Canada, the Guardian program to monitor environmental and wildlife parameters, and several research initiatives to investigate trends in environmental monitoring. Since 2014, the Government of the Northwest Territories has emitted Site Specific Fish Consumption Advice in several areas. Currently, 10 water bodies in the Dehcho are associated with advice to limit the consumption of certain fish species. The traditional diet of Dene, which was assessed in 1994 and 2016-2017, includes local fish consumption. Lake trout, the second most consumed fish in the region, is one of the species identified as having elevated mercury concentrations. The DFN initiated a program to collect long-term mercury data to understand the impact of this contaminant on the Dene lifestyle. Mercury data in water and fish, as well as complementary environmental data, are collected as part of an ongoing program facilitating community-based water monitoring: the Aboriginal Aquatic Resources and Oceans Management. Additionally, academic collaborative projects measuring mercury in traditional foods, as well as human hair, blood and urine were developed. These initiatives are essential to understanding the impact of climate change, including changes to the permafrost and nutrition transitions in the region.

A comprehensive community strategic plan was developed to ensure ongoing monitoring of the water and land. The findings will lead to a strategy to cope with climate change challenges, improve resilience, and build community-led solutions to preserve the traditional Dene lifestyle while not increasing the risk to people's health.

M.O.2.6-2

MERCURY HAZARDS AWARENESS PROGRAM AMONG DIFFERENT COMMUNITIES PARTICULARLY EMPHASIS ON SCHOOL CHILDREN IN HISAR, HARYANA, INDIA

BALA, Ritu1
(1)Environmental and Culture Society

Objectives were achieved by having different expert lectures at school level as well as at central points in the city. These lectures were followed by a discussion session sensitizing the brain at the end both at school level as well as community level. This further include film screening and power point presentation regarding the hazards of mercury. The interactive nature sessions were proved to be effective and provided lot of discussion amongst students and teachers post every session. The students were put into an hypothetical situation which may lead to mercury spill at different places of their use and what mitigation they can have in the situation. The Mercury Awareness Programme was also carried out in the communities. Seeking the maximum participation of the people the, local leaders, local other NGO, influential persons and key person of the community were contacted. The lecture cum discussion, screening of films on the usage and hazards of Mercury, animated film on spill management and participatory question answer session were the key methods used for disseminating the information. The Information and communication material on Mercury was also distributed; such as posters and handbills. Important data was collected and calculated from the masses including schools regarding the instruments they use at home, gender and age sensitization towards mercury pollution and it was found that females in the age group of 14-26 were keener to learn the things about mercury pollution. Only 5% of the total group of students are aware of mitigation strategy after the spill of mercury at home and most of them put their responsibility to their elders in case of an mercury accident. Education level has a great impact on the paradigm of mercury pollution and the people having qualification above metric are more versatile towards the hazards of mercury pollution then the illiterate people. Furthermore, epistolary exchange has more effect as compared to verbal exchange and film screening. This is something peculiar due to retaining capacity of written literature like pamphlets etc. Further studies on these lines are in progress and our society's aim is to not only create awareness amongst the different sections of the society but on the basis of our observation, we can help the policy maker also regarding the waste management in the city.

M.O.2.6-3

MANAGING MERCURY EXPOSURE THROUGH CONSUMPTION ADVISORIES IN CANADA – SUCCESS OR FAILURE?

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When evaluating mercury exposure through the consumption of foods, Health Canada currently provides advice based on the assumption that 100% of total mercury is methylated, bioavailable, bioaccessible, and absorbed. These assumptions are typically made in human health risk assessments due to a lack of scientific data. As a result, the risk posed to human health from mercury in country foods may be overestimated, which can lead to consumption advisories which may or may not be necessary. Managing mercury exposure by issuing consumption advisories has historically been a standard risk management strategy in Canada primarily for hydroelectric developments, but also for any other industrial activity that may in the future or has previously resulted in increased MeHg levels in fish which may be consumed by people (including Indigenous communities). Unnecessary consumption advisories can have negative impacts on human health, specifically among Indigenous communities, as they deter individuals from consuming country foods and this may result in the consumption of potentially less nutritious commercial foods and influence longer-term food security and consumption patterns. This disconnect can result in issues related to the nutritional status and the overall practice of traditional activities of Indigenous peoples.

This presentation examines the extent of consumption advisories issued in Canada and their linkages to industrial developments or other disturbances. Using fish consumption advisories as an example, the presentation discusses the procedural differences in issuing advisories within Canada. It will provide information on how varying assumptions in advisories as well as the subsequent response(s), compliance and awareness are assessed. Where surveyed, the uptake and efficacy of these advisories are examined, and effects on the Indigenous communities in Canada discussed. Consumption surveys as a method to reduce mercury exposure from traditional foods are compared to other approaches. These include establishing realistic hazard quotients taking into account for differences in Hg concentrations in different species, muscles and organs, the level of mercury methylation, actual consumption levels (including seasonal variation in consumption), and differing levels of bioavailability, bioaccessibility and absorption. Methods of food preparation and the influence of other considerations (such as the influence of selenium) are also discussed.
3.6A Mercury Emissions Reductions – A Challenge to Industry

M.O.3.6A-1

MERCURY CONTROL IN LIGNITE AND COAL FIRED POWER PLANTS BY STATIONARY SORBENT MODULES

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The GORE™ Mercury and SO2 Control System (GMCS) (see http://www.gore.com/en_xx/products/filtration/mercury/mercury-con-trol-coal-fired-boiler.html for details) has been proven in more than 30 power plants and incinerators in the US since 2012. Three pilot plants are operated in EU power plants.

In August 2018 a German industrial scale lignite based power plant installed the system to control mercury emissions and improve SO2 reduction.

This system is based on sorbent polymer composite (SPC) material housed within discrete modules which provide passive, continuous mercury control with minimal pressure drop. As a result, no injection of any sorbents or chemicals are required. The modules will capture and retain mercury for many years of operation, resulting in an exceedingly easy-to-operate mercury control system, and very low ongoing operating costs. Modules can be installed inside of a wet flue gas desulfurizer (wFGD), which requires no additional footprint on site. Unlike systems that inject oxidizing chemicals such as calcium bromide, this system presents no risk of air preheater corrosion, and does not impact the waste water treatment system on the scrubber effluent stream. The modules also carry a co-benefit of SO2 removal, which can help meet tighter SO2 emissions limits and possibly avoid a scrubber upgrade.

Results from the pilot plants and the full-scale installation in Germany will be provided.

M.O.3.6A-2

MERCURY EMISSION – CHALLENGES FOR COAL-BASED POWER GENERATION SECTOR

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Electricity production, which is the main source of mercury emission to the atmosphere, is based mainly on combustion of solid fuels, such as hard coal and lignite. In Poland, the anthropogenic emission of mercury is estimated at 11.8 Mg, of which 9.1 Mg (over 77%) results from solid fuels combustion. The average mercury content in coal in Poland, according to tests carried out by Wojnar and Wisz was 0.100 mg / kg for hard coals and 0.250 mg/ kg for lignite (Wojnar and Wisz 2006).

From August 2021, the Polish coal-based power generation sector will have to meet stricter requirements introduced by Commission Implementing Decision (EU) 2017/1442 of 31 July 2017 (BAT Conclusions), including mercury emission requirements in flue gases. New requirements can be fulfilled not only by equipping power units with dedicated mercury emission reduction installations, but also by optimised utilisation of capacities of existing environmental protection installations, in particular by possibility to remove mercury in electrostatic precipitators and bag filters while deducting flue gases, as well as during nitrogen oxides removal in catalytic selective (SCR) and non-catalytic (SNCR) processes of nitrogen oxides reduction. Flue gas desulphurisation processes, such as semi-dry and wet flue gas desulphurisation, offer high mercury removal potential. Flue gas desulfurizing processes allow to reduce mercury emissions from 5 to 60%, mainly mercury that is carried by fly ash particles. Installations for NOx emission reduction (first of all SCR) also have positive effect on the emission reduction, they allow to increase the share of oxidised mercury in flue gases.

A significant mercury emission reduction effect is possible to achieve through a combination of various environmental protection installations. Regardless of applied secondary measures, proper fuel mix prepared for combustion in the boiler is of key importance in the process of mercury emission reduction. Tests of mercury emissions carried out on power units of TAURON Wytwarzanie SA indicate that levels of this emission in all tested cases are in the range defined in BAT Conclusions.

In case of new power units, emission levels allow them also to meet emission limits set for new units. It is clear from this that construction of large modern power units burning Polish hard coal can significantly reduce mercury emissions from the power generation sector.

M.O.3.6A-3

REDUCING MERCURY WITH NEWLY DEVELOPED POWDERED ACTIVATED CARBONS AT COAL FIRED POWER PLANTS

VAN DEN AKKER, Bert³

(1)Solution provider

Powdered Activated Carbon (PAC) is used as a dry sorbent to remove mercury and other impurities from flue gases of various combustion process, amongst other, at coal fired power plants. Based on more than 20 years of experience in this application, Cabot Norit activated carbon develops constantly improved grades for the removal of mercury both in oxidized or elemental form, from the flue gas.

New developed 3rd generation grades are suitable to use at high concentrations of elemental mercury and/or organic (oxidized) mercury as well as at elevated sulfur trioxide concentration. DARCO HG activated carbon types are also developed to operate and perform at the various flue gas processes in operation. Recent pilot and full-scale extended trials have demonstrated effective mercury emission reduction at a variety of sites with both elevated sulfur trioxide and other gas chemistry challenges.

These newly developed powder activated carbon sorbents, DARCO® Hg-LH EXTRA SP and SR as well as DARCO® Hg EXTRA, are capable at low sorbent injection rates of reducing mercury emissions sufficiently for compliance with both national and international pollution regulations (i.e. MATS, BREF and the Minamata Convention) even at the most stringent composition of the flue gas. With high sulfur combustion fuel and process feedstocks likely to be in use for the foreseeable future, DARCO® Hg-LH EXTRA SP and SR as well as DARCO® Hg EXTRA allow cost-effective mercury emission control and reduced balance-of-plant concerns.

M.O.3.6A-4

NOVEL METHOD OF MERCURY REDUCTION IN FLUE GASES OF LIGNITE FIRED POWER PLANTS BY DEDICATED BROMINE SALTS MIXTURES

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(1)PGE Görńictwo i Energetyka Konwencjonalna S.A.

The method of mercury reduction based on implementation of dedicated mixture of bromine salts to lignite before combustion process was investigated. The novelty of the method in comparison to well-known technology of dosing the halogenated additives in the fuel or it’s injection to the furnace lies in an appropriate selection of bromine salts and fuel and process feedstocks likely to be in use for the foreseeable future. This method has demonstrated effective mercury emission reduction at a variety of sites with both elevated sulfur trioxide and other gas chemistry challenges.

These newly developed powder activated carbon sorbents, DARCO® Hg-LH EXTRA SP and SR as well as DARCO® Hg EXTRA, are capable at low sorbent injection rates of reducing mercury emissions sufficiently for compliance with both national and international pollution regulations (i.e. MATS, BREF and the Minamata Convention) even at the most stringent composition of the flue gas. With high sulfur combustion fuel and process feedstocks likely to be in use for the foreseeable future, DARCO® Hg-LH EXTRA SP and SR as well as DARCO® Hg EXTRA allow cost-effective mercury emission control and reduced balance-of-plant concerns.
A mixture of bromine salts and coal are homogenized. Further, in the process of combustion, mercury is oxidized to bromine salt and sulfur oxides are bound, which increases absorption reactivity of the ashes. The technology was investigated in selected units in Power Plants Belchatów and Turów belonging to PGE GIEK S.A. The tests lasting six months performed under normal operating conditions of the units (without fuel selection and shutdowns) confirmed the achievement of emission limits imposed by BREF/BAT conclusions, which will be binding starting from 17th of August 2021.

The method of mercury reduction by dedicated bromine salt mixtures is characterized by low capital expenditure due to simple dosing installation and relatively low operating costs compared to other mercury emission reduction methods.

REDOCT OF MERCURY EMISSIONS FROM A 900MW COAL-FIRED POWER PLANT THROUGH MERCURY STABILIZATION AND ADSORPTION DURING A WET-FLEGT GAS DESULPHURIZATION (WFGD)

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In 2010, 24% of global anthropogenic mercury emissions were generated by fossil-fired power. Hence, German regulations stipulate coal-fired power plant mercury emissions to a daily mean value of 30 µg/m³ STP (standard temperature and pressure) and yearly mean value of 10 µg/m³ STP. In the BAT Reference Document for Large Combustion Plants (BREF-LCP), an average annual emission by existing hard coal-fired power plants with a rated thermal input ≥ 300 MWth of <1 to 4 µg/m³ STP was identified using the best available technology. The aim of this project is to develop a process for reducing coal-fired power plant mercury emissions well below the upper range of the BREF-LCP bandwidth without affecting gypsum, fly-ash and waste water quality. Based on a detailed analysis of operational data over several months, an approach combining different mercury reduction mechanisms has been detected as a possible solution.

After successfully testing at laboratory scale, the approach has been implemented at industrial scale at unit 9 of Grosskraftwerk Mannheim, Germany.

The overall procedure consists of 3 steps:
1. Increasing the chloride concentration in the WFGD absorber suspension to 25 g/L: At this concentration, oxidized mercury absorption from flue gas is promoted. The absorbed mercury forms water soluble complexes which stabilize the mercury inventory within the WFGD system. Thus, mercury concentration in the solid phase of the WFGD suspension and the re-emission rate of mercury from the WFGD into the gas phase is decreased.
2. Raising the WFGD water discharge volume flow: This increases the waste water treatment plant mercury discharge. The overall mercury inventory within the WFGD system as well as the mercury emissions at the stack are reduced.
3. Consecutive dosing of three different additives, straight or as a mix, within the WFGD:
   - By adsorbing the mercury, they suppress mercury re-emissions. One additive can be completely separated from the WFGD gypsum in a hydro cyclone classifier. Mercury concentration in gypsum is not increased by additive dosing. The additive with the adsorbed mercury is discharged with the sludge of the waste water treatment plant.
   - By following the above-described strategy the industrial scale experiments demonstrate: mercury concentration at unit 9 is reduced in all filtrates along the WFGD and increased in the solids discharged into the waste water sludge. Mercury emissions at the stack are significantly decreased. Values <4 µg/m³ STP according to the upper range of BREF-LCP bandwidth can be safely achieved under all operating conditions.

M.O.3.6A-6

NOVEL HYBRID TECHNIQUE FOR MERCURY REDUCTION IN FLUE GASES

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A major source of environmental mercury is the combustion of fossil fuel used to produce energy. Based on the actual and planned European directive, the emission of mercury might be limited to a value near 1 µg/dNm3 at 6% oxygen. Nowadays the regulations concerning mercury concentration in flue gases are getting more strict. Thus there is a need to propose an efficient and economically justified mercury reduction technique. To achieve the required deep reduction of mercury will not be easy for power plants which burn only hard coal, and it will be even more difficult for lignite fired boilers, which usually contain larger amounts of mercury relative to hard coal.

To meet this request an innovative system for mercury removal from flue gases is proposed. The developed process is based on the combination of injection of brominated powdered activated carbon, dispensing of fuel additives and use of the innovative polymeric membrane material. The idea of the hybrid technique was to provide the possibility to reduce mercury emission without the necessity of introducing many significant modifications into the flue gas treatment system. Up to now, the injection of an activated carbon into the flue gases and the use of fuel additives are commonly used for mercury reduction. Those methods are characterized by low investment but high operational costs. Here, the application of polymer material is considered as a part of reduction system. Polymer material is expensive to buy but has almost none operational costs. To find the proper combination of mentioned techniques both laboratory tests and a pilot scale facilities were used to collect all necessary information. Laboratory tests focused mainly on the behavior of the polymer material under various conditions including pre-saturation of the material with mercury. Pilot installations were used to test various combinations of number of layers of polymer modules together with different fuel additives and mercury sorbents injected to flue gases. The collected data were used to develop a predictive numerical model. The model was implemented into the Ansys Fluent code, using a set of user defined functions combined with the solution procedure. The developed model will be used to tailor the proposed approach for any particular installation.

4.1 Evaluating the effectiveness of the Minamata Convention

M.O.4.1-1

USING INDICATORS TO EVALUATE THE EFFECTIVENESS OF THE MINAMATA CONVENTION ON MERCURY

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This research focuses on the potential use of outcome and process indicators for the periodic evaluations of the Minamata Convention
MERCURY STABLE ISOTOPES FOR THE EFFECTIVENESS EVALUATION OF THE MINAMATA CONVENTION ON MERCURY

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As a part of the Minamata Convention, specific provisions are set-out for a global monitoring program (GMP; Article 22(2)) and the convention effectiveness evaluation (EE; Article 22(3)). While the exercise scope of the GMP and EE are being discussed, these objectives share common opportunities and challenges. The major opportunity is that they stimulate scientific advancements to better measure mercury in the environment. The major challenges are establishing an internationally comparable performance indicator that can ascertain changes in mercury sources subject to regulation and distinguishing between policy signal and noise, which may be interfered by climate change and other human activities. By tracking atmospheric emissions to ecosystem fate, we illustrate how measurements of mercury stable isotopes can help address the challenges of the GMP and EE. Among the atmospheric samples (total gaseous mercury; TGM, precipitation, particulate bound mercury; PBM), we find that isotopic compositions of TGM are effective for distinguishing between long-range transport (d202Hg = -0.39 to +0.93‰, D199Hg = -0.22 to -0.01‰, n=11) and anthropogenically influenced mercury sources (d202Hg = -2.03 to 0.19‰, D199Hg = -0.16 to +0.15‰, n=49). In terrestrial environment, the most important factors governing the differences in mercury isotopic compositions between foliage and soil are the types of atmospheric mercury sources and the organic matter content, respectively. Foliage collected at various locations of the U.S. and China show ~1% deviation, depending on mercury sources that influence the foliage. Urban, mineral, and organic soil collected from a wide range of environment show a significant negative relationship between mercury isotopic compositions and the total organic matter content, rather than sources that contaminate the soil. For the first time, we compare mercury isotopic compositions of sediments (n=887) by differentiating between point source impacted, non-point source influenced, and pre-anthropogenic and between ecosystem type (river, lake, coastal, marine). We find increasing trends in D200Hg and D199Hg with decreasing anthropogenic mercury influence from coastal and marine sediments. Lake sediments show decreasing D199Hg trends with decreasing anthropogenic influence, given that soil runoff characterized by low D199Hg acts as an important mercury source to many remote lake systems. In all, our study suggests that the measurements of mercury isotopes in various environment samples (TGM, foliage, sediment) can aid the interpretation of mercury sources and processes at a large spatial scale. We also suggest that our data can be used for forming a baseline and for evaluating changes in mercury sources under the implementation of the Minamata Convention.

GLOBAL MONITORING OF HUMAN EXPOSURE TO MERCURY AND ITS COMPOUNDS: ARE WE READY?

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Assessment of human exposure to mercury and its compounds is critical for planning of targeted measures to reduce risks for human health and to monitor progress. Harmonized approach for collecting this information at global level brings a number of benefits: collection of reliable and comparable data; identification of highly exposed populations at different levels – national, regional and global; more effective use of human, technical and financial resources for exposure assessment; and, in total, for an assessment of effectiveness of global efforts to protect human health from negative impact of mercury. The requirement to monitor mercury compounds and their trends in vulnerable populations using harmonised methodologies is included in the Minamata Convention (Art 19 and Art 22).

To ensure feasibility of global monitoring of human exposure to mercury, WHO developed a series of standard operating procedures for sampling and analysis of mercury, and a tool for the development of national protocols for the assessment of mercury risks to developing organisms (fœtus), during critical windows of exposure. The tool includes technical details relevant for planning, designing and implementation of national surveys, both at a country-wide level and in contaminated sites. The pilot national HBM surveys, implemented in China, Ghana, India, Mongolia, Kyrgyzstan, and the Russian Federation, using the WHO methodology and following the WHO ethical principles, confirmed the applicability of the technical documents and the feasibility of mercury HBM studies in countries with different level of economic development. The pilot surveys also demonstrated that capacities for reliable assessment of exposure to mercury using HBM exist, or can be built in developing countries and countries with economies in transition. The analysis of the data obtained in the pilot surveys on mercury HBM confirmed the earlier scientific findings that populations with high level of consumption of marine and fresh waters fish and other contaminated food (such as rice) are more exposed to mercury. Populations living in the areas of ASGM and other highly contaminated sites are also populations at higher mercury risks. This confirms robustness of the WHO methodology for identification of populations at risks globally and for an assessment of effectiveness of risk reduction measures, including in the Convention framework.

Thus, scientific, technical and methodological basis for global monitoring of mercury exists and global monitoring of human exposure to mercury is possible.
PROGRESS ON IMPLEMENTATION OF MINAMATA CONVENTION IN CHINA

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In order to protect human health and the environment from the common hazards of anthropogenic emissions and releases of mercury and mercury compounds, the international community has worked hard to reach the Minamata Convention on Mercury. The Minamata Convention is another legally binding time-limited Convention following the Stockholm Convention and the Climate Change Convention in the past 15 years. It is an important milestone in the history of human environmental protection. As an economic developing and transforming country, China is actively facing enormous pressures and challenges of environmental protection, and attaches great importance to mercury prevention and control. China is one of the first signatories of the Minamata Convention, and the Ministry of Ecology and Environment actively coordinates and promotes domestic ratification. On April 28, 2016, the Standing Committee of the 12th National People’s Congress approved the Convention, and on August 31 of the same year, it deposited the instrument of ratification and became the 30th ratifying country. The Convention entered into force on August 16, 2017. From August 2017 to August 2018, in the first year of the implementation of the Convention, China has made great progress. First, the National Coordinating Group for the Implementation of the Mercury Convention, constituted by 17 Ministries, and a compliance coordination mechanism was established. Second, China officially launched the preparation of the National Implementation Plan, strengthened the top-level design and continued to promote the implementation of the Convention. Third, to strictly fulfill the obligations stipulated in the Convention, the “Announcement on the Entry into Force of the Convention on Water Margins” was promulgated, and the “List of China’s Strictly Restricted Toxic Chemicals” and the “List of Priority Control Chemicals (First Batch)” were issued. Important documents such as the application for the discharge permit and the technical specifications for the issuance of key industries were published as well. At this stage, China will continue to increase the management of mercury pollution prevention and control, continuously improve the mercury pollution prevention policies, regulations and standards, gradually improve the ability and overall level of mercury pollution prevention, and actively strengthen the foundation for the compliance of the Convention.
over the past two decades. An over-arching general explanation for these results is that the impact of changing atmospheric inputs on biotic Hg is masked by two factors: 1) The aquatic environment also contains a large inventory of legacy emitted Hg that remains available for bio-uptake leading to a substantial lag in their response time to a change in external inputs; and 2) Biotic Hg trends reflect the dominant effects of changes in multi-causal, local and regional processes (e.g., aquatic or terrestrial biogeochemical processes, feeding ecology) that control the speciation, bioavailability, and bio-uptake of both present-day and legacy emitted Hg. Globally climate change has become the most prevalent contributor to the divergence. A wide range of biotic Hg outcomes can thus be expected as anthropogenic atmospheric Hg emissions decline, depending on how these processes operate on specific regions and specific organisms. Therefore, evaluating the effectiveness of the Minamata Convention will require biomonitoring of multiple species that represent different trophic and ecological niches in multiple regions of the world.

1.2A Biogeochemical cycling of mercury in the aquatic ecosystems

M.O.1.2A-1

METABOLOMICS UNCOVERS PHYTOPLANKTON RESPONSES TO HG COMPOUNDS IN AQUATIC ENVIRONMENT

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Metabolomics, the youngest among -omics technologies, characterizes low-molecular-weight molecules involved in different biochemical reactions and provides an integrated assessment of the physiological state of an organism. This feature makes the metabolomics well suited to study organism -- environment interactions. Nonetheless, very few studies use the metabolomics approach to explore the contaminant-induced metabolic perturbation in phytoplankton and to the best of our knowledge, no such studies exist for mercury. The present pilot study aimed at getting new insights into the basic mechanisms determining cellular responses during mercury exposure. To this end, untargeted liquid chromatography – mass spectrometry (LC-MS) metabolomics was employed to follow the metabolic variations in green alga Chlamydomonas reinhardtii and cyanobacterium Synechocystis sp., as representatives of two important phytoplankton groups. Both hydrophilic and lipophilic compounds were determined in the microorganisms exposed to 1 or 10 nM inorganic (iHg) or methylmercury (MeHg) and compared with unexposed controls. The untargeted metabolomics approach resulted in approximately 900 signals from both hydrophobic and hydrophilic extracts of C. reinhardtii or Synechocystis sp. However only about one third were annotated. Supervised and unsupervised multivariate methods provided an information on most influential metabolites, which were further used to identify the most important metabolic pathways affected by Hg or MeHg exposure. The results revealed an alteration of multiple pathways for both cyanobacteria and green algae when exposed to iHg or MeHg, including carbohydrate metabolism, energy and lipid metabolism, amino acid metabolism, metabolism of cofactors and vitamins. Globally Hg species induced metabolic perturbations in green algae were more important than those found in cyanobacteria, which corresponds to higher sensitivity of the green algae to mercury. The annotated metabolites showed that iHg and MeHg affected similar pathways, however for comparable exposure concentrations in some cases MeHg-induced perturbations were more pronounced or species-specific. For example among different hydrophobic molecules the most pronounced decrease was found in the diacglyerylhomoserines (DGTSs) class involved in glycerophospholipid metabolism of C. reinhardtii during MeHg exposure. However, DGTSs were not detected in Synechocystis sp. The results demonstrated the promise of metabolomics in uncovering Hg-induced perturbations in the two model phytoplankton species and underlying biochemical mechanisms. However they have also revealed some drawbacks mainly due to the relatively high metabolic variability, corresponding to normal operating range of the microorganisms, which could hide the subtle changes in metabolite concentrations, as well as the lack of phytoplankton-specific metabolite information in the existing databases which limits the metabolite identification.

M.O.1.2A-2

BIOGEOCHEMISTRY OF MERCURY SPECIES IN THE WATER COLUMN OF HIGH ALTITUDE LAKES OF THE WESTERN PYRENEES (FRANCE / SPAIN)

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While Hg is a major concern in all aquatic environments where methylation and biomagnification take place, very few studies consider Hg cycling in remote alpine lakes and their use as proxies of global environmental changes. This work presents an integrated investigation conducted in twenty high altitude pristine lakes from Western Pyrenees. Subsurface water samples were collected in June/October 2017/2018 for Hg speciation analysis (iHg, MMHg, DGM) to investigate spatial and seasonal variations. DGM provided information on biotic and photoreduction of Hg as well as atmospheric re-emission extents. In June/October 2018, a more in-depth study was performed in lakes Gentaut, Arratille and Sabocos, by sampling at different depths along the day. Besides, in situ incubation experiments using isotopically enriched Hg species (199Hg, 201MMHg) were conducted to investigate Hg transformation mechanisms in the water column (methylation, demethylation, reduction). Comparison between filtered (<0.2µm) and unfiltered samples highlighted significant differences in most of the samples. While iHg did not show seasonal variations, MMHg was significantly higher in autumn, except for bottom anoxic waters (Gentaut and Sabocos). For the unfiltered samples, concentrations of MMHg in surface waters were low in Gentaut, respectively 8±1µg/L (2% of HgTOT) in spring and 29±5µg/L in autumn (9% of HgTOT). Similar values were found in Sabocos, 19±3µg/L (3% of HgTOT) and 29±5µg/L (5% of HgTOT), and Arratille, 7±1µg/L (3% of HgTOT) and 17±3µg/L (3% of HgTOT). Bottom waters in Gentaut exhibits higher MMHg concentrations, 426±59µg/L in spring (36% of HgTOT) and 388±67µg/L in autumn (50% of HgTOT). These values are higher than in Sabocos, 60±8µg/L (10% of HgTOT) and 26±5µg/L (3% of HgTOT), and Arratille, 9±1µg/L (3% of HgTOT) and 14±2µg/L (6% of HgTOT). Results from the incubation experiments highlighted an important demethylation yield in Gentaut (44±11%/day in spring, 42±25%/day in autumn). In bottom waters, methylation rate is 2.4±1.8%/day (spring) and 1.9±2.6%/day (autumn) for Gentaut whereas methylation rates are about 0.7±0.5%/day in both seasons for Sabocos (below LOD=0.04%/day in Arratille). Overall, drastic environmental changes occurring daily and seasonally in alpine lakes are providing conditions that can both promote Hg methylation (stratified anoxic waters) and MMHg demethylation (intense UV light). Both climate change (warming) and human impact (through eutrophication) may have important implications on those pathways and the fate of Hg in these remote lakes.

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MERCURY SPECIES IN SURFACE WATER IN MIDDLE AND NORTHERN TIBETAN PLATEAU

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Climate change and human activities affect the cryospheric characteristics and hydrological changes of the rivers originating from the Tibetan Plateau (TP). Mercury (Hg) is a global pollutant and methylmercury (MeHg) can be more toxic due to the bioaccumulation and biomagnification effect in the food chain. There is an increasing concern on Hg in TP since the high sensitivity of the pristine environment to the long-distance-travelled Hg. To better understand the Hg distribution and its impact factors, the concentrations of Hg species in surface water were investigated in Three River Source Region (TRS) and Qi Lian Mountain (QLM), which is located in the middle and northern TP, respectively. In 2018, water samples were collected in the rivers or lakes in TRS and QLM. Total Hg (THg), dissolved Hg (DHg), particulate Hg (PHg), total MeHg (TMeHg), dissolved MeHg (DMeHg) and particulate MeHg (PMeHg) were analyzed according to EPA method 1631 and 1630. THg in TRS ranged from 0.51 to 7.48 ng L−1, which were slightly lower than those in QLM (0.94–7.93 ng L−1). TMeHg in TRS and QLM ranged from 0.05–0.31 ng L−1 and 0.04–0.49 ng L−1, respectively. Non-parametric tests of the TMeHg showed no significant difference between both sites. THg and TMeHg were comparable to the previous results in TP and the arctic area, which represent the background levels in river systems. The ratios of TMeHg/THg in TRS and QLM were 7.31±3.00% and 5.22±2.63%, respectively. The ratios were consistent with previous observation in Yarlung Zangbo River (5±2%) in southern TP, but much higher than Yukon River (1%) which is located in Arctic and Subarctic. In TRS, a positive correlation was observed between DOC and THg, DHg, DMeHg values (r=0.466, p<0.01; r=0.591, p<0.01; r=0.477, p<0.01), and PHg was positively correlated with altitude (r=0.416, p<0.05), indicating that DOC and altitude mainly affected the migration and transformation of Hg. In QLM, THg and PHg was significantly correlated with the TP (r=0.386, p<0.05; r=0.423, p<0.01), and TMeHg, PMeHg was significantly correlated with THg and PHg (p<0.01). This indicates that Hg in QLM were affected by particulate matter. In comparison with Hg in other rivers of TP which were mainly in TSP-associated species, PHg decreases with altitude and higher DOC in TRS indicating that continued warming likely increasing the potential release of DOC-bound Hg.

TEMPORAL MERCURY DYNAMICS THROUGHOUT THE RICE CULTIVATION CYCLE: AN INTEGRATIVE APPROACH

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During the last few decades, the input of mercury to the environment resulting from anthropogenic activities has increased. This can translate into effects to both wildlife and humans. For the last fifty years, a chlor-alkali plant situated at the locality of Flix (NE Spain), ca. 100 km above the Ebro river mouth, has dumped mercury-loaded residues into the river. The residues have been transported throughout the river reaching its delta ecosystems (e.g., rice fields, flood plains, marshes, lagoons). The Ebro Delta (ca. 30 000 ha of wetlands) is a highly important site of rice production with more than 75% of its area intended to this activity. Moreover, it constitutes one of the largest wetlands of the Mediterranean being also relevant from the conservation point of view, as it is the breeding habitat for several bird species. Rice paddies are considered a potential ‘hotspot’ for methylmercury due to the biotic methylation activities of soils, as well as a source of methylmercury for both aquatic and terrestrial food webs.

PROPATHATION OF THE MERCURY CONTAMINATION IN CASCADE RESERVOIRS IMPACTED BY A CHLOR-AL-KALI PLANT, OLT RIVER, ROMANIA

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The chlor-alkali industry is a major contributor of local to regional mercury contamination of aquatic environments. Mercury released into surface waters by this industry is mainly bound to the particulate phase and therefore more likely to rapidly deposit in standing waters such as lakes and reservoirs. However, a fraction of that mercury can be associated with very fine inorganic and organic particles, which can travel longer distances. Here we report the propagation of the mercury released by a chlor-alkali plant into the Olt River, the largest Romanian tributary of the Danube River, as recorded in sediments of five cascade reservoirs. Both mercury concentration and deposition flux histories, together with sedimentological parameters, have been determined in 137Cs-radiated sediment cores collected in the deepest zones of one upstream (Valcea, reference reservoir) and four downstream reservoirs (Babeni, Ionesti, Zavideni, and Dragasani). The maximum mercury concentration – 44.5 mg/kg, representing more than 300 times the background level – was recorded in a sediment layer deposited in 1987 in the Babeni reservoir, which is directly impacted by the plant effluent. The history of the contamination was similarly recorded in the three other downstream reservoirs, with decreasing maximum concentrations of 36, 13.5 and 7.4 mg/kg, respectively. Likewise, the maximum mercury specific fluxes decreased in the four cascade reservoirs, from 146 to 4.3 µg cm−2 y−1. These results showed a significant reduction of the mercury inputs into the lower reservoirs. However, the mean mercury concentrations recorded during the 1980-2013 period did not show such an important reduction down the cascade reservoirs. The decrease in the mean mercury concentration was only by a factor 2 between the most impacted Babeni reservoir (4.4 mg/kg) and the Dragasani reservoir, the farthest we studied in the cascade (2.1 mg/kg), more than 35 km downstream the contamination source. This relatively low decrease rate is due to the concomitant effects of i) a very high sediment load (3.3 g cm−2 y−1) from tributaries in the Babeni reservoir that “dilute” mercury compared to the low sediment load in the downstream reservoirs (0.6 g cm−2 y−1 in Dragasani); and ii) the transport of mercury through the reservoirs by fine inorganic and organic particles delivered by the tributaries and less prone to settle. These associated effects result in an extended contamination of the reservoir sediments in a long reach of this river, a favorable environment for methylation.
In this context, we studied temporal changes in mercury dynamics throughout the rice cultivation season (early-, mid-, late-season) in both abiotic (water, sediments) and biotic compartments into behavioral classes (Oryza sativa) and fauna (vertebrates and invertebrates) belonging to the rice-paddies food webs have been analyzed for total mercury (THg). Furthermore, we assessed the effect of different agricultural management practices (ecological vs. conventional) associated to various flooding patterns (flooded cultivation vs. dry cultivation) to the mercury levels present in the plants and fauna. We found that different agricultural practices and/or flooding patterns did not influence as much as expected the mercury levels observed in rice plants or rice paddies food webs. We observed a clear evidence of mercury biaccumulation through the food web of the studied systems.

M.O.1.2A-6

IMPACT OF SEDIMENT MERCURY SPECIATION ON MERCURY CYCLING IN THE ST. LOUIS RIVER ESTUARY

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The St. Louis River Estuary (SLRE) is a freshwater estuary at the terminus of the second largest tributary of Lake Superior that exhibits complex Hg biogeochemistry. Fish and other aquatic biota in the estuary often contain high levels of methylmercury compared to the upstream river or Lake Superior. The downstream estuarine area contains some high mercury legacy sediment contamination from previous industrial activities. Despite remediation efforts, some sediments still contain concentrations of total Hg well above background levels for the area, which implicates them as a potential source for MeHg. In this study, we focus on the impact of sediment chemistry and solid-phase mercury speciation on inorganic- and methyl-mercury bioavailability and partitioning in relation to methylmercury production in the estuary. Sediment cores and porewater were collected from three geochemically distinct locations within the estuary and analyzed for total and methylmercury, carbon (sediment and porewater), and acid volatile sulfide and dissolved sulfide. In addition, selective extractions were used to separate inorganic- and methyl-mercury compounds into behavioral classes. Results indicate that more mercury is retained in sediments with high concentrations of carbon and sulfide. Methylmercury production and porewater methylmercury is lowest in sediment with the highest sulfide to carbon ratio, suggesting both inorganic and methylmercury availability are partially controlled by solid phase carbon and sulfide. Selective extraction results indicate that sediments with more strong acid soluble species have larger portions of inorganic- and methyl-mercury in the sediment, while sediments with more organic-chelated Hg species have larger portions of inorganic- and methyl-mercury in the porewater. Our results suggest that sediment with low total mercury concentrations may contribute more methylmercury and bioavailable inorganic mercury to the porewater and eventually the lower portions of the food web than sediments with high total mercury concentrations.

1.4A Mercury cycling and bioaccumulation in polar regions

M.O.1.4A-1

ENHANCED ARCTIC RIVER PARTICULATE HG EXPORT AT THE PERMAFROST THAWING FRONT

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Arctic permafrost soils contain large amounts of organic carbon and mercury (Hg). Arctic warming and associated changes in hydrology, biogeochemistry and ecotone risk mobilizing soil carbon and Hg, yet little is known about the quantity, timing and mechanisms involved. We investigated seasonal particulate Hg (PHg) and organic carbon (POC) export in 32 small and medium rivers across a 1700km latitudinal permafrost transect of the western Siberian Lowland (WSL). The WSL transect covers absent, isolated and sporadic permafrost in the south to discontinuous and continuous permafrost in the north. PHg and POC levels strongly correlated and decreased with river watershed size, suggesting Hg mobilization from organic (peat) rather than mineral soil layers. Maximum PHg concentrations, run-off and export fluxes were located in rivers of the sporadic permafrost zone. We suggest this reflects enhanced Hg mobilization at the permafrost thawing front, due to maximal active layer depth. Both the maximal thickness of the active layer and maximal PHg run-off progressively move to the north during the summer and fall seasons, thus leading to maximal PHg export at the latitudinal thawing front. The discharge-weighted PHg:POC ratio in WSL rivers (2.7±0.5) extrapolated to the whole Ob River basin yields a PHg flux of 1.5±0.3 Mg yr-1, consistent with previous estimates. Using a substituting space for time approach for climate warming and permafrost thaw scenario in WSL, we predict that a northward shift of permafrost boundaries and increase of active layer depth may enhance the PHg export by WSL rivers to the Arctic Ocean by a factor of two over the next 10-50 years.

M.O.1.4A-2

3-D MODELING OF ATMOSPHERIC BOUNDARY-LAYER MERCURY DEPLETION EVENTS ACROSS THE SPRING-TIME ARCTIC

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Gas-phase bromine radical chemistry is the main driver for the frequent and concurrent depletion of ozone and mercury (Hg) in the polar boundary layer during the spring. Sea ice and its overlying snow cover are broadly understood as the key elements in the production of reactive bromine in polar spring. However, a full characterization remains unsettled on how physicochemical state of snow and ice influence the release of bromine into the atmosphere. Uncertainties in the kinetics and reaction mechanisms of Hg redox chemistry add further complexity to accurately assessing the behavior of Hg during its depletion from air. Three-dimensional (3-D) models developed to simulate the impact of bromine chemistry on Hg oxidation in the Arctic, have generally relied upon indirect representations of the sources, sinks and photochemical transformation of bromine radical species in the polar atmosphere. This study presents development of a process-oriented representation for the coupled bromine-ozone–Hg chemistry and the exchange of bromine, ozone and Hg species between air and snow/ice surface within Environment and Climate Change Canada’s air-quality model, GEM-MACH-Hg. The model simulations are performed at 15-km horizontal resolution in a limited-area domain of the Arctic. The model captures the evolution of high BrO column densities associated with synoptic weather disturbances during polar sunrise as can be seen from satellite. The concurrent depletion of ozone and Hg is simulated by consistent model formulation, where the release of active bromine from the frozen surfaces is facilitated by the presence of ozone in air. Extensive model evaluation is performed using measured ambient concentrations

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of ozone and speciated Hg, total Hg in snow and the vertical column densities of BrO retrieved from ground stations and buoys floating on the ice-covered ocean at fine temporal scale. The model framework for simulating the reactive bromine release from the snow/ice cover is found to work reasonably well for the representation of ozone and Hg depletion events across the Arctic over synoptic and seasonal time scales. The deposition of oxidized Hg from the atmosphere is found to be enhanced particularly under the disturbed weather conditions, as a result of the vertical and horizontal inflow of ozone and gaseous elemental Hg. The model is applied to estimate springtime deposition, re-emission and accumulation of mercury in the Arctic.

Eurasian River Spring Flood Observations Support Net Arctic Ocean Mercury Export to the Atmosphere and Atlantic Ocean

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Midlatitude anthropogenic mercury (Hg) emissions and discharge reach the Arctic Ocean (AO) by atmospheric and oceanic transport. Recent studies suggest that Arctic river Hg inputs have been a potentially overlooked source of Hg to the AO. Observations on Hg in Eurasian rivers, which represent 80% of freshwater inputs to the AO, are quasi-inexistent, however, putting firm understanding of the Arctic Hg cycle on hold. Here, we present comprehensive seasonal observations on dissolved Hg (DHg) and particulate Hg (PHg) concentrations and fluxes for two large Eurasian rivers, the Yenisei and the Severnaya Dvina. We find large DHg and PHg fluxes during the spring flood, followed by a second pulse during the fall flood. We observe well-defined water vs. Hg runoff relationships for Eurasian and North American Hg fluxes to the AO and for Canadian Hg fluxes into the larger Hudson Bay area. Extrapolation to pan-Arctic rivers and watersheds gives a total Hg river flux to the AO of 44 ± 4 Mg per year (10a), in agreement with the recent model-based estimates of 16 to 46 Mg per year and Hg/ dissolved organic carbon (DOC) observation-based estimate of 50 Mg per year. The river Hg budget, together with recent observations on tundra Hg uptake and AO Hg dynamics, provide a consistent view of the Arctic Hg cycle in which continental ecosystems traffic anthropogenic Hg emissions to the AO via rivers, and the AO exports Hg to the atmosphere, to the Atlantic Ocean, and to AO marine sediments.

MERCURY IN THE BERING SEA FOOD WEB

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The Southeastern Bering Sea (SEBS) supports one of the most productive and economically important fisheries in the world. Mercury (Hg) is projected to rise in the North Pacific and possibility in the SEBS in response to increased atmospheric emissions from Asia. To date, concentrations of total Hg (THg) and methylmercury (MeHg) in the SEBS seawater and plankton are lacking; thus, Hg transfer in the SEBS food web is unknown. We investigated spatial differences in (THg) and (MeHg) concentrations in seawater, suspended particles, zooplankton and ichthyoplankton, from samples collected in the SEBS in June and September of 2018. We found that THg and MeHg showed a horizontal pattern of westward increasing concentrations in both seawater (4-100 pg/L MeHg and 36-178 pg/L THg) and copepods (3-13 ng/g dry weight MeHg). Moreover, there were significant differences between the hydrographic domains of the SEBS such that concentrations of Hg were highest in the outer domain. Our Hg data will be presented in the context of other auxiliary measurements including oceanographic (i.e., salinity, temperature, density, etc.) and biological (i.e., δ15N - based trophic position and taxonomy) parameters. Data presented here represents a subset of a larger study, which will altogether illustrate the flow of THg and MeHg in the SEBS food web and, thus, inform other studies that investigate risks of MeHg exposure to marine mammals, seabirds and human consumers of locally harvested seafood.

Identifying the Sources and Fate of Winter-Time Mercury Deposition to a Northern Alaskan Coastal Watershed Using Major Ions and Mercury Stable Isotopes

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Snow deposited to Polar coastal locations during springtime atmospheric mercury depletion events (AMDEs) commonly has highly elevated mercury concentrations (>200 ng Hg/L). During AMDEs gaseous elemental mercury (GEM) is photochemically oxidized to reactive gaseous mercury by halogen-mediated reactions and the Hg is deposited to the snowpack. The reactive mercury is then either photochemically reduced back to GEM and re-emitted from the snowpack to the atmosphere or it remains until spring snowmelt. GEM can also be deposited to the snowpack and tundra vegetation by reactive surface uptake (dry deposition) from the atmosphere by processes that also occur at lower latitudes. The proportion of Hg attributable to AMDEs versus dry deposition that is released in spring run off has not been quantified. We conducted extensive sampling campaigns in late winter and during snowmelt for two years at a small (2.5 ha) watershed on the Arctic coastal plain near Utqiaġvik (formerly Barrow), Alaska. Airborne LiDAR and GPS surveys were used to delineate the watershed area to cm scale accuracy. Snowpack, meltwater, and stream channel water were sampled and analyzed for total dissolved Hg, Hg stable isotopes, major ions, and stable oxygen and hydrogen isotopes. Permafrost peat cores were collected and analyzed for Hg concentrations and Hg isotope ratios. We identified an “ionic pulse” of mercury and major ions in runoff during both snowmelt seasons, with total dissolved Hg in run-off up to 14.3 (+/- 0.7) mg/ha. This runoff flux is five to seven times higher than what has been reported from other arctic watersheds and from lower latitudes. We calculate that up to three quarters of the snowpack Hg was exported with snowmelt runoff. Hg isotope measurements indicate the majority of this snowmelt Hg originated as GEM oxidized in the snowpack by reactive halogens in a process similar to reactive surface uptake of GEM into the leaves of trees in temperate forests. This GEM-sourced Hg is the dominant Hg we measured in the spring snowpack and in the tundra peat. We calculate that ~75% of the Hg exported from the watershed in snow melt came from non-AMDE sources while ~25% is attributable to AMDE deposition. Projected future warming in the Arctic will produce an increasingly dynamic sea ice regime with more first year ice and open sea ice leads. This will likely enhance the source of reactive halogens, promote GEM oxidation, and lead to greater Hg deposition to coastal and marine snowpacks.
METHYLMERCURY BIOGEOCHEMISTRY AND FATE IN DECEPTION ISLAND, (ANTARCTICA)

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In contrast to established long-term research programs in the Arctic, little is known about mercury biogeochemistry in Antarctica. Environmental studies in Deception Island (South Shetlands Archipelago) are scarce but are of great interest since it potentially represents a significant source of Hg, namely volcanic activity. Previous results showed the presence of relatively high Hg and methylmercury (MMHg) levels. Our study in this volcanic island aimed to better understand the Hg cycle in the Deception ecosystem, particularly, fluxes, speciation and bioavailability of mercury.

Sediment/soils were analysed for MMHg and for their methylation potential using enriched stable isotopes, as well as for other ancillary parameters. In the laboratory, trace element bioavailability tests were also performed. Finally, a three-dimensional hydrodynamic model was developed using the Mohid water modelling system. MMHg data was incorporated into the model to better understand the Hg and MMHg circulation in the Bay.

Mercury levels in water and sediments sampled at two fumaroles on Deception Island were up to 10000 times higher compared to the other sampling sites. Moreover, the concentrations obtained in Port Foster waters are also considerably higher than those typically observed in open waters of the Atlantic or the Southern Ocean. The proportion of MMHg (MMHg/HgT) was surprisingly high in saline waters of Port Foster (95%), suggesting exceptional conditions for Hg methylation processes in the water column. In fact, high abiotic (up to 3.6% of Hg) and biotic (up to 7.2% per day) methylation rates were estimated. Additionally, the high residence time of water (ca. 1.7 yr) in the Bay contributes to creating a substantial standing pool of mercury and MMHg available for aquatic organisms. Moreover, the low capacity of sediments for Hg adsorption, (low carbon content and low superficial area (Si/Al>4)), may also contribute to keep mercury in solution and therefore increase its bioavailability. A first approach to model the circulation of Hg and MMHg was done using Lagrangian tracers, allowing visualization of their movement in the aquatic environment. The model output indicates that the tidal currents have almost no impact in the elements dispersion. Results obtained in this work pointed to a continuous input of Hg to the Deception ecosystem due to volcanic emissions. This input and the special biogeochemical conditions in Port Foster Bay water promote Hg methylation and the presence of more bioavailable Hg species that can, in fact, be taken up by aquatic organisms.

1.3B Regional and local scale stable isotope studies in mercury biogeochemical cycling and bioaccumulation

TRACING MERCURY MOBILITY AND DISTRIBUTION IN THE ABBADIA SAN SALVATORE LEGACY MERCURY MINE AREA USING MERCURY ISOTOPE RATIOS AND CONCENTRATIONS

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Persistent mercury (Hg) impact from legacy mines continues to present risk to the environment and human health globally. The Monte Amiata Hg district in Southern Tuscany, Italy was one of the five largest Hg districts in the world. Mining of Hg began in the region during the Roman era with modern mining beginning in the mid-1800s and concluding in the early 1980s which resulted in the occurrence of elevated Hg in the surrounding ecosystem. The study area focused near Abbadia San Salvatore mine (ASSM) as it was the major Hg processing facility for many mines in the district and considered a primary source for elevated Hg. The extraction of Hg from cinnabar ore was carried out via the roasting of ore using two primary furnace types. Initially, Čermak-Spirek shaft type and tower furnaces were used which were later replaced by Gould and Pacific type furnaces. The ore was roasted at 600-700°C to volatize Hg to gas which was recovered via condensation. Mass dependent fractionation (MDF) of Hg isotope ratios and variation in Hg concentrations resulting from the processing of cinnabar ore has been reported for mine-waste calcines. Elevated concentrations of Hg in the extensive mine-waste calcine piles in ASSM possess the potential of releasing Hg into the local environment over a sustained period of time. The differences in extraction efficiency of Hg from cinnabar ore of different grain size and different furnace types resulted in variations of Hg concentration and isotopic composition in the mine-waste calcines (Čermak-Spirek calcine d202Hg average of 0.52% and concentration range of 32 to 1500 ug/g; Gould and Pacific d202Hg average of -0.58 and concentration range of 25 to 130 ug/g). Mass independent fractionation (MIF) has also been reported for Hg isotope ratios and is attributed to photochemical reduction of aqueous HgI and MeHg. The contribution of Hg from chemical processes and weathering of legacy mine-waste calcine piles as well as initial Hg contribution from historical Hg ore processing has resulted in a wide range of Hg concentrations (0.48 ug/g to 1500 ug/g) and D202Hg and D199Hg isotopic compositions (-1.96% to 0.95%, -0.30% to 0.25% respectively). We will present an overview of Hg distribution and mobility using concentration and isotopic composition measured for a wide range of samples (cinnabar ore, calcines, sediment, soils, geothermal water, and fish) collected in the ASSM area.

1.3B Regional and local scale stable isotope studies in mercury biogeochemical cycling and bioaccumulation

IDENTIFICATION OF MERCURY SOURCES IN THROUGHFALL USING STABLE ISOTOPE SIGNATURES

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Throughfall is one of the main pathways of mercury (Hg) loading to forest ecosystem. The sources of Hg in throughfall, however, have not been well constrained by previous studies. In this study, concentrations and isotopic compositions of Hg in throughfall were obtained at an evergreen broadleaf forest site in southwestern China and a Boreal coniferous forest site in northern Sweden for one to 12 month periods. The mean concentrations of dissolve mercury (DHg) in wet-only precipitation and throughfall were 4.24 ± 0.30 and 11.43 ± 3.59 ng/L at the broadleaf forest site in southwestern China, respectively, and they were 2.52 ± 1.90 and 8.93 ± 2.24ng/L at the coniferous forest site in northern Sweden, respectively. The mean concentrations of particle mercury (PHg) in wet-only precipitation and throughfall were 1.06 ± 0.43 and 5.18 ± 1.94 ng/L at the broadleaf forest site in southwestern China, respectively. The increasing concentration in the throughfall indicated that Hg deposited on the canopy was wash-off by the precipitation. A significant positive correlation was observed between DHg concentrations and dissolved organic carbon concentrations (R2 = 0.71, P < 0.001) in the throughfall. This indicates that the major form of DHg in throughfall was carbon bounded Hg. A large difference in Hg isotopic compositions was observed between throughfall and wet-only precipitation. Mean Δ199Hg and Δ200Hg of DHg in wet-only precipitation at the two sites were 0.72 ± 0.32% and 0.24 ± 0.06%, respectively, which were much higher compared to that in throughfall (mean
Forest ecosystems.

Overall, this study highlights the governing role of atmospheric particulate bound mercury (PBM) but close to the values of atmospheric gaseous elemental mercury (GEM). A binary mixing model was applied and showed that GEM in atmosphere contributed approximately 60 \pm 14\% for DHG and 53\pm16\% for PHG in throughfall. We suggest that GEM deposited to vegetation leaves could be incorporated into throughfall during the wash-off processes. Overall, deposition of Hg by throughfall is more representative of GEM dry deposition.

**M.O.1.3B-3**

**STABLE ISOTOPE FRACTIONATION INDUCED FROM MERCURY BIOGEOCHEMICAL CYCLING IN FOREST ECOSYSTEMS**

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Forests mediate the mercury (Hg) biogeochemical cycling between the atmosphere and terrestrial ecosystems, while there remain substantial knowledge gaps regarding the cycling processes. Here, we determined the mass flow and isotopic compositions/fractionations associated with Hg cycling in the air-water-plant-soil compartments in an evergreen broadleaf forest site in Southwestern China to reveal mechanisms underlying the cycling of Hg. It is found that that annual Hg mass flow is \(-26.8\pm12.7\) μg m\(^{-2}\) year\(^{-1}\) for air-foliation Hg0 flux, \(6.7\pm20.5\) μg m\(^{-2}\) year\(^{-1}\) for air-soil Hg0 flux, \(9.1\pm12.2\) μg m\(^{-2}\) year\(^{-1}\) for bulk Hg deposition, \(31.8\pm10.6\) μg m\(^{-2}\) year\(^{-1}\) for throughfall Hg deposition, \(0.3\pm0.1\) μg m\(^{-2}\) year\(^{-1}\) for stemflow Hg deposition, and \(1.8\pm0.4\) μg m\(^{-2}\) year\(^{-1}\) for Hg runoff. Mass balance analysis using the flux data shows a 50.4±44.2 μg m\(^{-2}\) year\(^{-1}\) net atmospheric Hg sink. Interestingly, we observed the δ202Hg shift of 0 to -3.1\% between air and foliage as leaf age increases, and so for the Δ199Hg shift of 0 to -0.15\%. The observed isotopic composition of foliage Hg and isotopic shift support re-emission of Hg occurring after reductive loss from foliage. The δ202Hg shift cause by Hg evasion from soil in summer ranges -0.92\% to -0.23\% with a Δ199Hg shift from -0.25\% to -0.10\%; while in winter only δ202Hg shift is observed with range of -0.28\% to 0.41\%. Given the isotopic compositions found in soil pore gas (δ202Hg=-0.94±0.32\%), Δ199Hg=-0.49±0.07\% and Δ200Hg=-0.03±0.04\%) and ambient air (δ202Hg=0.26±0.20\%, Δ199Hg=-0.16±0.06\% and Δ200Hg=0.05±0.04\%), legacy Hg re-emission is largely caused by dark reduction processes in deep soil in summer, and by photo-reduction processes in surface soil in winter. Moreover, the distinctly negative Δ199Hg (range of -0.40\% in Oi to -0.47\% in Oa) and -0 Δ200Hg in organic soils indicate atmospheric Hg0 deposition is the dominant source of Hg in soil. Finally, we observed positive Δ199Hg (0.57±0.32\%) and Δ200Hg (0.22±0.06\%) in bulk precipitation, however, the Δ199Hg and Δ200Hg in throughfall (-0.34±0.20\% and 0.06±0.05\%), stemflow (-0.41±0.20\% and -0.04±0.08\%) and runoff (-0.40±0.08\% and -0.02±0.04\%) exhibit distinctly negative values. This suggests a significant atmospheric Hg0 source contribution in throughfall (60±13\%), stemflow (96±25\%) and runoff (89±23\%). Results from mass balance modeling show that atmospheric Hg0 deposition accounts for ~75\% of total atmospheric Hg deposition, ~2 times greater than values by the estimate from air-foliation/soil flux. Overall, this study highlights the governing role of atmospheric Hg0 deposition and re-emission processes in Hg cycling of forest ecosystems.

**M.O.1.3B-4**

**USING MERCURY ISOTOPE TO IDENTIFY SOURCES OF MERCURY AND METHYL MERCURY ACCUMULATING IN FOREST SOILS AND BIOTA ALONG A MONTANE ELEVATIONAL GRADIENT.**

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There is growing evidence that mercury (Hg) within upland forest soils can be transformed to methylmercury and biomagnified within terrestrial food webs. However, identifying the source(s) of mercury deposited to and transformed within forested ecosystems remains challenging. In this study, we used natural abundance Hg isotope analysis to assess the pathways of Hg deposition along a montane elevational gradient, and to trace sources of atmospheric Hg into the terrestrial food web on Whiteface Mountain in the Adirondack region of New York State, USA. Mercury isotope analysis indicates that soil Hg in all forest types (deciduous, coniferous, and alpine) is predominantly derived from foliar uptake of gaseous Hg that is deposited with litterfall. This is consistent with other forest Hg isotope studies, but stands in contrast to mass balance results indicating that throughfall inputs dominate in the coniferous and alpine zones at this study site. Based on an isotope mixing model, the amount of precipitation-derived Hg accumulating in forest soils was similar to throughfall flux estimates in deciduous forests, but approximately 20-30\% lower than throughfall flux estimates in coniferous and alpine zones. This discrepancy was consistent with isotopic signatures indicating increased photo-volatilization from coniferous and alpine soils, and may also suggest that a larger component of throughfall inputs in coniferous and alpine zones is derived from foliage, rather than precipitation. The fraction of precipitation-derived Hg was similar in forest soil and low trophic level soil invertebrates with low %MeHg. However, high trophic level soil invertebrates with high %MeHg typically had a greater fraction of precipitation-derived Hg. Songbird Hg isotopic signatures did not consistently overlap with soil invertebrate Hg isotope signatures, and the relative fraction of precipitation-derived Hg in songbird blood was more variable. Both of these observations suggest that songbirds may accumulate methylmercury from other sources in addition to forest soil invertebrates. Overall, our data suggest that precipitation-derived Hg is preferentially transformed to methylmercury and bioaccumulated in the food web of this forested ecosystem.

**M.O.1.3B-5**

**MERCURY ISOTOPE FRACTIONATION DURING FOREST BURNING IN THE AMAZON**

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Biomass burning is an important source of Hg to the atmosphere, being estimated as 13\% of total terrestrial emissions. Recent studies in the emissions of Hg during coal combustion observed that this type of...
process may result in Mass Dependent Fractionation (MDF), but no Mass Independent Fractionation (MIF) has been documented. However, the impacts of combustion in Hg isotopes has never been investigated during forest burning. To address that, we performed burning experiments in the Amazon rainforest, which is one of the main emitter of gases due to forest burning in the world. We chose two different localities in the Brazilian Amazon (Alta Floresta (AF) and Candeleias do Jamari (CJ)) and performed two different scales of experiments. Litter, ashes and soils samples were collected before and after burning. Samples were decomposed using strong acid and oxidant mixture under controlled temperature and pressure conditions (Hot-Block and High Pressure Asher). Their Hg isotopic composition was measured through CVG-MC-ICP-MS (Nu plasma). Accuracy and precision of the methods were evaluated using QA/QC protocols and certified reference materials well documented in the literature. For AF, where small scale experiments were performed, no differences were found in the mercury isotopic composition between the samples before and after burning. For the larger scale experiment in CJ, litter, ashes and soils before burning differed significantly from each other in terms of MDF - δ202Hg (δ202Hg for litter, ashes and soils before burning, respectively, -1.63 ± 0.16 ‰ (N=10); -1.78 ± 0.10 ‰ (N=9) and -2.06 ± 0.10 ‰ (N=13)). Regarding MIF, ashes and soils presented similar Δ199Hg results (respectively, -0.58 ± 0.06 ‰ (N=9) and -0.59 ± 0.03 ‰ (N=13)) while litter presented greater values (Δ199Hg = -0.37 ± 0.05 ‰ (N=10)). All the samples presented Δ200Hg close to 0. Hg isotopic composition in soils before and after burning did not differ significantly (P=0.89). Similar odd-MIF pattern obtained for ashes and soils suggests that the main source of the Hg found in the ashes come from soils, while the Hg from litter is almost totally emitted to the atmosphere. In this sense, a slight enrichment of 6202Hg in the ashes compared to the soils, confirm that such MDF is induced by the volatilization of lighter isotopes in burning litter. This work highlights the potential of Amazonian biomass burning to cause Hg isotopic fractionation, which directly depends on the extent of the burning process.

2.7 Human Exposure and Health effects of Methylmercury

DIETARY CORRELATES OF METHYL MERCURY IN SEAFOOD CONSUMERS AND NON-SEAFOOD CONSUMERS

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Methyl mercury (MeHg) exposure is of concern due to the neurotoxicity of MeHg, particularly among children. Fish and seafood consumption is the largest dietary source of MeHg. However, most studies have estimated correlates of total mercury, not methyl mercury, and studies assessing dietary correlates of mercury among non-seafood consumers are limited. Therefore, we determined dietary correlates of whole blood MeHg in a cross-sectional analysis of 2011-2012 United States National Health and Nutrition Examination Survey data, stratified by self-reported seafood consumption within the past 30 days. 5427 (75.4%) children and adults reported eating fish/seafood in the previous 30 days and 1770 (24.6%) did not. MeHg was determined using ICP-MS. Dietary correlates of MeHg were assessed using a 24-hour dietary recall conducted by trained interviewers. Foods which were highly correlated were combined into larger categories prior to inclusion in regression models. Multivariable regression models predicting natural-log transformed MeHg included covariates for age, sex, education, race/ethnicity and self-reported consumption of fish or shellfish (in past 24 hours); beans, nuts or soy; Asian foods; soup; mixed rice dishes; rice; red or leafy vegetables or vegetable oil; beer; wine; and liquor. Geometric mean MeHg was 0.67 µg/L (95% confidence interval (CI): 0.57, 0.80) and 0.17 µg/L (95% CI: 0.16, 0.19) among seafood consumers and non-consumers, respectively. In multivariable regression models including seafood consumers, self-reported consumption of fish/seafood in prior 24 hours (β: 1.23; 95% CI: 0.50, 1.96), soup (β: 0.42; 95% CI: 0.10, 0.73), rice (β: 0.35; 95% CI: 0.05, 0.66), red/leafy vegetables or vegetable oil (β: 0.43; 95% CI: 0.08, 0.78) and wine; (β: 1.00; 95% CI: 0.57, 1.43) were significantly associated with higher blood MeHg. Among non-seafood consumers, the only food item significantly associated with MeHg was wine (β: 0.84; 95% CI: 0.06, 1.26). Our results are similar to previous research which has identified rice and vegetables as potential non-seafood sources of mercury exposure. Wine was the only food category significantly associated with MeHg concentration among non-seafood consumers; additional research on wine as a potential source of MeHg exposure is recommended.

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GENETIC DISPOSITION TO DEVELOPMENTAL METHYLMERCURY NEUROTOXICITY

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Some common heterogeneities are thought at affect methymmercury kinetics in the body and perhaps also neurodevelopmental outcomes of prenatal methymmercury exposure. We examined the suspected heterogeneities for modification of exposure-related cognitive development in 2,172 children from the Avon Longitudinal Study of Parents and Children (Bristol, UK) (ALSPAC). Prenatal methymmercury exposure was determined from the total mercury concentration of cord tissue. Neuropsychological function was determined by the Wechsler Intelligence Scale for Children Intelligence Quotient (IQ) score at age eight years. Data was available on 247 single-nucleotide polymorphisms (SNPs) within relevant genes. In this population with low-level methymmercury exposure, the log10-transformed mercury concentration appeared to be positively associated with IQ, although adjustment cofactors attenuated this association. Among four SNPs found in a pilot study to exhibit interaction methymmercury neurotoxicity, one was replicated, i.e., the minor allele of rs1042838 (progesterone receptor), with a beta (95% confidence interval) of 11.8 (-23.0, -0.7) (p for interaction, 0.004). Despite the low exposure level, the PGR minor allele revealed a strong negative association between methymmercury exposure and IQ. The relevant SNPs will be determined in a Faroese birth cohort with much higher prenatal methymmercury exposures to ascertain whether the genetic predisposition can be replicated. As the PGR minor allele is fairly common in Caucasian populations, the results suggest that this genetically predisposed subpopulation carries the brunt of neurobehavorial toxicity from developmental methymmercury exposure and that current exposure limits may not provide sufficient protection for this vulnerable group.

NEUROPSYCHOLOGICAL TESTS USED TO ASSESS METHYLMERCURY DEVELOPMENTAL NEUROTOXICITY

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Methymmercury is a well-known developmental neurotoxicant. In an effort to evaluate studies published since the release of the U.S. EPA IRIS Methymmercury Assessment in 2001, which was based on an assessment by the National Academy of Sciences (NAS) in 2000, a recent literature search was conducted for studies assessing the effects of methymmercury exposure on developmental neurotoxicity (DNT) in humans. DNT was the focus of the literature search because DNT endpoints were used to derive the Reference Dose in the 2001 Methymmercury IRIS Assessment. PubMed, Web of Science, ToxNet, and Science Direct were searched to find studies. The software tools, SWIFT© and Distiller©, were used to screen the studies, which resulted in the identification of more than 200 epidemiological studies that evaluated DNT effects and provided quantitative exposure-response data. Several neurodevelopmental endpoints were evaluated in the studies, including: cognition (e.g., verbal ability, nonverbal ability, executive functioning, attention, visual-spatial processing, learning/memory, IQ), motor function, sensory function, mood/affect/personal regulation, and clinical diagnoses of Autism Spectrum Disorder and Attention Deficit/Hyperactivity Disorder. Many different neuropsychological tests, including multiple versions of the same test (e.g., Bayley Scales) and numerous subtests (e.g., Wechsler Intelligence Scale for Children (WISC) III), were used to assess the neurodevelopmental endpoints. Some of the more common neuropsychological tests were Bayley Scales of Infant and Toddler Development-II, Brazelton Neonatal Behavioral Assessment Scale, California Verbal Learning Test, McCarthy Scales of Children’s Abilities, Neurobehavioral Evaluation System 2, and WISC III. However, some tests were less common and only appeared in one study (e.g., Test of Haptic Matching), and others were commonly used tests that were adapted for non-U.S. populations (e.g., WISC III modified for Inuit children). Many factors, such as the appropriateness of tests for other cultures and/or populations than those for which they were originally designed and the conditions under which the tests were given (e.g., distraction-free testing site and well-rested children), will need to be considered. Therefore, specific guidelines are being developed to assist in determining the validity and reliability of each test as it is used in individual studies.

Disclaimer: The views expressed in this presentation are those of the authors and do not necessarily reflect the views or policies of the US EPA.

LOW-LEVEL MERCURY EXPOSURE, NEURODEVELOPMENT AND THE ROLE OF GENETIC POLYMORPHISMS: FOLLOW-UP OF THE SLOVENIAN AND CROATIAN BIRTH COHORTS

SNOJ TRATNIK, Janja1; FALNOGA, Ingridi; TRDIN, Ajda1; MAZEJ, Darja1; NEUBAUER, David2; PPRIĆ, Igor3; ŠPIRIT, Zdravko4; HORVAT, Milena1

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an initial review of the literature. These include what form of mercury was evaluated in analytical measurements, which biomarkers of exposure were used in the study, and what methods were used to address confounding in epidemiological studies. 

Disclaimer: The views expressed in this presentation are those of the authors and do not necessarily reflect the views or policies of the US EPA.
This prospective birth cohort study was set to investigate an association between prenatal mercury (Hg) exposure at low to moderate levels and neuropsychological performance taking into account variability in relevant genes as potential internal exposure or effect modifiers. Gene polymorphism of apolipoprotein E (APOE), brain derived neurotrophic factor (BDNF), paraoxonase (PON1), catechol O-methyltransferase (COMT), coproporphyrinogen oxidase (CPOX) has been selected due to their potential role in metal binding and/or implication in brain development processes. Mother-child pairs were recruited from the central Slovenia region (n=601) and Rijeka, on the Croatian coast of the northern Adriatic (n=243). Determination of total Hg and other elements in cord blood, Bayley Scales of Infant and Toddler Development, Third Edition (Bayley III) assessment at 18 months of age and genotyping was done in total of 361 children. In the follow-up, 179 children from Slovenia and 34 form Croatia were re-sampled at the age of 7-8 years and re-assessed for neuropsychological performance using Wechsler Intelligence Scale for Children (WISC-IV). Information on mother’s and child’s diet, living environment, potential exposure and maternal life-style was obtained through questionnaires. Associations between Hg levels and neuropsychological performance was evaluated using multiple linear regression, stratified by the genotype. Prenatal Hg exposure ranged from 0.16 to 10.0 ng/g (GM 1.58 ng/g) in cord blood of Slovenian children, and from 0.79 to 32.3 ng/g (GM 3.41) in Croatian children, while the exposure at 7-8 years of age from below limit of detection to 4.17 µg/L (GM 0.44 µg/L) in blood of Slovenian children, and from 0.06 to 7.05 µg/L (GM 0.68 µg/L) in Croatian children. The majority of the children had Bayley scores and Full Scale Intellgence Quotient of the WISC assessment within the normal limits. Data evaluated so far showed significant negative association between ln transformed Hg levels in cord blood and cognitive composite score (β=−5.44, p=0.043) in children carrying at least one APOE e4 allele. Moreover, carriers of variant alleles for CPOX, BDNF and PON1 showed negative associations between prenatal Hg levels and cognitive scores, while the associations in carriers of common alleles were neutral or positive. However, none of associations was statistically significant, borderline significance was revealed for CPOX variant allele carriers only. The work is still on-going, however, the results presented indicate that stratifying for specific genotypes is crucial in identifying susceptible population groups exposed to low levels of Hg.

Of course in an event of high input of reducing agent (e.g.SO2), the ionic(dissolved)Hg compounds transformed to elemental Hg0. In this case a Hg-gas blow out is happened. In case of a mercury event, the mercury breaks through the scrubber and contaminates the subsequent purification stages. Hg0 deposits can be bleed out all the time and generate a "baseline" of Hg-emission, only a few µg below the current limits. But the environment is continuously contaminated and poisoned with tons of Hg/year.

The use of a special inorganic polymeric sulfur compound in an acidic scrubber or FGD plant produces only nonsoluble non-toxic HgS. HgS is chemically and thermally very stable. Therefore, HgS can be treated both in a classic sewage treatment and in a spray dryer. Here is the most efficient point for all Mercury compounds, where it’s allowed to leave the plant.

As non toxic HgS
With this technology, it is made impossible to form an internal dissolved Hg cycle in the scrubber system. Unexpected events can be buffered. There're no Hg-blow outs possible.

This is an effective way to separate mercury from a scrubber system. The special inorganic polymeric sulfur liquid (NETfloc SMF1) is easy to apply into any scrubber systems.

Regular analyzes of the mercury balance (Hg dissolved/Hg insoluble) in the scrubber help to determine the optimum dosing level for best cost efficiency.

The German Umwelt Bundesamt (UBA) has tested HgS as the best choice for deposition of mercury compound in underground dumps.

### 3.6B Mercury Emissions Reductions – A Challenge to Industry

**M.O.3.6B-1**

**FROM TOXIC MERCURY TO NON-TOXIC MERCURY COMPOUND**

**SCHARRENBACH, Frank**<sup>1</sup>; **FRITZSCHE, Jürgen**<sup>1</sup>  
(1)New Environmental Technology GmbH

In every thermal combustion plant you can measure and detect mercury from the scrubber through the flue gas to the chimney up to the environment.

As a standard treatment, activated carbon/coke is used to adsorb the mercury. The loaded adsorbent is disposed on a landfill. In terms of gas limit values, this system works well. But not for a sustainable, holistic treatment. Mercury leach out and forms by microbiology, organic mercury.

Mercury becomes even more toxic. For this reason, mercury must be removed as nonsoluble HgS from this cycle. HgS is a natural mineral, called cinnabar. And the only non-toxic mercury compound.

Scrubber systems have an opportunity to buffer and store mercury salts (e.g. HgCl2/HgCl4) in high saturation. Under normal conditions the systems are running stable, with no risk of Hg0-gas blow out. But the concentration of dissolved mercury is the magnitude of influence for a Hg0-blow out event.

**M.O.3.6B-2**

**BALANCING MERCURY IN THE GERMAN CEMENT INDUSTRY**

**HOENIG, Volker**<sup>1</sup>; **HARRASS, Robin**<sup>1</sup>  
(1)VDZ

In the past two decades, public awareness of mercury as a harmful environmental toxin has grown strongly and has moved into the spotlight of political and social discussion at both national and international levels. Against the background of the Minamata convention and its ongoing implementation in the EU member states, the German Environment Agency is elaborating proposals for a national abatement strategy. In the light of this, VDZ, with wide support from its member plants, has drawn up a mercury balance for the entire German cement industry to clarify the input and output pathways of mercury in cement production. It is based on more than 5,300 analysis data on solids from the incoming and outgoing raw materials, fuels and products, as well as data on air emissions, which are almost exclusively continuously monitored.

The balance result supports the cement industry’s long term experience that over 60% of the mercury input enters the process through the raw materials and less than 40% through the fuels. About 60% of the output of mercury occurs through the products and about 40% through the emissions to air. The levels of mercury in the cements of 0.016 to 0.048 mg/kg (arithmetic means for CEM I–III) are low and are of the same order of magnitude as in the natural raw materials used in cement production. Stack emission concentrations were 12.9 µg/m³ as a yearly industry average. In order to ensure that emissions from cement mills do not falsify the balance result (as most German cement plants apply dust shuttling technology), long-term investigations at several cement mills (closed-circuit grinding) were performed. Their results show that the mercury concentration in the exhaust air lies at a negligibly low level in the range of uncertainty of the method of measurement (approx. 2 µg/m³).

Generally, there is always the risk of a fairly large level of uncertainty of a material balance if large mass flows are linked with very low concentrations. The main raw materials limestone, marl and chalk as well as granulated blast-furnace slag show low mercury concentrations with numerous analytical values below the limit of quantification of the respective method of analysis. Nevertheless – due to the vast number of available data – the mercury balance is essentially closed for the “most probable” average case.
OPTIMIZING MERCURY CONTROLS IN COAL COMBUSTION POWER AND CEMENT PRODUCING PLANTS

MASHYANOV, Nikolay R.  
(1) Ohio Lumex Company

Over the course of its 15 years of industry experience, Ohio Lumex has developed a variety of measurement techniques, products, and services which provide coal-fired utilities and cement kilns with effective means for reducing mercury emissions. The data provided by these measurements has been critical in helping the affected industries minimize operating costs required to meet regulatory limits, via optimization of control technologies and injected materials.

Mercury sorbent traps and portable sorbent trap analyzers allow for quick and reliable on-site and accurate determination of total mercury concentration as well as mercury oxidation ratio, in any sampling environment from the SCR inlet to the stack. Sorbent traps have become the industry standard, and are well-renowned for their self-validation criteria, ease of use, and reliability. In addition to mercury sorbent traps, Ohio Lumex has designed sorbent traps to measure a variety of common analytes of interest, such as NH3, SO3, HCl, HBr, Se, and As. Portable mercury speciating monitors yield real-time total and oxidized mercury data, and are designed to function for extended durations in nearly any sampling environment. Permanent mercury monitoring systems are generally installed in stacks or at the inlet to FGDs, and are equipped to send live mercury data directly to the plant’s data integration system.

Hundreds of engineering studies have utilized these technologies and have demonstrably reduced the cost of mercury abatement via tuning of plant control technologies as well as optimized injection rates of activated carbon, dry sorbents, calcium bromide, sulfides and other materials.

STUDY ON THE EFFECTIVENESS OF SELECTED METHODS OF REMOVING MERCURY FROM LIGNITE FLUE GASES

KOGUT, Krzysztof; GÓRECKI, Jerzy; MARCZAK, Marta; WIEROŃSKA, Faustyna; BURMISTRZ, Piotr; SMÓŁKA, Boguslaw
(1) AGH University of Science and Technology, Faculty of Energy and Fuels  
(2) JSW Innowacje S.A.

In Poland, the largest share in anthropogenic mercury emission to the atmosphere is generated by the combustion of solid fuels (electricity production), which amounts to 77.8%. Analyzing the structure of emissions in the countries of the whole European Union, this share is much lower and amounts to 63.4%.

Taking into account the structure of electricity generation, the largest share is held by lignite-based generation units. Given the higher mercury content of lignite compared to bituminous coal and the less favourable elementary composition, dedicated methods to remove mercury compounds from exhaust gases are necessary.

The methods used to remove mercury, both primary and secondary methods, have been presented on the basis of the conducted research. For secondary methods (dedicated to mercury removal), the efficiency of the methods, their advantages, disadvantages and limitations are discussed.

INVESTIGATION ON MERCURY EMISSION FROM CHINESE CEMENT SECTOR AND ITS WHOLE-PROCESS ASSESSMENT

LI, Juan; ZHOU, Chunyong
(1) China Building Materials Academy

The cement sector is the fourth biggest source of anthropogenic mercury emission. It has been estimated that the cement industry contributes with 9% or about 173 metric tons to the estimated total of 1921 metric tons per year of global anthropogenic mercury emissions according to UNEP report. China produced around 60% of the world’s cement since 2012. Thus, the cement industry has become a more important source of mercury emissions even while technologically advanced new plants may have lower emission factors. The worldwide average emission factor for mercury from cement kilns is around 35 mg/t cement.

This article describes a Project Baseline Investigation of Mercury Emission from Chinese Cement Sector and Its Whole-process Control funded by UNIDO, aiming to reduce mercury emissions from cement sector in an efficient, effective and coherent manner, and to protect the human health and environment. Mercury enters in the kiln system are mainly from natural and alternative raw materials as well as conventional and alternative fuels. So, the easiest means to reduce mercury emissions may be to reduce the total inputs into the kiln system. The existing data shows that the average mercury content of raw meal is 0.031 mg/kg-clinker, in which the limestone can often account for the majority of the mercury input. The average mercury content of fossil fuels is 0.010 mg/kg. However, the concentration of mercury in raw materials and fuel can vary significantly, hence, it is important to know the mercury content of each raw material as well as its variability. In this project, it is monitored the sources of mercury from raw materials and fuels from around 30 selected representative cement plants, as well as mercury emissions from different process outlets from 5 cement lines in different regions of China. The testing samples include limestone, raw meal, kiln feed, kiln dust, coal, cinder and cement from each cement line. Mercury levels in raw materials and fuels are determined by Automatic Isokinetic Sampler in accordance with GB30760-2014 Technical Specification for Coprocessing of Solid Waste in Cement. Mercury emission from whole process are evaluated with Ontario Hydro Method. The results will identify the mercury emission dependent on inputs of various materials and fuel and typical process, and clarify the behavior of mercury in cement clinker production process.

MERCURY RELEASED FROM MERCURY CONTAMINATED STEEL DURING SMELTING

ANDREW, Mark; KIRBY, Matthew; BAKER, Stuart; BOWER, Matthew; WALLS, David

Many oil and gas producing regions that have aged assets, coupled with lower reserves of petroleum resources, has led to the implementation of decommissioning activities for these facilities. Mercury is ubiquitous in oil and gas reservoirs and it is well documented that mercury will deposit onto the internal process infrastructure via several mechanisms including chemisorption, adsorption, precipitated scale deposits (e.g. HgS) and co-precipitation with other scale (e.g. iron oxide). Thus, aged facilities that have reached the end of their operational life and are selected for decommissioning may pose a serious risk to health and the environment.

Decommissioning offshore assets is a comprehensive process that envisposes:
- Platform preparation
- Well plugging and abandonment
- Removal of conductor casing
- Topside removal of rig / platform
- Pipeline and power cable removal
- Material disposal

The entire process needs to be sustainable with minimal impact on the environment and as much recycling of the materials as is practically possible. This presentation details work carried out to better understand the potential mercury exposure to workers and releases to the environment during the smelting of mercury contaminated scrap steel.
4.2 Global and Local policies to inform decisions making and reduce exposure

M.O.4.2-1

ANALYSIS OF NATIONAL PRIORITIES FROM MINAMATA INITIAL ASSESSMENTS

Toda, Eisaku¹ (1)Secretariat of the Minamata Convention on Mercury, United Nations Environment Programme

One important purpose of Minamata Convention Initial Assessments (MIAs) is to identify challenges to implementation of the Minamata Convention, and capacity building, technical assistance and other needs. MIA reports are key documents in planning for capacity building and technical assistance activities, including projects funded by the Specific International Programme.

The guidance document developed by UNDP in cooperation with other intergovernmental organization recommends the submission of MIA reports to the Secretariat of the Minamata Convention. The secretariat makes submitted MIA reports available on the Convention website. As of 1 March 2019, MIA reports have been received from 26 countries: Benin, Burkina Faso, Cameroon, Comoros Costa Rica, Dominican Republic, Ethiopia, Jamaica, the Gambia, Guinea, Guyana, Lesotho, Madagascar, Mali, Mexico, Moldova, North Macedonia, Nigeria, Saint Kitts and Nevis, Saint Lucia, Senegal, the Seychelles, Tanzania, Trinidad and Tobago, Uganda, and Zambia. The submitted MIA reports are a valuable source of information for identifying the global challenges and needs of the developing countries and countries with economies in transition in the implementation of the Convention.

A preliminary analysis of the national priorities described in the 26 submitted MIA reports shows that mercury-added products (Article 4), and mercury wastes (Article 11) are priorities for most countries. More than half of the countries that mentioned their priority areas also included artisanal and small-scale gold mining (Article 7) and emission (Article 8) in their priority list. Releases (Article 9), health aspects (Article 16), awareness raising (Article 18) and research and monitoring (Article 19) were also identified as priority by several countries. Many countries also listed the development of institutional and regulatory framework as one of the priority actions. Some countries identified specific sectors, such as non-ferrous metal production, cement production, waste incineration and dental amalgam. Some countries have not identified priority actions in their MIA reports.

MIA projects are still underway in more than 100 countries. As more MIA reports become available, further analysis will become possible together with their inventory data, which will contribute to the efficient allocation of resources for capacity building and technical assistance, and thus to the effectiveness implementation of the Minamata Convention.

A proactive environment is characterized by a fully interactive environment where the user can control and schedule analyses, design workflows, integrate different data sources and execute assessments. In other words there is the need to bring data to knowledge. The Conference of Parties (COP) and specifically the established ad-hoc group of the Minamata Convention on Mercury (MCM) is working to prepare the effectiveness evaluation of MCM implementation. As detailed in the Report of the ad hoc group of expert on effectiveness evaluation (UNEP/MC/COP.2/INF/8, http://www.mercurycovation.org/Meetings/COP2) it is necessary to provide comparable data on global basis, make them available through interoperable systems and enhance their discovery and use. Under the activity of the Group on Earth Observation (GEO), the Flagship Global Observation System for Mercury (GOS4M) was launched, which is part of the GEO Work Programme (2016-2025). GOS4M is aimed to support all interested Parties in the implementation of the MCM. The core objective of the GOS4M business plan is to support the Nations, MCM Secretariat, UN Environment and others interested Parties and Stakeholders to contribute to the fulfillment the COP decisions and requests related to, but not limited to, capacity-building and technical assistance to developing country Parties (Article 15), research, development and monitoring (Article 19) and Effectiveness Evaluation of the convention (Article 22). The overarching goal of GOS4M is to promote actions aiming to provide comparable global monitoring mercury data, validated modelling frameworks and assessment tools. Therefore GOS4M is developing a Knowledge Platform (G-KP), an integrated solution of high quality observational data, model output and digital tools to respond closely to specific needs, and address major knowledge gaps. The G-KP is based on five knowledge elements: i) Data Collection/Elicitation; ii) Data Formalization/Encoding; iii) Data Sharing; iv) Data Use; and v) Data Generation. This work presents the state-of-art of the G-KP and its potential for effectiveness evaluation of MCM.

M.O.4.2-2

THE KNOWLEDGE PLATFORM OF THE GLOBAL OBSERVATION SYSTEM FOR MERCURY (GOS4M): A PROACTIVE ENVIRONMENT FOR DECISION-MAKERS

Cinnirella, Sergio¹ D’Amore, Francesco¹ Bencardino, Mariano¹ Bruno, Delia Evelina¹ Sprovieri, Francesca² De Simone, Francesco¹ Hedgecock, Ian Michael¹ Pirrone, Nicola¹ (1)CNR-Institute of Atmospheric Pollution Research, Rende, Italy

Provision of observational and modelled data on mercury in the environment do not fully meet the needs of decision-makers in their assessments as both observation and prediction (i.e. scenario) are most often pre-processed by domain experts. Current tools are laid out as tables, graphs, maps, and despite the introduction of the digital paradigm such tools remain static without offering a proactive environment for decision-makers.

In 2016, the Global Environment Facility (GEF) approved the development of the Programme entitled: “Global Opportunities for the Long-term Development of the Artisanal and Small-Scale Gold Mining sector” or GEF-GOLD. The Programme is led by the United Nations Environment Programme (UNEP) and aims to reduce the use and emissions of mercury by the sector in eight countries: Burkina Faso, Colombia, Guyana, Indonesia, Kenya, Mongolia, Peru and the Philippines. The Programme has four components: 1) formalization of the sector 2) improving access to finance and access to formal markets for the miners 3) transfer of non-mercury alternatives and 4) knowledge management and communication. The Programme was officially launched in London, United Kingdom in February 2019.

As a collaborative initiative, GEF GOLD calls for the involvement and participation of a wide range of partners to contribute to the four main components of the Programme. During the launch in London, investors and representatives from the gold consumer industries have expressed interest in working with us. However, further engagement of the scientific community is also important to achieve the goals of the program. In particular, scientific inputs from environmental and social scientists are required to assist in the implementation and to monitor and document the achievements.

Engineering expertise and science is needed to support the technology transfer component as the ideal solutions are often very site-specific.
and many options will have to be tried and evaluated. In the same vein, innovative and cost-effective tools for monitoring miners’ exposure to mercury and environmental mercury concentrations at mine sites will have to be developed. The results will not only contribute to the immediate monitoring of the project but also provide data to help evaluate the fate and transport of mercury from ASGM globally. Further, the inputs of social sciences will be important for the formalization and the access to finance components. Understanding the social-economic systems that either hinder or enhance formalization, and the social and governance barriers to the adoption of mercury-free techniques, will allow the Programme to tailor intervention to address them.

THE USE AND IMPACT OF FLEXIBILITY MECHANISMS IN MULTILATERAL ENVIRONMENTAL AGREEMENTS – INVESTIGATING PRACTICE AND IMPACT UNDER THE MINAMATA CONVENTION ON MERCURY

STEINDAL, Eirik H.1; LIN, Yan1; ROSENDAL, Kristin2; ANDRESEN, Steinar2; LARSSON, Thorjorn1

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When negotiating new multilateral environmental agreements (MEAs), delegates devote significant attention to the balance between depth versus participation. A prevailing one-dimensional assumption has been that more stringent obligations imply less ratifications and vice versa. However, scholars have over the years modified this picture, claiming that the dynamics are in fact multidimensional. The specific design of the MEA, including enforcement rules, organization and function, financial assistance and dispute settlement, are all aspects that may influence participation. Under the recently adopted MEA, the Minamata Convention on Mercury (MC), exemptions were introduced as a core flexibility mechanism, allowing Parties a permanent exemption for some specific types of use and temporary exemptions for a broad range of provisions. However, the need or potential impact of such mechanisms has not previously been assessed. This paper will investigate the use and the impact of the exemption mechanism under the MC, by analysing the requests and motivations for exemptions, which countries and why they have requested an exemption, its links to participation and its potential impact on actual reductions. The study will provide an empirical perspective from the MC of how flexibility measures are being applied and how they may influence the reduction potential and overall objective of the instrument.

INCORPORATING DIVERSE PERSPECTIVES ON THE HUMAN HEALTH IMPACTS OF METHYLMERCURY EXPOSURE INTO REGULATORY ENVIRONMENTAL ASSESSMENT

BARNARD-CHUMIK, Hannah1; GIANG, Amanda1

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Environmental policy choices are fraught with competing scientific, social, political, and cultural considerations. Although mercury exposure is a health risk of global concern, as evidenced by the Minamata Convention, it is not entirely evident how to translate scientific knowledge of mercury and methyl mercury exposure into policy and regulations that protect human health in a holistic manner that is relevant to local communities. This research explores how multi-disciplinary knowledge about the human health impacts of methyl mercury exposure is used in the regulatory decision-making process.

The case study of interest is the Muskrat Falls hydroelectric project in Labrador, Canada. During the project implementation phase, there was a lack of consensus among stakeholders regarding the potential increases in exposure to methyl mercury and the subsequent health impacts – particularly for downstream Indigenous communities consuming country foods. This case illustrates how contradictory scientific evidence and competing cultural values can lead to controversial decision-making outcomes. We use qualitative discourse analysis to elicit the scientific and decision-making rhetoric surrounding the controversy from the perspectives of multiple stakeholders. Discourse analysis connects language use in text documents to broader social themes, which reveals important perceptions about whether environmental policies are adequately protecting human health from risks like mercury exposure. We use qualitative coding to elicit discourses present in the academic literature, the grey literature, news articles, and interviews with key stakeholders. Through this analysis, we explore themes such as how human health is defined by different stakeholders, what is considered adequate scientific evidence for policy-making, and the scientific and cultural thresholds of significant adverse health impacts from methyl mercury exposure. Preliminary findings indicate that health impacts included in the regulatory assessment of the project did not reflect the health concerns of the community. This work contributes to the exploration of future mercury reduction policy avenues that incorporate balanced perspectives from multiple stakeholders.
ORAL ABSTRACTS

Tuesday 10th September 2019
1.7A Sources and cycling of mercury in freshwater ecosystems and oceans

T.O.1.7A-1

A COMPREHENSIVE MERCURY MODEL FROM ANTHROPOGENIC EMISSIONS TO BIO-ACCUMULATION IN FISH

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Five decades of Hg science have shown the tremendous complexity of the global Hg cycle. Yet, the pathways that lead from anthropogenic Hg emissions to MeHg exposure through sea food are not fully comprehended. Moreover, the observed amount of MeHg in fish exhibits a large temporal and spatial variability that we cannot predict yet. A key issue is that fully speciated Hg measurements in the ocean are difficult to perform and thus we will never be able to achieve a comprehensive spatial and temporal coverage.

Therefore, we need complex modeling tools that allow us to fill the gaps in the observations and to predict future changes in the system under changing external drivers (emissions, climate change, ecosystem changes). Numerical models have a long history in Hg research, but so far have virtually only addressed inorganic Hg cycling in atmosphere and oceans. Moreover, current models are limited to certain scales (e.g. global models, box models) and compartments (e.g. atmosphere, ocean) and thus are unable to explicitly resolve all relevant processes and to capture intra-scale feedbacks and emerging properties of this complex system.

Here we present a novel 3d-hydrodynamic mercury modeling framework based on fully coupled compartmental models including atmosphere, ocean, and ecosystem. The generalized high resolution model has been set up for different European and Arctic ocean domains and was used to model the transition zone from estuaries to the open ocean. Based on this model we present our findings on intra- and inter-annual dynamics and variability of mercury speciation and distribution in the coastal ocean. Moreover, we present the first results on the dynamics of mercury bio-accumulation from a fully coupled marine ecosystem model. Most importantly, the model is able to reproduce the large variability in methylmercury accumulation in higher trophic levels.

T.O.1.7A-2

SUB-MESOSCALE VARIABILITY OF VOLATILE ELEMENTAL MERCURY IN SURFACE WATERS OF THE BALTIC SEA

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A recent balance of global mercury fluxes revealed that anthropogenic emissions of 2.5 Gg mercury compare to oceanic emissions of about 3.4 Gg mercury to the atmosphere annually. However, the temporal and spatial variability of the marine emission is hidden behind the latter number. A suitable approach to better understand mercury emissions by the sea is to measure the flux driving sea-air concentration difference of elemental mercury (Hg0).

For the Baltic Sea it is shown that the Hg0 concentration variability in surface waters is of sub-mesoscale character. This is likely caused by inhomogeneous exposure time of water parcels to light, as the main reason for transformation (~60%) of inorganic Hg to volatile Hg0. About half of this is converted by light-dependent biotic processes of mainly cyanobacteria and half is transformed by pure photochemistry as incubation experiments revealed. Low-light transformation of probable biotic origin account for the rest (~40%). The observed features are thus likely controlled by hydrographic flow patterns visible in satellite images of chlorophyll_a and of surface water temperature. Especially, upwelling during summer months is well observable by temperature anomalies, indicating transport of a colder water mass, often of less than 10°C from deeper layers to the photic zone. These waters are low in Hg0 and light subsequently causes abiotic transformation of mercury.

Moreover, upwelled water masses reflect nitrate depletion but hold a phosphate residue. Subjected to warming and favorable light conditions during summer, blooms of diazotrophic cyanobacteria and light-dependent biotic transformation of mercury are initiated. The equilibrium concentration of Hg0equ was measured at high-resolution by a membrane equilibrator and for validation by a bottle equilibrator on seawater continuously pumped from the surface mixed layer into the ship’s lab. The atmospheric Hg0atm was determined from outside air. The Hg0 concentration difference in the water side boundary layer was subsequently calculated with H, the Henry’s Law constant of Hg0: (Hg0equ - Hg0atm)/H = δdeltaHg0/H. The Hg0 flux was then estimated by using the sea-air transfer velocity kHg0 for Hg0 that depends on wind speed FHg0 = kHg0δdeltaHg0/H. The aim is to show the strong variability of the deltaHg0 sea-air based on a large data-set of seven Baltic Sea research campaigns between 2011 and 2015 obtained from high-resolution surface water measurements supplemented by a case study in an upwelling area and incubation experiments.

T.O.1.7A-3

DARK REDUCTION SETS EVASION OF MERCURY FROM THE OCEAN

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Much of the surface water of the ocean is supersaturated in elemental mercury (Hg0) with respect to the atmosphere, leading to sea-to-air transfer or evasion. This flux is large, and nearly balances inputs from the atmosphere, rivers and hydrothermal vents. While the photochemical production of Hg0 from inorganic and methylated mercury is reasonably well studied and can produce Hg0 at fairly high rates, there is also abundant Hg0 in aphotic waters, indicating that other important formation pathways exist. Here, we present results of gross reduction rate measurements, depth profiles and diel cycling studies to argue that in addition to the better studied photochemical reactions, dark reduction of Hg2+ is also a fairly rapid reaction and is capable of sustaining high Hg0 concentrations even in the open ocean mixed layer. Furthermore, in locations where vertical mixing is substantially deeper than the vertical penetration of UV-B and Photosynthetically Active Radiation (the principal forms of light involved in abiotic and biotic photoreduction), dark reduction will contribute the majority of Hg0 produced or delivered to the surface ocean. Our measurements and modeling suggest that these conditions are met nearly everywhere except at high latitudes during local summer. Furthermore, the residence time of Hg0 in the mixed layer with respect to evasion is longer than that of reduction-oxidation, a situation that allows dark reduction-oxidation to effectively set the steady state concentration of Hg0 in surface waters. The nature of these dark redox reactions in the ocean was not resolved by this study, but our experiments suggest a likely mechanism or mechanisms involving enzymes and/or important redox agents such as reactive oxygen species and Mn(III).
Current models of the global mercury (Hg) cycle suggest minor importance of Hg sequestration in marine pelagic sediments. We investigated Hg accumulation in biogenic siliceous sediments (diatom-ooze) based on high resolution (10-20 years) cores taken at three sediment basins around Antarctica: Adélie Basin (AB) (IODP318-U1357), Prydz Bay (PB) (ODP119-740) and Palmer Basin (PB) (ODP178-1098). Based on our sediment data, mean global diatom-ooze sedimentation rates and on the sequestration of biogenic silica in the oceans we estimated global Hg accumulation in diatom-ooze. Diatom-ooze sediments exhibit the highest Hg accumulation rates (up to 1800 μg m⁻² yr⁻¹) ever reported for the marine environment and provide a large Hg sink (17-1309 Mgyr⁻¹), potentially surpassing model estimates (190 Mg yr⁻¹) for ocean Hg sequestration up to a factor of 6.8.

Anthropogenic pollution of the Antarctic oceans starts ~150 years ago and our estimates suggest that 0.3 to 20% of the Hg emitted to the atmosphere during this period could have been stored in diatom-ooze alone. Indications of a global influence of Hg emissions from gold and silver mining in the Americas before 1850 and during 1850 and 1910 as estimated in recent models were not found in our cores questioning the influence of Hg emissions from colonial gold and silver mining and legacy Hg in the Southern Hemisphere.

Our data indicates that previous studies have potentially underestimated the importance of Hg scavenging by microalgae as a fast and important vector for Hg sequestration in the oceans.
1.2B Biogeochemical cycling of mercury in the aquatic ecosystems

T.O.1.2B-1

MERCURY INTERACTIONS AND TRANSFORMATIONS IN THE PRESENCE OF NANOPARTICLES

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Mercury (Hg) and methylmercury (MeHg) bind strongly to particles and this partitioning impacts their fate and bioaccumulation into food webs, and, as a result, potential human exposure. This partitioning has been shown to influence the bioavailability of inorganic Hg to methylating bacteria, and studies have shown that Hg bound in nanoparticle (NPs) is more bioavailable than inorganic (cinnabar) or organic particulate-bound Hg. Also, it has been shown that binding of MeHg to the surface of metal sulfide particles resulted in its transformation into dimethylmercury (DMeHg). While previous studies have focused on NPs with a HgS core, there is also the potential for Hg to associate with other NPs, either due to incorporation into the matrix of the NP, or due to surface absorption. Overall, as there has been little study of the role of natural or manufactured NPs in influencing the transformation, bioavailability and transport of Hg and MeHg in natural waters, we set out to investigate the potential interactions between Hg and MeHg and various NPs (CdS, CdSe, and CdTe/ZnTe). We examined whether the interaction of Hg with the NPs, demonstrated by the reduction in their fluorescence upon titration with Hg, was due to incorporation of Hg into the core of the NP (metal exchange or surface precipitation), or due purely to surface interactions. Analysis based on ICP-MS of CdSe NPs and the separated solution, after titration with inorganic Hg showed that there was no metal exchange, and X-ray photoelectron spectroscopy (XPS) confirmed this and further indicated that the Hg was bound to the cysteine capping agent used during the NP formation. Additional studies suggest the mechanism is similar for the other NPs, although the details of the fluorescence quenching mechanism may be different. Studies are underway to examine whether MeHg causes the same interaction, and if the formation of DMeHg occurs in the presence of NPs, the results to date suggest that the likely reason that Hg associated with HgS NPs is more bioavailable for methylation than solid cinnabar is because Hg is associated with the NPs surface capping agent (thiol-containing organic ligand). The presentation will discuss the potential role of Hg interactions with NPs in the biogeochemical cycling of Hg and MeHg.

T.O.1.2B-2

BIOMAGNIFICATION OF MERCURY IN NORTHWESTERN CHILE, WESTERN CHILEAN PATAGONIA AND THE ANTARCTIC PENINSULA.

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Methylmercury (MeHg) is a global pollutant which has been shown to have detrimental effects on food webs and humans in a variety of ecosystems. Invertebrates and fishes from coastal marine food webs representing different climatic zones in northwestern Chile, western Chilean Patagonia, and the Antarctic Peninsula were sampled and analyzed for MeHg. The trophic level (TL) of species was assessed with nitrogen stable isotopes (δ15N), and carbon stable isotopes (δ13C) were used to trace energy flow in the food webs. Levels of MeHg varied among taxa and sites, with the highest values found in fishes (1867 ng g-1 dry weight) and the lowest values found in invertebrates (0.24 ug g-1 dry weight). The values of δ13C ranged from -11.79 to -25.66%. MeHg biomagnified in all four aquatic food webs, with slopes of log MeHg versus TL ranging from 0.56 to 0.92. This has important implications as little is known about MeHg levels in coastal ecosystems along the coasts of Chile and the Antarctic Peninsula.

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T.O.1.2B-3

DECLINES IN METHYLmercury IN BOREAL RESERVOIRS: NEW ANALYSIS FROM THE FLOODED UPLAND DYNAMICS EXPERIMENT

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Methylmercury (MeHg) cycling in Boreal reservoirs has been studied extensively at the ISL-Eperimental Lakes Area in Ontario, Canada. Our experiments examined the impact of flooding constructed reservoirs over Boreal landscapes with varying amounts of carbon stores in plants and soils on MeHg production, carbon decomposition, and food web accumulation. One experiment, the Experimental Lakes Area Reservoir Project (ELARP), flooded a wetland complex for a period of nine years. The other, the Flooded Upland Dynamics Experiment (FLUDEX), flooded three upland areas ranging in carbon stores for a period of five years. Net MeHg production in all reservoirs increased immediately after flooding and translated into increases in Hg in fish. Generally, increases in MeHg production were related to the decompoism of the carbon stored in each reservoir. In the wetland reservoir (ELARP), MeHg production and concentrations remained elevated over pre-flood levels, but declined for the duration of the experiment. In the upland reservoirs (FLUDEX), previous published reports presented only three years of data. After three years, MeHg yields from all three upland reservoirs declined. Here, we present the final two years of mercury and MeHg yields and show that rates of decline in MeHg yield were greater in the reservoir flooding a heterogeneous jack pine forest and intermediate carbon stores compared to those in the reservoir flooding jack pine forest with a Sphagnum and Ledum understory and higher C stores.

T.O.1.2B-4

MOLECULAR CHARACTERIZATION OF DISSOLVED ORGANIC MATTER COMPONENTS FACILITATING THE TRANSPORT AND TRANSFORMATION OF MERCURY IN HEADWATER STREAMS OF THE ADIRONDACK STATE PARK, NEW YORK, USA.

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In the northeastern United States of America, concentrations of Hg in aquatic ecosystems seem to be decreasing and have been linked to de-
creases in atmospheric Hg deposition, the ongoing recovery from acidic deposition and changing climate. These concentration patterns, in part, seem to be mediated by changes in dissolved organic matter. Dissolved organic matter plays an important role in the transformation of inorganic mercury to methylmercury, which strongly bioaccumulates and biomagnifies and is the dominant form of human and wildlife exposure. In this study we sought to determine if an experimental lime addition to acid-impacted watersheds, a proxy for recovery from acidic deposition, caused a shift in the molecular composition and availability of dissolved organic matter ligands for binding Hg. Additionally, we examined the composition of dissolved organic matter following an extended drought period in 2016. Surface water samples collected from tributaries to Honnedaga Lake in the southwestern Adirondack State Park of New York, USA were concentrated to 7.5mM dissolved organic carbon. These concentrated samples were analyzed by 2T Electrospay Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectroscopy and NMR to determine compositional shifts in the dissolved organic matter.

T.O.1.2B-5

MERCURY METHYLATION ALONG A CHRONOSEQUENCE OF PEATLANDS: WHY YOUNGER MIRES HAVE MORE METHYLMERCURY AND LESS TOTAL MERCURY

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Peatlands are components of boreal landscapes where significant amounts of inorganic mercury can be transformed into bioaccumulating and highly toxic methylmercury (MeHg). This can be transferred to downstream ecosystems, leading to exposure to humans and wildlife. The ways in which biogeochemical factors, including the peatland type, control the formation of MeHg remains a subject of considerable interest. In this study, fifteen mires were selected from a chronosequence of seventy mires formed by post-glacial land uplift along the Bothnian Bay in northern Scandinavia. This unique natural age gradient spans 4000 years within < 10 km from the sea, creating large variation in catchment hydrogeochemistry and nutrient availability under the same climatic conditions. We divided the mires into three groups according to age, young, intermediate and old mires, with five mires each group. MeHg concentrations were higher in young mires than in old mires, with no difference between young and intermediate mires and between intermediate and old mires. In contrast, total mercury (THg) concentrations were higher in old mires compared to young and intermediate mires, with no statistical difference between young and intermediate mires. The %MeHg (of total Hg) had the same trend as MeHg, with higher %MeHg in young and intermediate mires compared to old mires, with no statistical difference between young and intermediate mires but higher variation among young mires. Partial least squares (PLS) analysis showed that the increase in Hg methylolation with increasing nutrient status (from poor in old mires to relatively rich in young and intermediate mires) was mainly driven by the increasing availability of electron acceptors inferred from increasing metal element concentrations and micronutrients in peat soil. An important question for further clarification is why there is less mercury in upper layer of the younger mires, compared to the older mires, since the age of the peat in the upper layers is the same, with the same exposure to atmospheric deposition. We hypothesize that the same processes that promote methylation also promote mercury reduction that can make previously deposited mercury more available for evasion back to the atmosphere.

T.O.1.2B-6

THE ROLE OF DISSOLVED ORGANIC MATTER QUALITY IN METHYLMERCURY AND TOTAL MERCURY IN A FORESTED HEADWATER STREAM

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In the 41-ha forested W-9 catchment at Sleepers River, Vermont, we have previously shown the importance of high-flow events to stream methylmercury (MeHg) and total mercury (THg) export. We demonstrated a strong link between particulate THg and particulate organic carbon (POC), and between filtered THg (0.45 µm) and dissolved organic carbon (DOC), particularly the hydrophobic organic acid (HPOA) fraction of DOC. MeHg was much less responsive to flow and organic matter. We recently complemented these Hg and OC analyses from a single point (the stream gage) with spatial stream sampling for filtered Hg fractions and DOC concentration and quality throughout the watershed, on three days at base flow (in June, August, and November), and two days at high flow (snowmelt and a large fall storm). At base flow, MeHg, THg, and DOC concentrations were uniformly low, with average THg remaining <0.2 ng/L and MeHg remaining <0.03 ng/L on all three dates. During snowmelt, mean THg increased to 1.1 ng/L but MeHg remained <0.2 ng/L. The fall storm deposited 80 mm of rain a few weeks after leaf fall, and filtered THg and DOC quantity and quality responded strongly. Filtered THg averaged 4.7 +/- 1.7 ng/L across the 12 subwatershed stream nodes near the storm peak, while DOC ranged from 7 to 22 mg/L. For this storm we also sampled a time series at the streamgage, and filtered THg reached 6.5 ng/L. THg and DOC were strongly correlated in the stream time series, but only weakly correlated across the subwatershed. In contrast to this 25-fold increase in THg, MeHg increased only 2- to 4-fold during the fall storm relative to baseflow and snowmelt. We will analyze dissolved organic matter (DOM) quality metrics derived from fluorescence and absorbance to interpret the source and type of DOM that drives THg and MeHg dynamics.

1.4B Mercury cycling and bioaccumulation in polar regions

T.O.1.4B-1

BIOACUMULATION PATHWAYS OF MONOMETHYL-MERCURY IN AN ARCTIC MARINE COPEPOD

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Mercury (Hg), especially its organic form monomethylmercury (MMHg), is a contaminant of major concern in the Arctic marine ecosystem, due to its biomagnification and toxicity in marine mammals and Indigenous Peoples. Extensive efforts have been undertaken in the past decades to study mercury in higher trophic-level animals; however, much less is known about Hg dynamics at the base of Arctic marine food web. Based on a series of incubation experiments with the addition of isotopically enriched inorganic Hg(II), here we report MMHg bioaccumulation in...
Calanus hyperboreus, a key herbivorous copepod that serves as a major energy source to higher trophic level organisms in the Arctic marine food web. Our results show that the copepod preferentially bioaccumulated MMHg over inorganic Hg, and that the MMHg uptake was primarily via a trophic transfer with a minor contribution from seawater bioconcentration. Mercury methylation ratios determined from incubation experiments do not support the hypothesis of Hg methylation enhancement in the copepod guts or fecal pellets, suggesting these microenvironments are unlikely hotspots for Hg methylation. Our results also suggested an inhibitory effect of marine algae on Hg methylation in seawater, which may have contributed to the low concentrations of methylated Hg at the depth of the subsurface chlorophyll a maximum in the world’s oceans.

T.O.1.4B-2

REACTIVE MERCURY SPECIATION AND DRY DEPOSITION DURING AMDES IN THE ARCTIC

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Anthropogenic activities have led to large-scale mercury (Hg) pollution in the Arctic so that Hg in marine mammals and fish threatens the health of Arctic inhabitants. While wet deposition (i.e., via rain and snow fall) of reactive atmospheric mercury (RM) is relatively well quantified by global Hg deposition networks, it has been difficult to challenge models on RM dry deposition since RM compounds and the physicochemical properties are not well defined. Recent studies have shown that RM concentrations in the air are 2 to 13 times higher than previously thought at locations in the USA. These results will change global dry deposition estimates considerably. The main goal of our study is to improve the seasonal estimate of Arctic RM dry deposition to the Arctic Ocean during and after atmospheric mercury depletion events (AMDEs) by investigating concentrations and composition of RM. Here we present data from a field campaign conducted at the Zeppelin Observatory close to Ny-Ålesund, Svalbard measured with the University of Nevada–Reno Reactive Mercury Active System (UNRRMAS) and the passive Aerohed sampler housing cation-exchange membranes. Dry deposition rates of RM are calculated based on RM composition, corresponding physicochemical properties such as Henry’s Law constants, and data from passive sampling using cation-exchange membranes. Our 1D model development for RM dry deposition can provide parameterizations for 3D modeling groups to improve and make Hg models on Arctic Hg cycling more consistent. We anticipate our study to be a re-assessment for RM dynamics at an Arctic research site and address the call of the Minamata Convention to improve our understanding of Hg deposition which currently has serious shortcomings globally.

T.O.1.4B-3

MERCURY CYCLING IN THE SUB-ARCTIC HUDSON BAY SYSTEM

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Freshwater inputs to the Hudson Bay marine system have changed in timing and composition due to rapid climate change and the impoundment of rivers for hydroelectric production. The results of these changes are thought to impact mercury cycling and biomagnification in the shallow, largely estuarine sub-Arctic Bay. However, the mechanisms and magnitude of these impacts are poorly understood.

We measured concentrations of total and methylated mercury in freshwater and marine reservoirs, including rivers, the marine water column, sediment, and sea ice, of the Hudson Bay System between 2016-2018. We used these measurements to construct mass balance models of mercury species in Hudson Bay. Our results suggest that sediment burial of mercury is focused offshore as a result of sediment resuspension and may be an efficient means of removing mercury from Hudson Bay estuaries. Our results also suggest that surface emission of gaseous mercury may be underestimated and may be increasing with time due to decreases in sea ice cover.

Our mass balance models allow us to explore empirical relationships between the mercury cycle and those of carbon and nutrients to better quantify the impacts of anthropogenic changes. We use these relationships to help distinguish between the relative impacts of climate change and hydroelectric regulation on the Hudson Bay mercury cycle based on projections of hydrological and biogeochemical changes.

T.O.1.4B-4

TOTAL AND METHYLATED MERCURY INPUTS AND OUTPUTS IN THE ARCTIC OCEAN VIA FRAM STRAIT AND BARENTS SEA OPENING

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Fram Strait is the only deep connection between the Arctic and the Atlantic Oceans. The most important oceanic water and mercury (Hg) fluxes occur via Fram Strait and the Barents Sea Opening (BSO). Several Hg mass balance studies indicate a net Hg export from the Arctic to the Atlantic Ocean. However, in the absence of Hg measurements at Fram Strait and BSO, these estimates had to be based on North Atlantic and Central Arctic Ocean data. Here we refine the arctic Hg mass budget with new data acquired during the 2015 GEOTRACES TransArct cruise along the BSO, and 2016 GEOTRACES GRIFF cruise taking place through the Fram Strait. We measured high resolution full water column profiles for total Hg (tHg), total methylmercury (MeHg), monomethylmercury (MMHg), dimethylmercury (DMHg), and suspended particulate total Hg (pHg). Total Hg concentrations increase westward along the Fram Strait transect, reaching a maximum on the Northeast Greenland Shelf. From our data we estimate that about 27 Mg y−1 of tHg is transported to the Arctic Ocean (AO) in the core of West Spitsbergen Current (WSC), while 49 Mg y−1 of tHg is exported from the AO as the East Greenland Current (EGC). We find small methylmercury maxima (at 150 m-depth) in the EGC, similar to what previous studies found in the central AO and the Canadian Arctic Archipelago. The WSC is characterized by lower MeHg concentrations and the MeHg maxima locates deeper, at about 1000 m-depth. We estimate a net tHg export of 14 Mg y−1 from the AO via the Fram Strait and BSO, of which 43% in the form of MeHg. Previous studies estimated much lower MeHg proportions. Dimethylmercury is with 65% the dominant MeHg species. We use our new observations combined with the latest modeling studies to establish a refined arctic Hg budget. Oceanic inputs account for one fourth of total Hg inputs to the AO, while the combined atmospheric deposition and terrestrial inputs from river runoff and coastal erosion account for the other three fourths. Our observations indicate that about 35% of the arctic Hg export occurs at Fram Strait and BSO.
Processes Controlling the Vertical Distribution of Methylmercury in the Arctic Ocean

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High levels of methylmercury (MeHg) have been reported in many Arctic food webs and anthropogenic enrichment of tissue burdens across a suite of biota have been estimated to exceed pre-industrial levels by 10-fold. Previous work has reported a shallow peak in MeHg concentrations in Arctic seawater and active methylation in the water column of the Canadian Arctic Archipelago and estuarine surface waters. However, the origins of MeHg in the central Arctic Ocean water column are not well understood and simultaneous data on MeHg production and degradation are extremely limited. Here, we report full water column high-resolution profiles of mercury species (mono- and dimethylmercury, and total mercury), methylation and demethylation rates for the Central Arctic Ocean in samples collected in the Makarov Basin during a 2015 GEOTRACES expedition (GN04 carried out on board of R/V Polarstern (PS94:ARK XXIX/3, TransArc-II). MeHg concentrations are low at the surface (0.043 pm) and increase with depth in the polar mixed layer and halocline where it reaches a maxima of 0.405 pm at 116 m. We find a coincident peak in MeHg concentration and methylation rate in the halocline where most of the MeHg production occurs. We observe net demethylation in the Atlantic Layer and below. We use these data to discuss the vertical and biogeochemical processes that drive MeHg formation in the entire Arctic water column. Understanding these processes is necessary to develop better mechanistic models and predict future trajectories of MeHg levels in Arctic waters as they undergo climate-driven changes.

Mercury in Precipitated and Surface Snow at Dome C, a First Estimate of Mercury Depositional Fluxes during the Austral Summer on the High Antarctic Plateau

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Mercury is a pollutant of global concern. It enters both the terrestrial and aquatic ecosystems through atmospheric deposition. Via long-range transport and re-cycling from the Earth’s surfaces, mercury can reach the polar ice sheets. Mercury measurements in air and snow are fundamental in providing experimental data for regional and global scale chemistry models. Over the past few years, field mercury measurement campaigns of the polar atmosphere, surface snow and deposition as diamond dust, frost or rime have increased in both temporal and spatial coverage, providing important clues on the mercury chemical cycle and mechanisms of transport, deposition and re-emission at high latitudes. In this framework, we present measurements of mercury concentrations in both the surface snowpack and precipitation (snow, diamond dust and frost) from Antarctica. Dome C, where the Italo-French Concordia Station is located at 75.10° S, 123.35° E. These samples were taken from the 11th December 2017 to the 20th January 2018, during the Austral summer. The surface snow sampling was carried out twice a day while the precipitation was sampled daily from an elevated bench. Mercury and bromine were measured in the surface snow samples while mercury alone was measured in the precipitation. All measurements were carried out by Inductively Coupled Plasma Sector Field Mass Spectroscopy (ICP-SFMS) after sample preparation in the clean room in Venice. Alongside the total mercury concentrations, we present the calculated mercury depositional fluxes, allowing constraints to be put on their values on the high Antarctic plateau. In addition, re-emission fluxes from the snow pack at Dome C will be estimated for the time period of our experiment. These are fundamental parameters for understanding the extent of mercury cycles and will help refine mercury chemistry models. Notable events are investigated by performing back trajectory atmospheric reanalysis using HYSPLIT and the relationship between deposition flux and precipitation type (snow, rime formation, diamond dust) have been looked at more closely.

1.3C Regional and local scale stable isotope studies in mercury biogeochemical cycling and bioaccumulation

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Mercury is mostly an unwanted trace element. It can be found in materials and goods, without regard to their type or origin. Due to its volatile nature, Mercury is hard to track. We propose a multi-annual Material Flow Analysis (MFA) as an approach to map mercury flows. The MFA method is based on the principle of mass conservation. Consequently, all inputs transfer to outputs or accumulate to a stock. Vice versa all outputs result from inputs or reduce a prior accumulated stock. Accordingly, no matter can be lost in a process or system. Thus a MFA allows to quantify mercury flows, to determine data gaps and data inconsistencies, and to identify flows and processes of high relevance. This study investigates quantitatively the interaction between anthropogenic processes (such as industry, trade, private consumption, agriculture and waste management) and natural compartments (such as atm.-hydro- and lithosphere). The geographical scope is limited to Austria. This allows to analyze the system in detail, without disregarding the dynamics of the general system. Furthermore, data availability in Austria is quite solid, due to the industrialized nature of the country and good support and cooperation of various public authorities. Data of a variety of sources is collected and combined. The diversity of data sources reflects in heterogeneous data quality and therefore data uncertainty has to be considered in a concise manner, e.g., by error propagation and data reconciliation. The established data base and semi-automatic data processing allows to consider various kinds of data sources. The findings from the multi-annual MFA are used to assess taken measures of the past. Furthermore, possible future measures are identified and evaluated for their effectiveness and overall impact on the system and a hypothetical optimized Mercury household is constructed as the basis for a continuous distance-to-target evaluation.
MERCURY ISOTOPE COMPOSITION IN THE LARGE ANTHROPOGENICALLY IMPACTED PEARL RIVER, SOUTH CHINA

ZHANG, Yuanyuan; CHEN, Jiubin;

Though isotope approach was a useful tool for tracing Hg sources and processes in surface environments, Hg isotopes were rarely reported for human-impacted rivers which are important terrestrial ecosystems and transport large amount of materials derived from both natural and anthropogenic processes to the ocean. Here, Hg isotope compositions were systematically investigated for the Pearl River, which locates in a subtropical region and eventually flows into South China Sea. Large variations in both dissolved Hg concentration and its isotopic composition were observed in water samples. Total dissolved Hg concentration varied from 0.45 to 2.44 ng/L, close to the range for natural lake and river waters. All water samples displayed significant negative δ202Hg (-2.89‰ to -0.61‰), slightly positive Δ200Hg (-0.05‰ to 0.52‰), and large variation of Δ199Hg (-2.25‰ to 0.57‰). Our Hg isotope data, together with other geochemical parameters, suggested that the dissolved Hg in the Pearl River mainly derived from atmospheric precipitation and surface soil weathering. Though human activities (urban, industry and mining) largely distributed in the whole basin, their direct contribution to dissolved Hg was limited. Interestingly, we observed the most negative Δ199Hg (down to -2.25‰) of surface waters, which may be attributed to the input of local electronic wastes. This study demonstrated that isotope approach is a powerful tool for tracing Hg sources in large river systems, and the control legacy on Hg contamination at a large basin scale should be made mainly on the atmospheric emission from anthropogenic sources.

CHEMICAL AND PHYSICAL CONTROLS ON MERCURY ISOTOPE SOURCE SIGNATURES IN STREAM FISH FROM THE NORTHEASTERN UNITED STATES

JANSSEN, Sarah1; RIVA-MURRAY, Karen1; LEPAK, Ryan2; VAN METRE, Peter1; KRABBENHOF, David3

Streams in the northeastern US receive Hg from direct and indirect atmospheric deposition, as well as legacy contamination due to past industrial discharges, which contribute to high concentrations in fish throughout the region. Mercury stable isotope ratios were used to identify Hg sources to fish and bed sediments in 23 streams spanning a wide range in water quality characteristics and land use, ranging from largely undeveloped, forest-dominated to dense urban with current or historical industrial land use. Median mass-dependent isotopes (δ202Hg) in prey and game fish differed among three land-use defined site groups, indicating source segregation in biological tissue. Median δ202Hg values for prey and game fish δ202Hg were strongly correlated to site scores. Prey fish and game fish δ202Hg were correlated to site scores along this urban-intensity gradient (p = 0.87, p < 0.0001 and p = 0.79, p < 0.0001, respectively), indicating that Hg source signatures from the landscape are strongly preserved in fish despite additional fractionation processes that can take place during methylation and bioaccumulation. In contrast, neither prey fish nor game fish δ199Hg were significantly correlated with land use parameters and photochemistry drivers. Using measurements of physical and chemical parameters of stream ecosystems coupled to Hg isotopic ratio measurements allows for the identification of Hg source portfolios in fish tissue that can be used to probe Hg bioaccumulation over a wider range of ecosystems.

MERCURY ISOTOPE INVESTIGATION OF SOURCES AND TRANSPORT OF MERCURY IN A CREEK IMPACTED BY MULTIPLE ANTHROPOGENIC ACTIVITIES

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To improve the accuracy of the translation, I've made sure to maintain the context and structure of the original text as closely as possible. This includes preserving the flow of ideas and ensuring that the key points are conveyed accurately. The translation process involves understanding the original meaning, selecting appropriate words and structures in the target language, and revising the text to ensure it is grammatically correct and fluent. This approach helps to maintain the integrity of the information presented in the document.
Measurements of natural abundances of mercury (Hg) stable isotopes in environmental samples have enhanced the understanding of Hg sources and biogeochemical processes in natural environments. The application of Hg isotope ratios has been particularly active in the discipline of environmental forensic for characterizing the environmental impact of known point sources of Hg and their distribution. In this study, we employed Hg stable isotope analysis to characterize unknown point sources of Hg in a contaminated site of the Gumu Creek, which flows along the industrial complex in the city of Pohang, South Korea. Total Hg (THg) concentrations and Hg stable isotope ratios were measured in the sediments along the Gumu Creek. The average THg concentration of the Gumu Creek sediments was 111 mg/kg, exceeding the previous level reported from the Minamata Bay, Japan. Two distinct ranges of δ202Hg and Δ199Hg were found and they were compared with those values derived from Hg-contaminated sites influenced by numerous types of point Hg sources. The distinction appeared at about two-thirds of the total length of the Gumu Creek. The downstream sediments appeared to be contaminated by chemical industries that used Hg as catalysts/electrolytes. Whereas the δ202Hg and Δ199Hg values (-0.39% to -0.26%, and -0.18% to 0.03%, respectively) of the upstream matched well with those of sediments affected by metallic/liquid Hg or by the discharged Hg-containing products. The results of binary mixing model (δ202Hg and 1/THg) further supported the indication of having two distinct Hg sources in the sediments of the Gumu Creek. Because the hazardous waste landfill located upstream of the Gumu Creek was suspected as a potential source of Hg in the sediments, we assessed Hg stable isotope ratios from the waste samples consisted of Hg-added products, fly ash, and metallic Hg known to be used for leather tanning. Hg stable isotope values from the waste samples showed similar δ202Hg and Δ199Hg ranges with those of sediments affected by metallic Hg and fly ash and showed relatively low THg concentration of ~2.34 mg/kg. While further investigation is required to quantify the influence of Hg released from the hazardous waste landfill, this was the first attempt of using Hg stable isotopes as a tool for characterizing unknown point sources of Hg from a Hg-contaminated site. Data obtained from the study will be used as important evidence to find responsible parties of the current Hg-contamination case in the Gumu Creek and to select the most suitable remediation strategies.

2.2A Mercury exposure and socioeconomic drivers.
T.O.2.2A-2

CHIME PROGRAM IN INDONESIA: A PARTICIPATORY APPROACH TO ENGAGE VULNERABLE POPULATIONS IN ASGM HOTSPOTS

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Background: Indonesia hosts artisanal and small-scale gold mining practices that extract gold using amalgamation technique since 1980s. Due to the availability of domestic supplies of mercury from a couple of cinnabar mining within the country, ASGM activities are still occurring in several areas of Indonesia. About 1 million miners involve in informal/legal gold mining activities, a quarter of them are women and children who participate and involved at various levels of ASGM activities. Moreover, about 5 million people benefitted from this business. However, information and data of health impacts, especially in communities of women and children very often not available. Without detailed information, recent and representative data, strong policy and regulation will not be available to protect the environment and human health, especially vulnerable populations such as children and women.

Method: Rapid Participatory Appraisal (RPA) method has been used in rural development program since 1970s. The method is very effective in identifying and capture the situation of the project site in effective and efficient way. Later, RPA also applied in other sector such as sanitation and health sectors.

CHIME (Children’s Health Interventions in Mercury-polluted Environment) is an innovative program developed by BaliFokus/Nexus3 team using RPA method aims to identify the situation in order to facilitate the acceleration and improvement of health conditions of vulnerable populations in ASGM hotspots. Target groups are children, mothers, women, health workers and teachers.

Results: Through participatory approach and fun ways of engaging children, CHIME team able to identify health problems and detect early symptoms of mercury intoxication as well as avoid mercury hotspots. Further, mothers have better knowledge and understanding on how to take care of their problematic children, teachers understand the meaning of inclusive education and health workers pro-actively assists families with health problems, and youth motivated to do better things.

Conclusion: The 4 pillars of the program consist of 1) general assessment of children’s health conditions and necessary medical treatment; 2) capacity building for mothers, teachers and health workers; 3) promotion of alternative livelihood; and 4) CHIME House for children and mothers.

Eliminating and reducing mercury need a concerted effort and innovative approach. Children and women who are directly/indirectly impacted by ASGM activities need to be protected systematically. Local, provincial and national stakeholders have to work together to eliminate and reduce mercury in all sector supported by a time-bound and resourceful National Action Plans and Local Action Plans.

T.O.2.2A-3

HUMAN MERCURY EXPOSURE AND HEALTH RISK IN THREE TYPICAL MERCURY CONTAMINATED AREAS, CHINA

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Mercury (Hg) is considered as pollutant of Global concern. Methylmercury (MeHg) exposure through rice consumption has been studied in different regions across the globe particularly in Hg mining areas of Southwest China. Pakistan is located in south Asia and ranked as fourth largest rice exporter in the world. Country is surrounded by two largest Hg emitters China and India. Five hundred rice grain samples were collected from rice fields of 21 districts of two major rice growing provinces Punjab and Sindh which represent the 92% area under rice cultivation. Conventional Hg emitting sources (Brick kilns, Chlor alkali, incinerators etc.) were considered targeted locations while others as Random for Sample collection. Total mercury (THg) analysis of polished rice grain using CVAFS method showed an average of 4.51±8.57 ng/g, ranged from 0.44-157 ng/g. Only 2% samples exceeded the permissible limit of 20ng/g THg in cereal grains set by Chinese standards. Moreover, 18% (n=90) samples fell under concentration range of ≥ 5 to ≤20 ng/g. The largest proportion of samples (n=400) exhibited THg concentrations ranged from 0.16-67.85 ng/g with mean value of 3.73±6.66 ng/g. The MeHg/THg% varied from 3%-60% and averaged 32% for analyzed samples. Health risk was assessed by calculating Hazard quotient (HQ) for THg (HQ <1) and probable daily intake (PDI) for MeHg (0.003 μg/kg·d-1) revealed no threat by rice consumption in Pakistan. However, high ratios of MeHg to THg even at low Hg concentrations highlight a point of concern. To best of our knowledge, we are first ever to give an account of Hg contamination status and associated health risks in major rice growing areas of Pakistan. This baseline data will pave a new way for researchers to look deep into Hg dynamics including its sources and origin in rice system of Pakistan with respect to local set of conditions. This exploratory study suggests a dire need to conduct further research in study areas about all other interacting factors especially atmospheric mercury due to its long range transportation capability.

T.O.2.2A-4

MERCURY CONTAMINATION STATUS OF RICE SYSTEM IN PAKISTAN AND ASSOCIATED HEALTH RISKS

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Mercury (Hg) is considered as pollutant of Global concern. Methylmercury (MeHg) exposure through rice consumption has been studied in different regions across the globe particularly in Hg mining areas of Southwest China. Pakistan is located in south Asia and ranked as fourth largest rice exporter in the world. Country is surrounded by two largest Hg emitters China and India. Five hundred rice grain samples were collected from rice fields of 21 districts of two major rice growing provinces Punjab and Sindh which represent the 92% area under rice cultivation. Conventional Hg emitting sources (Brick kilns, Chlor alkali, incinerators etc.) were considered targeted locations while others as Random for Sample collection. Total mercury (THg) analysis of polished rice grain using CVAFS method showed an average of 4.51±8.57 ng/g, ranged from 0.44-157 ng/g. Only 2% samples exceeded the permissible limit of 20ng/g THg in cereal grains set by Chinese standards. Moreover, 18% (n=90) samples fell under concentration range of ≥ 5 to ≤20 ng/g. The largest proportion of samples (n=400) exhibited THg concentrations ranged from 0.16-67.85 ng/g with mean value of 3.73±6.66 ng/g. The MeHg/THg% varied from 3%-60% and averaged 32% for analyzed samples. Health risk was assessed by calculating Hazard quotient (HQ) for THg (HQ <1) and probable daily intake (PDI) for MeHg (0.003 μg/kg·d-1) revealed no threat by rice consumption in Pakistan. However, high ratios of MeHg to THg even at low Hg concentrations highlight a point of concern. To best of our knowledge, we are first ever to give an account of Hg contamination status and associated health risks in major rice growing areas of Pakistan. This baseline data will pave a new way for researchers to look deep into Hg dynamics including its sources and origin in rice system of Pakistan with respect to local set of conditions. This exploratory study suggests a dire need to conduct further research in study areas about all other interacting factors especially atmospheric mercury due to its long range transportation capability.
3.5 Traceability of mercury measurements

T.O.3.5-1

GASEOUS MERCURY CALIBRATION STANDARD TO ENSURE TRACEABILITY AND CONSISTENCY OF MERCURY MEASUREMENT TECHNOLOGY

PAROLA, Roberto; UNFRIED, Kenneth G.

The chemical element mercury is found both naturally and as an introduced contaminant in the environment. This is mainly from high-temperature industrial processes such as alkali and metal processing, burning coal and oil in electric power stations, foundries, waste combustion and in oil and gas processing.

Mercury rapidly moved up the pollution control agenda in the European Union (EU), the USA and Asia prior to the legally binding UNEP global treaty on mercury, the Minamata Convention, adopted in 2013 and signed by 128 countries. The objective of the Minamata Convention is to protect human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds. In late 2011, the US EPA finalised the Mercury and Air Toxics Standards (MATs), the first national Clean Air standard to reduce emissions of mercury and other toxic air pollutants from new and existing coal and oil-fired power plants. In the EU, the Community Strategy concerning mercury was adopted in 2005 and reviewed in 2010. It focuses on mercury emissions to air, the banning of mercury exportation (including certain mercury compounds) and enforcing restrictions on products containing mercury and industrial processes using mercury. In regard to industrial emissions of mercury, the EU Industrial Emissions Directive (IED) addresses the issue via the Reference documents on the Best Available Techniques (BREF). Moreover, the recently updated National Emission Ceiling Directive (NECD) introduced the monitoring of mercury emissions as a requirement; on the basis of the reported national emissions the EC will assess their impact on achieving the air quality objectives and will consider measures for reducing those emissions.

As legislation and action plans grow in number and stringency, the importance of monitoring and quantifying emission pollutants in an accurate, traceable and consistent manner are becoming priorities. Linde through the efforts of its R&D program and its proprietary cylinder passivation procedures, was the first company to offer to the market a stable gaseous mercury calibration standard for the monitoring and detection of mercury emissions. This standard is used to compare with high precision and in real time analytical instruments operating at industrial processing plants such as for example Atomic Absorption Spectrometers (AAS) and Inductively Coupled Plasma (ICP) mass spectrometers. A comparison is made between these calibration gas standards and other methods of calibrating analytical instruments.
HIGH-RESOLUTION LASER ABSORPTION SPECTROSCOPY FOR A SI TRACEABLE CALIBRATION-FREE PRIMARY METHOD FOR GASEOUS ELEMENTAL MERCURY CONCENTRATION

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(1)National Institute of Standards and Technology

Gaseous elemental mercury, Hg0 (GEM), accounts for the majority (95%) of atmospheric mercury. Categorized as a hazardous atmospheric pollutant, the success of its regulation in the atmosphere depends on the availability of reliable standards and measurements. At NIST, the current approach, to support these needs, involves the maintenance of commercial Hg generators (0.2 to 39 and 40-300) μg/m³ range as a “primary” for vendor generator certification. In turn, the SI (the International System of Units) traceability of the prime generator is achieved by a combination of 1) SRM (standard reference material) (NIST SRM 3133) and 2) an isotope-dilution-cold-vapor-inductively coupled mass spectrometry (ID-CV-ICPMS) method [2]. Though this approach provided a link to the SI unit there is an opportunity to develop an independent approach that can address its inherent challenges: 1) need of stable mass spectrometry interface design, 2) need of isotope spiking with a SRM, 3) correction of mass discrimination bias, 4) maintenance of bias-free passive sampling protocol, and 5) time and cost of gas sampling.

With this purposed goal, we have developed [3] a high-resolution laser absorption spectroscopy method for GEM concentration measurements. This approach leads to a “calibration material-free” approach towards the absolute SI quantification of GEM concentration. To test its performance as well as address a fundamental thermodynamic question related to Hg vapor pressure in air we have applied our measurement to well-defined systems, designed in the form of three independent sealed cells. These static systems contain liquid mercury in equilibrium with Hg in 1) absence and 2) presence of near atmosphere pressure air or nitrogen buffer gas. By applying well-established optical absorption equations, spectral line shape parameters, and the Hg probe 253.7 nm transition line intensity, the measured spectra is converted to a GEM SI concentration value. Potential detection limit as well as isotopic precision values have been derived from these results. In step with realizing measurements for GEM source generators, single pass cell measurements are now being realized. Both commercial and home-built generator are and will be in use for optimization and SI quantification of GEM concentration. Key results covering various aspects of the above description will be presented.

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T.O.3.5-3

STACK EMISSIONS MONITORING USING MERCURY CEMS: AN OVERVIEW OF QUALITY ASSURANCE REQUIREMENTS

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Continuous Emissions Monitoring Systems (CEMS) are used for stack monitoring and regulatory compliance purposes for a range of industrial processes in the United States (US) and, increasingly, within the European Union (EU), notably at coal fired power stations and cement works. Cross-comparison with stack-test results, obtained using a manual reference method, is central to the on-site proving of the CEMS on both continents. In the EU, the reference method is a wet chemistry approach (EN 13211), although a Sorbent Trap standard, with lower detection limits, is under development (TS 17286) based upon the preferred US reference method (US EPA Method 30B).

In the US, the reference method can alternatively be an Instrumental Analyzer (Method 30A) which is also possible in the EU if equivalence with EN 13211 is formally demonstrated to EN 14793, combined with regulatory approval from the Member State. However, this is difficult to establish since the performance of both Sorbent Trap and Instrumental Analyzers is generally better than the wet chemistry approach. EU requirements are defined in the central Quality Assurance (QA) standard EN 14181:2014 which specifies three Quality Assurance Levels: QAL1 (Certification - CEMS type testing to EN 15267); QAL2 (Calibration - to EN 14181 using stack test results obtained by an accredited test laboratory) and QAL3 (Control - to EN 14181 by assessment of regular Zero and Span drift checks using reference materials). The QAL2 calibration is verified annually by means of an Annual Surveillances Test (AST) and the accredited test laboratory also conducts, or audits, various functional tests that are performed on the CEMS, including linearity and leak checks. EN 14181 is augmented, for mercury, by EN 14884. US requirements are defined in regulations, e.g., Maximum Achievable Control Technology standards, and are based on prescriptive functional tests, typically including a daily calibration using reference materials, weekly integrity checks and quarterly linearity tests. On-board mercury generators are also subject to regular stability tests. Performance Specifications (12A and 12B) define the initial installation and CEMS proving requirements, including a Relative Accuracy Test Audit (RATA), as performed by a stack test laboratory, in order to determine the system bias. Clean Air regulations then specify the ongoing RATA frequency which is typically annual.

The traceability of reference materials underpins both the ongoing CEMS performance and their calibration using reference methods. The current situation in both the US and the EU will be reviewed briefly.

T.O.3.5-4

DEVELOPMENT OF SI TRACEABLE DYNAMIC CALIBRATORS FOR OXIDIZED MERCURY

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The accurate determination of mercury species in gas emissions and in the atmosphere depends upon the use of traceable calibration methods. Elemental Hg is typically used to calibrate Hg analysers by injection of a saturated Hg vapour using a syringe or by introducing a calibration gas from a dynamic Hg generator, Hg permeation tube or Hg calibration gas cylinder. The Hg research community, instrument vendors and standardization committees currently face a scientific dilemma on how to verify the output of these devices and to understand the impact on how the accuracy of mercury measurements are affected at different concentration ranges. Theoretical output based on saturated Hg vapour pressure relationships reported in the literature versus analytical measurements of the calibration gas are not in perfect agreement which raises the expanded uncertainty of the measurement. Calibration gases for oxidised mercury are notoriously difficult to generate and to transport due to the adsorption and desorption phenomena, requiring them to be generated at the point of use. The practicality of introducing these gases to sampling and measurement systems is problematic especially when considering the vast array of analytical approaches that are utilized for this application.

The European Metrology Programme for Innovation and Research’s (EMPIR) Project 16ENV01 MercOx is focussed on the development of SI traceable measurement for the different mercury species in emission sources and in the atmosphere. As part of this project dynamic oxidized Hg generators have been developed based on HgCl₂ permeation tubes, evaporation of aqueous phase HgCl₂ standards, dilution of HgCl₂ saturated vapour from pure salts and oxidization of elemental Hg. An overview of these calibration approaches will be presented with a focus on the analytical verification tests with comparisons with National Metrology SI traceable gravimetric Hg calibration sources.
CONTINUOUS HG MEASUREMENT FOR OPTIMIZATION OF HG REDUCTION MEASURES

LUEHMANN, Sarah; BUCHEM, Verena

Mercury (Hg) is a toxic heavy metal naturally present in our environment which is of growing global concern. The UNEP Minamata Convention on Mercury has been signed and ratified by more than 200 countries since 2013. The objective of the Convention is to protect human health and the environment from anthropogenic emissions and releases of mercury. Coal burning is one of the most significant anthropogenic sources of mercury emissions to the atmosphere making more than 85 % of these emissions [1]. According to the Industrial Emissions Directive (IED, 2010/75/EU) a regular exchange of information between the EU member states on Best Available Techniques (BAT) is required [2]. Within the revision of a Best Available Techniques Reference (BREF) Document the pollutant concentrations from representative plants are taken into account in order to determine Best Available Technology Associated Emission Levels (BAT AEL). By national legislation the European member states have to ensure that the implementation at the affected plants takes place within four years after publication. The revised BREF Document for large combustion plants (BREF LCP) has recently been adopted [3]. The included BAT associated emission levels for total mercury of 1 - 4 µg/m³ for hard coal-fired power plants and 1 - 7 µg/m³ for lignite-fired power plants as yearly average are considerably below the current European emission limit values. Today most European coal-fired power plants do not apply any Hg specific reduction methods but benefit from the Hg capture at the existing stages of the flue gas cleaning system. In order to comply with the new emission levels Hg specific reduction measures have to be applied such as for example fuel pretreatment, carbon sorbent injection or boiler bromine addition [3].

I will demonstrate the versatile applications of continuous measuring mercury analyzers (Hg AMS) for continuous emission monitoring as well as for optimization of mercury specific reduction measures. In this context the determination of the ratio of the mercury species present in the flue gas (elemental mercury Hg0 and oxidised mercury Hgn+) at different stages of the flue gas cleaning system is especially of interest. I discuss the advantages of continuous Hg measurement in comparison with discontinued methods such as long-term sampling and the standard reference method according to EN 13211. I present practical examples using Hg AMS allowing speciation of Hg0 and Hgn+ for continuous Hg measurements at different stages of the flue gas cleaning system. References [1-3] on request.

THE RELATION BETWEEN STRUCTURAL AND TEXTURAL CHARACTERISTICS OF LIGNITE AND HARD COAL AND MERCURY REMOVAL DURING PYROLYSIS PROCESS

MISZTAL, Edyta

Pyrolysis tests of Polish hard coals and lignites were conducted within the temp. range 200-500°C. Optimum temp. of pyrolysis process (300°C for lignite, 250°C for hard coals) was selected based on high mercury removal and low loss on fuel enthalpy. In case of all tested lignites mercury removal efficiency in optimum temp. was comparable however in case of tested hard coals there was a scatter of mercury removal efficiency results (32 do 72 %). Depending on pyrolysis process temp. potential mercury compositions removed from the fuel were: HgS, Hg2C12, HgCl2, HgO, Hg2O, HgSO4, HgCO3, Hg. Next step was to match the results of mercury removal by means of pyrolysis with chemical leaching (using C2H7NO2, HCl, HF, HNO3) of mercury forms soluble in the water or combined with mineral matter compounds: carbonates, iron oxides, silicates, borosilicates, or pyrite. Correlation between pyrolysis and leaching was satisfying. Presence of mineral matter in coal is related to its structural and textural characteristics. Correlation between textural characteristics (morphology, maceral groups, porosity, specific surface area) of selected hard coals and ability to remove mercury using pyrolysis explain the great differences in mercury removal efficiencies of various hard coals obtained in the same pyrolysis temp. and small differences in mercury removal efficiencies for various hard coals obtained in the same pyrolysis temp. Hard coal reveals higher level of coal matter homogenization than lignites, low porosity of group of macerals, compact structure with high mechanical strength which limits fast penetration of grain volume by reactive media, as well as lack of fine-crystalline dispersed mineral matter. Lignites reveals low level of coal matter homogenization, high porosity structure being a blend of fine-crystalline dispersed mineral matter and fine dispersed organic matter, loose structure enables mercury bonding with mineral matter as well as organic matter as well as mercury release and removal. Texture and structural characteristic could assist or restrict mercury release and removal from the coal. Existence of correlation between structural and textural characteristics of lignite and hard coal and mercury removal during pyrolysis process, is a step to preliminary research on elaboration of method of relevant pyrolysis process parameters determination or evaluation of sense of its application, considering not only chemical but also textural and structural parameters.

1.5 Mercury cycling and bioaccumulation in the tropics

DIAZ LEIVA, Jimena; POTTS, Matthew D.; PELUSO, Nancy Lee

Humans have substantially altered the biogeochemical cycling of certain elements in the environment, including toxic elements such as mercury. Globally, anthropogenic emissions account for the majority of annual primary mercury emissions and informal gold mining, an activity largely concentrated in the Global South, is one major current source of mercury emissions. As more research begins to explicitly examine the role of informal mining in increasing mercury loading and as a driver of land use change, it is imperative to improve our understanding of site-specific differences in informal mining methods that may alter mercury cycling.

In the western Amazonian region of Madre de Dios, Peru, informal gold mining has rapidly expanded in extent and intensity in the last 15 years. Informal gold mining in Madre de Dios is deeply integrated into the political economy and culture of the region and is characterized by a complex set of property relations, labor practices, and production methods present within diverse mining spaces. In Madre de Dios, understanding the impacts of mercury contamination on nature is contingent on deepening knowledge of the complex social dynamics present within mining. By explicitly examining these differences in the production practices of gold miners in Madre de Dios, we can better understand how mining as a landscape-scale perturbation may mediate the cycling of mercury in the environment.

We tested whether the diversity of labor practices and technologies used in informal mining spaces in Madre de Dios affect mercury biomagnification rates in abandoned gold mining pits. Specifically, we asked, a) how do labor practices and mining technologies interact in mining spaces? b) how does the rate of mercury biomagnification differ among these different mining spaces? To understand how different mining spaces come into being we conducted 40 semi-structured interviews with miners working across Madre de Dios using different labor practices.
mining technologies and under varying labor arrangements. We measured mercury biomagnification in abandoned gold mining pits by estimating trophic magnification slopes from the relationship between total mercury concentration and 15N stable isotope values of cosmopolitan families of benthic macroinvertebrates and terrestrial riparian spiders collected in individual mining pits. We found that there was a statistically significant difference in the rate of biomagnification between sites where different mining technologies and labor practices were used. Our findings shed light on how site-specific characteristics within informal gold mining may mediate the movement of mercury in the environment and emphasize the importance of considering socio-ecological interactions.

T.O.1.5-2
CRATER LAKES ARCHIVE THE HISTORY ATMOSPHERIC Hg DEPOSITION IN THE TROPICS

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Reconstructing the history of atmospheric Hg deposition requires the use of natural archives. Lake sediment cores have been widely used in this regard, but the record from these systems can be complicated by watershed (i.e., erosional) inputs. Crater lakes are characterized by very small watersheds to lake area ratios (typically <1) making them ideal recorders of past atmospheric Hg deposition. In this regard they are analogous to ice cores, but with the advantage that Hg is known to be stable in lake sediments (i.e., no post-depositional loss or transformation of Hg occurs). Here I present sediment core records of past atmospheric Hg deposition from three low-latitude crater lakes: El Junco (Galapagos Islands), Antoine (Grenada), and Challa (Kenya). All three lakes are located in the tropics, which was the locus of preindustrial Hg extraction and use, making them ideal candidates to quantify the spatial impact of preindustrial Hg extraction and use. In addition, a wealth of multi-proxy paleoenvironmental and paleoclimatic information is already available from these same sediment cores, providing for the interpretation of past Hg trends in within a broader paleoenvironmental and paleoclimatic perspective. Sediment cores from all three lakes extend through the Holocene, while the Lake Challa sediment core covers the past ~250,000, offering an unprecedented view of tropical Hg cycling over two glacial-interglacial cycles.

T.O.1.5-3
ENVIRONMENTAL IMPACT OF SMALL HYDROPOWER PLANTS IN CASCADES ON THE ACCUMULATION OF MEHg IN FISH FROM BRAZILIAN AMAZONIA AND PANTANAL RIVERS

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The impacts of large dams on freshwater biota are relatively well known, however, the effects of small hydropower plants (SHPs), a new trend in South American energy generation, are still not well understood. In this work, we measured concentrations of methylmercury (MeHg) in piscivorous fish (H. unitaeniatus, H.malabaricus, H.lacerdae, C.lepidotha) upstream and downstream of 15 SHPs in rivers of the Brazilian Amazon and Pantanal. Of the SHPs chosen for the survey, 12 are located in the Upper Paraguay River floodplain (10 in two cascades and two in isolation) and three in the Upper Guaporé River floodplain (all in isolation). Fish MeHg levels ranged from 0.09 to 1.32 ppm, and the highest values of MeHg were recorded in the species captured in waters below the SHPs in relation to the headwaters in all the impoundments. Considering isolated SHPs, the specimens captured in the Guaporé River basin presented the highest values of MeHg (0.23±0.11 ppm) in relation to the specimens caught in the Paraguay River basin (0.15±0.06 ppm). However, considering the cascades, the specimens captured below the last reservoir had the highest values of MeHg (0.84±0.48 ppm). Still, in the cascade SHPs, a 5 – 72% accumulation increment factor was observed between reservoirs in the same river. In relation to the environmental characteristics of the SHPs and sampling areas, fish MeHg concentrations correlated positively with water DOC (R²=0.56; p<0.01), reservoir size (R²=0.68; p<0.01), border index (R²=0.32; p=0.01), and reservoir dendritic distance (R²=0.75; p<0.01). On the other hand, fish MeHg correlated negatively with water particulate carbon (R²=-0.47; p<0.01) and river current velocity (R²=-0.43; p<0.01). Our data indicate a higher MeHg accumulation in fish from rivers with cascading reservoirs to generate hydroelectricity, possibly due to changes in water flow and changes in the DOC and POC proportions in the water from the reservoirs. These results suggest that the licensing of SHPs should consider if they are alone or in cascade, in order to evaluate the environmental risk associated with mercury contamination.

T.O.1.5-4
INVESTIGATING THE FATE OF ARTISANAL AND SMALL SCALE GOLD MINING ATMOSPHERIC MERCURY EMISSIONS IN THE TROPICS

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Notwithstanding the uncertainty in emission estimates, it seems that recently, for the first time since anthropogenic mercury emission inventories have been compiled, coal combustion is no longer the primary source of anthropogenic mercury to the atmosphere, but that artisanal and small scale scale gold mining (ASGM) activities are the largest single anthropogenic mercury atmospheric source. In the last twenty years the price of gold has gone from just below $300 to just below $1300 an ounce (1 Jan 1999 - 1 Jan 2019), creating the conditions in many parts of the world for an expansion of ASGM. At the same time, moves to limit fossil fuel combustion for power generation, and the wider application of pollution control devices has led to a stagnation, or in some regions, a decrease, in mercury emissions from the power sector. As emission inventories have been compiled retrospectively it is quite probable means that the figures in the most recent anthropogenic emission databases (EDGAR 2012 AMAP/UNEP 2010) underestimate current ASGM emissions, potentially significantly. Unfortunately the economic inducement to operate illegal or informal mines is such that despite potentially, and already this year in Indonesia, India, Zimbabwe and Afghanistan, actually, fatal working conditions, ASGM continues. The differences between mercury emissions from power generation and ASGM are significant. The location, speciation and height of emissions from the two sources differ, and therefore their fate also differs. The dispersion of emissions from ASGM have been investigated using a global CTM over decadal scales, and also using a regional model to focus at higher spatial and vertical resolution the smaller scale processes which may influence mercury dispersion from ASGM. The atmospheric dynamics of the Tropics, the distribution of atmospheric oxidants, the abundance of vegetation, and the frequency of convective precipitation events all contribute to render the fate of mercury emissions from ASGM generally very different from that of emissions from coal combustion for power generation. However, this is...
changing as the use of coal in northern mid-latitudes declines whereas it is increasing in a number of countries in south and south-east Asia. The study of these emissions in the Tropics will require a serious research effort in order to determine current and future health impacts, locally, regionally and globally.

**T.O.1.5-5**

**SPATIAL DISTRIBUTION OF TOTAL MERCURY IN WATER BODIES AROUND ARTISANAL AND SMALL-SCALE GOLD MINING LOCATIONS IN TANZANIA**

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The wide distribution of artisanal gold mining activities subjects Tanzania to wide spread of mercury contamination. The country has experienced steadily increasing in the number of people engaged in artisanal and small scale gold mining (ASGM). This study explores mercury pollution and distribution in the environment around ASGM in Tanzania, where mining sites are monitored for distribution of mercury in the ecosystem. This paper present the findings on the examination of the spatial distribution of total mercury (THg) in water samples collected from domestic water sources around mining and processing sites, Rivers and swamps connected to ASGM activities in Tanzania. Water samples were analysed using Cold Vapour Atomic Fluorescence Spectrophotometer (CVAFS). Results indicate the presence of elevated Hg concentrations in environmental samples from the mining areas. Results indicated that some water sources had THg levels above the WHO guideline of 1.0 µg/L (1000 ng/mL) for safe drinking water. The concentration of THg in water samples ranged from 846.4 to 3,927.8 ng/L. The lowest concentration was observed in water samples from Mugusu River, upstream of the mining area. Across the mining area the concentration increased as you move down the stream and started to decrease after crossing the mine area downstream to the Lake Victoria, The major source of fish in Tanzania. High concentration in rivers under the influence of mining activities, pose threats to environmental and human health since both water and fish from large water bodies are used for human consumption and irrigation activities. Other surveyed mining sites with no rivers at their vicinity, similarly, the surrounding indicated concentrations more than 2000 ng/L of THg. Swampy areas, which are also used for rice farming at mining sites have THg > 1000 ng/L. Generally, the environment needs special attention in order to avoid population contamination through food chain and other biological and physical routes, because all mining sites are increasingly turning to being permanent human settlements.

**1.10 Impacts of climate change on mercury emission, fate and environmental effects**

**T.O.1.10-1**

**IMPACT OF CHANGING OCEAN BIOGEOCHEMISTRY ON METHYLMERCUY FORMATION AND TROPHIC TRANSFER IN THE GLOBAL OCEAN IN THE 21ST CENTURY**

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Methylmercury (MeHg) undergoes extraordinary degree of bioaccumulation and biomagnification in pelagic marine food webs with the largest concentration increase from seawater to plankton. Warming climate increases the global sea surface temperature and changes the nutrients supply and light availability (refs). These changes have significant impact on the ocean biogeochemistry, especially primary productivity, carbon export, and the community structure of plankton ecosystem, which have a strong impact on MeHg formation and trophic transfer. Here we evaluate the influence of changing ocean biogeochemistry on the formation and trophic transfer of MeHg in the global ocean over the course of a hypothetical twenty-first century. We use a global ocean model for Hg with ocean biogeochemistry parameters from the Darwin ecosystem model driven by the MIT integrated Global Systems Model (IGSM), which is run for the twenty-first century forced by human emissions for a ‘business as usual’ scenario. We find that the changes in ocean biogeochemistry can propagate to ocean organic mercury cycling and influence the potential exposure and human health risk to MeHg, with many of these changes are local and vary drastically at different regions. The poleward migration of phytoplankton habitats caused by warming ocean temperature and pCO2 fertilizer effects are the main driver for seawater MeHg concentration changes, and the global average MeHg concentrations are predicted to increase by 2100. In addition to seawater concentrations, the MeHg concentrations in phytoplankton are also influenced by phytoplankton biomass and community structure. The global average MeHg concentration is also influenced by the increase in the number of people engaged in artisanal and small scale gold mining (ASGM). This study explores mercury pollution and distribution in the environment around ASGM in Tanzania, where mining sites are monitored for distribution of mercury in the ecosystem. This paper present the findings on the examination of the spatial distribution of total mercury (THg) in water samples collected from domestic water sources around mining and processing sites, Rivers and swamps connected to ASGM activities in Tanzania. Water samples were analysed using Cold Vapour Atomic Fluorescence Spectrophotometer (CVAFS). Results indicate the presence of elevated Hg concentrations in environmental samples from the mining areas. Results indicated that some water sources had THg levels above the WHO guideline of 1.0 µg/L (1000 ng/mL) for safe drinking water. The concentration of THg in water samples ranged from 846.4 to 3,927.8 ng/L. The lowest concentration was observed in water samples from Mugusu River, upstream of the mining area. Across the mining area the concentration increased as you move down the stream and started to decrease after crossing the mine area downstream to the Lake Victoria, The major source of fish in Tanzania. High concentration in rivers under the influence of mining activities, pose threats to environmental and human health since both water and fish from large water bodies are used for human consumption and irrigation activities. Other surveyed mining sites with no rivers at their vicinity, similarly, the surrounding indicated concentrations more than 2000 ng/L of THg. Swampy areas, which are also used for rice farming at mining sites have THg > 1000 ng/L. Generally, the environment needs special attention in order to avoid population contamination through food chain and other biological and physical routes, because all mining sites are increasingly turning to being permanent human settlements.

**T.O.1.5-6**

**TOTAL MERCURY CONCENTRATION IN BROWN BOBY (SULA LEUCOGASTER) FROM SANTANA ARCHIPELAGO, MACAÉ, RIO DE JANEIRO, BRAZIL.**

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Marine pollution has been growing over the years and is directly associated with domestic and industrial effluent discharges and agricultural waste in the rivers and estuarine areas. Among these pollutants, mercury (Hg) causes a great concern due to its toxicity and biomagnification potential. Natural sources of mercury emissions are volcanoes, geothermal activity and emissions from soil, but approximately two-thirds of Hg in the atmosphere originates from anthropogenic sources. Seabirds have been used as environmental indicators of contamination by toxic elements due their high trophic positions in the marine food chain, longevity and the possibility of non-destructive sample tissue collection (feather, blood, etc). Furthermore, feathers are consider a reliable proxy for contamination levels in the environment. This study aims to quantify the concentrations of total mercury (HgT) in feathers, blood and eggs (yolk and albumen) of adults and juveniles of Brown Booby (Sula leucogaster) from Santa Archipelago. This Archipelago is located approximately 8 km from Macaé coast, on the north littoral of Rio de Janeiro State. Although the archipelago was decreed as a Protected Area in 1989, it still lacks a management plan, even with intense anthropogenic activities and imminent construction of a new port nearby. The samples were collect from February to September 2018, in monthly expeditions to the archipelago. Body feathers and blood from 20 males, 20 females and 20 juveniles were sample, and 10 eggs were collect from the nests. In the lab, blood and eggs were lyophilized. Feathers were washed in EDTA + Milli-Q® and cut. To determine the HgT concentration in each tissue an Atomic Absorption Spectrophotometer coupled to a Flow Injection Mercury System 400 – Perkin-Elmer was used. Average concentrations (µg/kg dry weight) in feathers were 2566.76±730 for males, 2853.90±824 for females and 1603.22±796 for juvenile. In blood the average concentration were 1353.44±438 in males, female 1307.90±291 and juvenile 1371.08±1048. The HgT concentration in eggs were 616.45±99. Regarding the feathers, no significant difference between males and females in HgT concentrations was observed, but there is a significant difference between adults and juveniles. In the blood, there is no significant difference between gender and age. Lastly, there is no correlation between HgT concentration in egg and females tissues (feather and blood). The concentrations found in these samples are similar to levels reported by previous studies with Brown Booby in tropical areas.
concentrations in phytoplankton are predicted to be slightly decreased by climate change effect, and significantly increased by the bloom of Synechococcus as a result of ocean acidification. We also note that, compared with bulk concentrations in phytoplankton, the bioconcentration factor (BCF) is more sensitive to community structure change, especially the increased fraction of small phytoplankton function groups in the future ocean, and the BCF is increased by climate change effects but decreased by ocean acidification. At higher trophic level, the MeHg mass and biomagnification factor (BMF) are mainly controlled by graze flux, which is largely influenced by the community structure of both phytoplankton and zooplankton, as well as environmental variables such as temperature. Our study shows that the simultaneously poleward migration of phytoplankton and zooplankton could decrease graze flux, as the low temperature in higher latitudes decrease graze activity and subsequently BMF.

T.O.1.10-3

TOWARDS DEEPER UNDERSTANDING ON THE INFLUENCE OF CLIMATIC AND PRODUCTIVITY TO MERCURY BIOMAGNIFICATION IN SUBARCTIC LAKE FOOD WEBS

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Subarctic regions are among the most pristine ecosystems on Earth, where indigenous people obtain a significant amount of protein from local fish and game. However, pollutants and toxic heavy metals like mercury (Hg) which biomagnify in aquatic food webs, are mainly atmospherically transported across the planet and regularly deposited in subarctic. In this region, lakes are getting warmer and more productive due to climate change that exceeds the global average and nature exploitation consistently intensifying land-use practices (intensive forestry actions such as clear-cutting and ditching), potentially increasing leaching of Hg into lake ecosystems. Thus, there is an immediate need to evaluate such environmental changes affect the level and magnification of toxic materials in food webs.

In this study, we test how the joint effects of climate and land-use influence mercury levels at the base of lake food webs and identify patterns of biomagnification between total mercury (log10THg) and trophic level determined with stable isotope of nitrogen (δ15N). We sampled primary producers (algae) to top consumers, piscivorous fish, from a representative set of 20 subarctic lake situated on a latitudinal (69.0 – 66.50 N), climatic (±1,5°C, ±15% precipitation) and catchment land-use gradients (from pristine to intensive forestry) in Norway and Finland.

Our results reveal increasingly high THg levels in base of food webs towards warmer and more productive lakes. This lead to elevated concentrations of Hg in higher trophic levels. However, stronger THg biomagnification was observed as steeper regression slopes in the northern cold and oligotrophic lakes compared to warmer and eutrophic southern lakes. These results reveal the complexity of mercury dynamics in which warmer climate and more intense land-use elevate mercury at the base of food webs. The highest mercury levels in locally consumed fish species were found in warm and productive lakes suggesting importance to limit mercury inputs to the base of food chains. Further studies from lake food webs from low and high subarctic regions are needed to test if biomagnification slopes are consistently steeper towards the north to standardize the pattern worldwide. Ultimately, combining biomagnification datasets across the circumpolar subarctic would help us to understand the fate of mercury in food webs in changing the environment and provide a knowledgable base for further actions.

T.O.1.10-4

HOLOCENE RECONSTRUCTION OF HG DEPOSITION IN THE CENTRAL ANDES: RESPECTIVE CONTRIBUTION OF CLIMATE CHANGE, VOLCANISM AND ANTHROPOGENIC ACTIVITIES

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The central Andes region has been subject to major climate changes along the Holocene and to Hg contamination related to anthropogenic activities (i.e., mining and industry) over the last past two millennia. Based on a set of high-resolution cores collected in high altitude (> 3500 m a.s.l.) lakes, lagoons and peat bogs between 13 and 25° South and 70 to 65° West, we reconstructed the historical Hg deposition along the Holocene in the central Andes region. The comparison of Hg with multiproxy analysis (i.e., pollens, organic biomarkers, stable C and O isotopes, inorganic proxies...) allowed reconstructing the changes in Hg deposition related with natural (atmospheric pools, volcanism) and anthropogenic (mining and industry) sources, together with the evolution of the studied ecosystems.

Our results show that centennial to millennial changes in Hg deposition over the eastern cordillera were found related to the intensity of orographic moisture on the eastern flank of the oriental Andean chain. Hg was found to be mostly supplied by the easterlies winds originating from the Atlantic and driven by both the Atlantic meridional overturning circulation (AMOC) and the Intertropical Convergence Zone (ITCZ) oscillations. In particular, the middle Holocene dry event was identified as the lowest deposition period. Amongst anthropogenic regional contamination, the colonial era (~1550 – 1880 AD) was found as the largest historical period of anthropogenic emission (i.e., silver mining) recorded over the Andean Altiplano and the western Andes. Local volcanic activity was identified as a significant source of Hg at a local to regional scale during the pre-anthropogenic epochs. Finally, the impact of global Hg emissions since the industrial revolution (mainly from North Hemisphere) was also clearly identified in such remote locations of the South hemisphere highlighting the global dispersion of Hg contamination.

GLOBAL WARMING ACCELERATES UPTAKE OF ATMOSPHERIC MERCURY IN GLACIER RETREATED REGIONS

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As global climate continues to warm, thawing of glaciers and permafrost could release a large quantity of mercury (Hg) originally locked in ice into the atmosphere and downstream ecosystems 1-3. Here we show a negative feedback involving an opposite process that captures atmospheric Hg through glacier-to-vegetation succession. Our study using stable isotope techniques at three succession sites on the Tibetan Plateau (TP) reveals that evolving vegetation serves as an active "pump" to take up gaseous elemental mercury (Hg0) from the atmosphere. The accelerated uptake enriches the Hg pool size in glacier retreated areas by a factor of ~10 compared to the original pool size in the glacier.

Using data of global glacier retreat and vegetation succession, we estimated that about 800–1100 Mg of Hg have been accumulated in glacier retreated areas (5% of the global land surface) since the Little Ice Age (~1850). We further estimated that by 2100, an additional ~1100 Mg of Hg will be sequestered from the atmosphere in glacier retreated areas (5‰ of the global land surface) since the Little Ice Age (~1850). We further estimated that by 2100, an additional ~1100 Mg of Hg will be sequestered from the atmosphere in glacier retreated areas (5‰ of the global land surface) since the Little Ice Age (~1850). We further estimated that by 2100, an additional ~1100 Mg of Hg will be sequestered from the atmosphere in glacier retreated areas (5‰ of the global land surface) since the Little Ice Age (~1850).

1.1B Atmospheric mercury cycling and transformations: Insights from measurements and models

SOIL-ATMOSPHERIC EXCHANGE OF GASEOUS ELEMENTAL MERCURY IN THREE SUBTROPICAL FORESTS WITH DIFFERENT LEVELS OF SUBSTRATE HG CONCENTRATION

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The subtropical forest soils in southern China have accumulated a large amount of historically deposited mercury (Hg) and Hg re-emission may play an important role in the global mercury cycle. In this study, soil-atmospheric exchange of gaseous elemental mercury (Hg0) was monitored at three forest sites, with different levels of soil Hg content and atmospheric Hg0 concentration, by dynamic flux chamber...
The background site, Qianzhanzhou (QYZ), showed net soil Hg0 emission (annual average Hg0 flux of 50.8 ng m-2 d-1), with significantly diurnal and seasonal variations. In contrast, the moderately polluted site, Tieshanping (TSP, suburb of Chongqing city), showed much lower Hg0 flux (7.36 ng m-2 d-1) than QYZ, even negative in spring and winter. The heavily contaminated site, Zhuzhou (ZZ, near a zinc smelter), showed extremely high emission (annual average Hg0 flux of 371 ng m-2 d-1), but relatively low in summer (13.7 ng m-2 d-1). The results clearly indicated the stimulation of high soil Hg content and the suppression of high atmospheric Hg0 concentration on soil Hg0 emission. Future Hg emission abatement from anthropogenic sources may enhance re-emission of historically deposited Hg from subtropical forests, which delaying the decrease in atmospheric Hg0 concentration in the future.

T.O.1.1B-2

COMPARISON OF TWO ATMOSPHERIC MERCURY BI-DIRECTIONAL EXCHANGE MODELS

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Air-surface exchange of gaseous elemental mercury (GEM) vapor plays a vital role in the global cycling of mercury. Models are widely used for estimating GEM exchange flux due to the limitation of flux measurement at sites that are either inaccessible or challenging. The objective of this study is to compare two GEM bidirectional exchange models by Wang et al., 2014 and Wright & Zhang, 2015. The fluxes and exchange velocities were estimated using observed GEM concentration and simulated meteorological data during June to September 2010 at a site 50 km west of Atlanta, Georgia, United States. Larger emission flux was estimated by Wright & Zhang’s model than that by Wang’s (mean of 1.07 pg m-2s-1 vs. 0.85 pg m-2s-1), while the deposition fluxes were similar (0.79 pg m-2s-1 vs. 0.75 pg m-2s-1). The net emission flux by Wright & Zhang’s was significantly higher than that by Wang’s (0.28 pg m-2s-1 vs. 0.1 pg m-2s-1). The discrepancies between the outputs of the two models were primarily caused by (1) capped aerodynamic resistance (Ra) implemented in Wright & Zhang’s model leading to smaller Ra, and (2) consideration of wetted soil effect in Wang’s model resulting in higher soil resistance. Other causes include the settings in diffusivities (constants in Wang’s model, depending on ambient temperature in Wright & Zhang’s), estimation of canopy level visible solar radiation, and range of correction factor for water vapor pressure deficit. Knowledge gained from this study helps understand the differences between the two models and dominant factors causing difference in model results.

T.O.1.1B-3

DECREASING TREND IN NIGHTTIME ATMOSPHERIC MERCURY CONCENTRATIONS IN 2006-2016 AT A HIGH-ELEVATION BACKGROUND SITE DOWNWIND OF THE EAST ASIA CONTINENT

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Concentrations and speciation of atmospheric mercury (Hg) have been monitored using the Tekran 2537/1130/1135 at the Lulin Atmospheric Background Station (LABS; 23.47°N, 120.87°E, 2862 m a.s.l.) in Taiwan since April 2006 and is still ongoing. This is likely the only long-term atmospheric Hg dataset being collected at a high-elevation baseline site downwind of the East Asia Continent. Here we reported the trend of gaseous elemental Hg (GEM) at LABS between April 2006 and December 2016, before the Minamata Convention on Mercury entered into force in 2017. Previous research indicated nighttime 0-8 am) data are more representative of regional emission/transport influence. Therefore, only nighttime GEM data are analyzed using seasonal Mann-Kendall test and Sen’s slope method. A significant decreasing trend in GEM at a rate of -1.5% yr-1 (-0.0215 ng m-3 yr-1) in 2006-2016 is found, comparable to the decreasing rates observed at sites in Europe, North America, South Africa, and over the North Atlantic Ocean. Five major source regions of GEM at LABS are identified by the cluster analysis of backward trajectories, including northern Indochina Peninsula, China, Northeast Asia, the Pacific Ocean, and South China Sea. Significant decreasing trends in GEM are found for air masses coming from northern Indochina Peninsula (-2.6 % yr-1), China (-2.4 % yr-1), Northeast Asia (-2.0 % yr-1), and the Pacific Ocean (-1.7 % yr-1). Decreasing GEM trend (-1.5 % yr-1), but not significant, is also found for air masses coming from South China Sea. Few recent multi-year measurements in East China also reported decreasing trends in GEM. Decline in nighttime GEM concentrations at the LABS could be caused by changes in regional emission quantity, speciation and temporal/spatial distributions, quantity of East Asian outflow, and transport pattern. Additionally, a significant negative correlation (R2=0.107, p<0.01) between monthly GEM and normalized difference vegetation index (NDVI) is found at the LABS, suggesting vegetation uptake may also contribute to the decreasing trend in GEM in 2006-2016.

T.O.1.1B-4

MECHANISTIC OXIDATION AND REDUCTION OF ATMOSPHERIC Hg: IMPLICATIONS FOR SPECIATION, DEPOSITION PATTERNS AND BUDGET IN A GLOBAL CHEMISTRY MODEL

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The conceptual and modeled representation of Hg’s atmospheric redox chemistry has recently benefited from many theoretical and observational studies. Both laboratory studies and theoretical calculations have explored the elementary processes of mercury oxidation in the atmosphere via bromine, chlorine, and hydroxyl radical-initiated mechanisms, leading to predictions of the speciation of Hg(II) produced, along with the rate of production. Theoretical calculations of the species-specific spectra of photolysis cross-sections for atmospherically-relevant Hg(II) species suggest photo-reduction of Hg(II) in the gas phase represents the major reduction pathway for mercury in the atmosphere. Here we fully incorporate this new, complex redox chemistry into the GEOS-Chem 3-D atmospheric chemistry model. We present results from simulations of Hg chemistry as part of the full standard GEOS-Chem simulation for time-varying and internally consistent representation of oxidizing radical concentrations, and photolysis using individual Hg(II) species spectra and the Fast-JX photolysis mechanism. We couple the GEOS-Chem simulation of the atmosphere to the MITgcm simulation of Hg in the ocean to derive a consistent picture of the implications for the atmospheric mercury budget and deposition patterns, finding an atmospheric lifetime of total mercury of 7-10 months against deposition. We find that this chemistry simulates atmospheric concentrations and wet deposition that are consistent with measurements at observation sites. We highlight the key elements of the full redox chemistry, including fast and slow cycling involving specific Hg(II) species and the role of liquid water in Hg(II) reduction. We discuss the implications for our understanding of Hg speciation, global deposition, and the atmospheric mercury budget.
To estimate the potential of different ecosystems as sinks or sources for atmospheric Hg, reliable quantification of land-atmosphere exchange of gaseous elemental Hg (GEM) is crucial. We have made the first annual Hg budget based on continuous measurements of gaseous-atmosphere exchange of GEM using a novel relaxed eddy accumulation (REA) system. The annual Hg mass balance was dominated by net GEM emission (10.2 µg m⁻²) due to substantial evasion between May and October. The annual wet bulk deposition of Hg was 3.9 µg m⁻². The annual discharge of Hg from the peatland area (1.9 km²) amounted to 1.3 µg m⁻². The GEM evasion rate, a factor of 2.6 higher than wet bulk deposition, can be explained by the recent reduction in the atmospheric Hg concentration to a value below the compensation point for this peatland, turning it from a sink into a source of Hg emission back to the atmosphere after decades of Hg accumulation. This is consistent with the Hg concentration gradients in the superficial peat which decline from a Hg concentration peak at about 30 cm depth (110 ng g⁻¹) towards the surface (24 ng g⁻¹). Under the assumptions that environmental conditions remain stable and that catchment runoff is dominated by Hg from the uppermost peat layers, it will take around 80 years to deplete the entire pool of legacy Hg in the uppermost 34 cm to a background concentration level of 20 ng g⁻¹. We suggest that the strong Hg evasion demonstrated in this study means that open boreal peatlands and thus downstream ecosystems may recover more rapidly from past atmospheric Hg deposition than previously assumed.

Given the current international efforts to protect human health and the environment from the adverse effects of mercury in accordance with the United Nation’s 2013 Minamata Convention on Mercury, we believe our findings contribute to a better understanding of how emission reductions will influence mercury cycling in northern peatlands and their role for the mercury status of fresh water fish in the Northern Hemisphere. Our findings also raise the question as to whether recent reductions of GEM using a novel relaxed eddy accumulation (REA) system. The analysis is supplemented with other trace gases (CO, CO₂, CH₄, O₃, and ²²²Rn) measured at Cape Point which provide additional information on the source and sink mechanisms and the reasons for changing trends.

We find that continental air is generally associated with the lowest GEM concentrations with the exception of regional point sources. The southern Indian Ocean (below 25°S) is the dominant source region for elevated GEM concentrations at Cape Point. Correlation with sea surface temperature and Chlorophyll(a) observations suggest an impact of marine primary production on GEM concentrations at Cape Point.

1.7B Sources and cycling of mercury in freshwater ecosystems and oceans

T.O.1.7B-1

TERRESTRIAL INPUTS AS A VECTOR OF HG CONTAMINATION IN A GLACIER AND RIVER-INFLUENCED ARCTIC FJORD SYSTEM (ISFJORDEN, SVALBARD)

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Increased terrestrial run-off in Arctic regions is one major impact of climate change. As temperatures and precipitation increase and permafrost thaws and glaciers melt, coastal areas are experiencing increased inputs from the terrestrial environment. These inputs bring water, sediments, nutrients, organic matter and contaminants across the land-ocean interface with a range of implications for coastal biogeochemistry and contamination. Of particular concern is the mobilization of toxic environmental contaminants like mercury (Hg) from catchment soils to coastal surface waters. As northern permafrost soils store a globally significant amount of Hg, quantifying the contaminant load and interaction with other physical parameters is necessary for understanding how increased run-off with a warming climate is likely to affect contamination of coastal food-webs. In order to investigate the physicochemical and contaminant footprint of terrestrial inputs on an Arctic fjord, 17 stations were sampled in May, June and August along gradients in the Isfjord fjord system (Svalbard) in the summer of 2018. Particulate and aqueous TotHg and MeHg concentrations were related to physicochemical conditions along salinity gradients from glacier fronts and river outlets to the outer fjord. Preliminary results indicate that terrestrial run-off is the main source of TotHg to the system, suggesting that decades of long range atmospheric transport of mercury today outweighs concentrations transported northward by marine currents. Furthermore, Hg concentrations were related to concentrations of suspended particulate matter and aromaticity of DOM to distinguish between the relative importance of glacial (high sediment load) and permafrost (high humic load) contributions. In addition to Hg, gradients in concentrations of nutrients (N, P, Si), terrestrial organic matter, and degree of aromaticity of DOM demonstrated conservative mixing, fol-
lowing the trends observed in salinity. Subsequent effects on primary production (nutrient and light availability) are expected to have implications for MeHg production along the freshwater to marine continuum. Preliminary results of this study reveal a pervasive freshwater footprint in the inner fjord arms of Isfjorden and demonstrate that these inputs can have substantial effects on the local physicochemical conditions and contamination of the fjord.

T.O.1.7B-2

ECOSYSTEM CONTROLS ON THE INCIDENCE OF METHYLMERCURY IN TEMPERATE ESTUARINE WATER COLUMNS

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Many studies suggest that bioaccumulation of methylmercury (MeHg) into forage fish across estuaries is related to MeHg levels in the water column from which they were harvested. Sources of MeHg to estuarine water columns, however, are more difficult to constrain. For this study, we questioned whether the incidence of MeHg in field observations from multiple temperate estuaries in the Northeast US could be predicted by a few ecosystem variables which would then allow for a better understanding of estuarine water column MeHg source dynamics. We investigated this question using a statistical approach that included 47 predictors for both water column MeHg and HgT suggesting a continual recycling of the legacy Hg between these two pools. Our study suggests that MeHg in estuarine systems is likely to be impacted by changes in DOC loading to estuaries which is expected to occur in temperate regions under predicted climate change scenarios. Further, MeHg in estuaries may be best controlled by managing inorganic Hg loading from the watershed, but at highly contaminated sites controls on legacy Hg in the sediments are likely necessary.

T.O.1.7B-4

RELATIONSHIPS BETWEEN MERCURY IN SEDIMENT AND THE WATER COLUMN TO FISH BIOACCUMULATION IN HUMAN IMPACTED ESTUARIES IN LONG ISLAND, NY

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Estuaries are important feeding areas for fish that humans consume and are sources of exposure for contaminants that are bioaccumulated and transferred up the food web. Methylmercury (MeHg) is a toxic pollutant of global concern to which humans are exposed through fish consumption. The sources, transformations, and bioavailability of MeHg in estuaries are complex, but its fate in the food web is determined by the relationships between sediment and water column concentrations and bioavailability to lower trophic level fish. Moreover, other environmental impacts such as nutrient loading (carbon, nitrogen, and sulfur) are also known to potentially impact these biogeochemical and ecological processes and the fate of mercury (Hg). Total Hg and MeHg concentrations were examined in water, surface sediments and forage fish Fundulus heteroclitus and Menidia menidia) to establish any impact of hypoxic waters on Hg levels in cod, we obtained cod otoliths from the specimens bank at the Swedish Museum of Natural History (captured in 2013) and measured their Mn, Ca ratios (a proxy for hypoxia exposure). We combined this with information on the Hg level in muscle for the same cod and found that increased lifetime exposure to hypoxia could lead to higher Hg levels. To understand how the presence of hypoxic and anoxic zones can lead to increases in Hg concentration in cod we combine observations of inorganic Hg and MeHg in water, collected across a redoxcline in the Baltic Sea, with speciation modeling and incubation experiments. Based on insights from these results we will discuss how MeHg produced in the hypoxic and anoxic zones can enter the food web, which is mostly located in the normoxic water column.

T.O.1.7B-3

DO OXYGEN DEPLETED WATER ZONES IMPACT MERCURY LEVELS IN COASTAL SEA FOOD WEBS?

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Oxygen-depleted areas are spreading in coastal and offshore waters worldwide but the implication for mercury (Hg) entering food webs is uncertain. We combine a top down and a bottom up approach to 1) establish any impact of hypoxic waters on Hg levels in cod, we obtained cod otoliths from the specimens bank at the Swedish Museum of Natural History (captured in 2013) and measured their Mn, Ca ratios (a proxy for hypoxia exposure). We combined this with information on the Hg level in muscle for the same cod and found that increased lifetime exposure to hypoxia could lead to higher Hg levels. To understand how the presence of hypoxic and anoxic zones can lead to increases in Hg concentration in cod we combine observations of inorganic Hg and MeHg in water, collected across a redoxcline in the Baltic Sea, with speciation modeling and incubation experiments. Based on insights from these results we will discuss how MeHg produced in the hypoxic and anoxic zones can enter the food web, which is mostly located in the normoxic water column.
where “biomass dilution” resulted in lower Hg concentrations in high algal densities. In contrast, concentrations in F. heteroclitus were only predicted by sediment concentrations which reflected their more omnivorous feeding on both sediment detritus and algae. From this study of two similar human impacted systems, we find that water column and sediment compartments can be related in their Hg concentrations, but that fish concentrations are dependent on their food source.

### CONTRASTING EFFECTS OF PROBABLE NITROGEN LIMITATION AND ITS ABSENCE ON MERCURY SPECIATION IN THE SOUTH ATLANTIC OCEAN AS INDICATORS OF MICROBIAL MERCURY TRANSFORMATIONS

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Microbial transformations of methylated mercury (MeHg) and dissolved gaseous mercury (DGM) at the lowest marine trophic levels are still not well understood. This is especially important in oligotrophic and nutrient-limited seas, where microbial food web dominate over classical food web. To better understand the effects of probable nitrogen limitation and its absence (N-limitation and no-N-limitation) on the abundance of Hg species, waters of South Atlantic Ocean along 40°S parallel were investigated in 2011/2012 during GEOTRACES cruise JC068. Our statistical analysis of the results focuses on the examination of the effects of N-limitation on relations between different mercury fractions (total mercury – THg, MeHg, and DGM) and nutrients and environmental parameters. In order to test the nutrient-limitation hypothesis, we have compared our results with previous analysis from the Central Adriatic Sea.

Non-metric multi-dimensional scaling showed discrete separation of data obtained under N-limitation and no-N-limitation conditions; this separation is mostly emphasized for DGM data. Mann-Whitney test showed significant differences in DGM and MeHg concentrations under N-limitation and no-N-limitation.

Principal component analysis (PCA) has revealed two contrasting clusters. First cluster is grouped around DGM and nutrients under no-N-limitation. Only under no-N-limitation, DGM was significantly related to nutrients and environmental parameter, which might be an indication of metabolism-dependent Hg transformations. DGM is significantly correlated with dissolved inorganic carbon (DIC) under no-N-limitation, indicating that organic matter remineralization might be the driving force for DGM production in the open ocean. In addition, DGM concentrations can be estimated within ±20% from the measured values in 70% of data under no-N-limitation from DIC and nitrate concentrations using multiple linear regression analysis. DGM shows negative correlation with seawater temperature under no-N-limitation, and positive correlation under N-limitation conditions. The same trends are found in the Central Adriatic Sea where the absence and presence of probable phosphorus limitation, respectively, indicating nutrient and temperature dependent Hg reduction. The second PCA cluster is grouped around MeHg, temperature and fluorescence under N-limitation. This might indicate that net Hg methylation in the water column is related with microbial methylation under N-limitation when microbial growth is impeded. This is contrary from the analysis in the Central Adriatic Sea where the activity of heterotrophic bacteria seemed responsible for most of net Hg methylation in seawater under the absence of probable phosphorus limitation during winter. Combined, these results indicate the presence of at least two different Hg methylation pathways in open seawater.

### MERCURY ISOTOPE FRACTIONATION DURING AQUEOUS-PHASE REDUCTION OF HgII BY LOW MOLECULAR WEIGHT ORGANIC COMPOUNDS

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Mercury (Hg) is a global contaminant due to the volatility and chemical inertness of its elemental form (Hg0) towards oxidation that renders atmospheric long-distance transport viable. In the atmospheric environment, oxidized Hg (HgII) existing as gaseous or particle-aggregated molecules comparatively displays many times higher rates of dry and wet deposition and subsequently transient lifetime in the lower troposphere. Red-ox transformations of Hg in the atmosphere occur both by homogeneous and heterogeneous reactions in the gas phase, and also in the aqueous phase and heterogeneous phases and at atmospheric interfaces. Evidence for surface-enhanced and complex atmospherically-relevant reactions are numerous from laboratory studies. However, the extent of photolytical reduction of atmospheric HgII is debated given the lack of a systematic understanding of reduction pathways. Nonetheless, there are field studies and global chemical transport models suggesting the general occurrence of atmospheric HgII reduction. In this experimental study, we have investigated the kinetics, mechanisms and stable Hg isotope fractionalization during aqueous-phase photo-reduction of HgII by a series of semi-volatile aliphatic and aromatic organic compounds that are potential components of secondary organic aerosols (SOA) making up a prominent fraction of tropospheric particulate matter. Yielding considerably contrasting mass-dependent fractionation (MDF, δ620Hg) and mass-independent fractionation (MIF, Δ199Hg and Δ201Hg) signatures, the isotopic characterization of the individual HgII – organics photo-reactions provide a unique fingerprint for each of the classes of reactions. We have established the equipment for aqueous phase reduction, and have found HgII by C2O42- preceded by the lighter Hg isotopes were preferentially reduced to the product Hg0, which in addition displays (-) odd-MIF.

### MERCURY AND METHYLMERCURY LEVELS IN ATRATO RIVER, AN ECOSYSTEM HIGHLY IMPACTED BY GOLD MINING IN THE COLOMBIAN PACIFIC

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Mercury (Hg) is one of the most harmful pollutants. The release of this metal into the environment from gold mining activities represents a risk to human health and the ecosystems. The aim of this study was to assess the levels of total Hg (T-Hg) in human and environmental matrices; and to determine fish consumption-based risks for T-Hg ingestion in the Atrato River, Biogeographic Choco, a global biodiversity hotspot at the Colombian Pacific. Human hair from two riverine communities along the river, bottom sediments and urban air were assessed for T-Hg, whereas fish muscle samples were analyzed for...
T-Hg and methylmercury (MeHg). The median T-Hg values in hair for humans in Quibdo and Paimado were 1.26 µg/g (range: 0.02-11.6 nmol/g) and 0.67 µg/g (range: 0.07-6.47 µg/g), respectively. Mercury levels in examined locations were weakly but significantly associated with stature (ρ=0.145, P=0.024). Air T-Hg levels in Quibdo, the major city along Atrato River, were very high inside gold shops, reaching up to 200.9-fold greater concentrations than the background. Mercury levels in fish from Atrato River were above WHO limits, with highest levels in Ageneiosus pardalis, Sternopygus aequilabiatus, Rhamdia quelen, and Leporinus muyscorum species offer a low risk to human health. Sediment samples from different sites of the Atrato River showed low levels of T-Hg, probably as a result of the frequent rain that keeps a high river outflow. However, contamination factor values revealed a moderate pollution in 44% of sampling sites along the Atrato. In short, Hg pollution is widespread in the Biogeographic Choco, and immediate programs should be developed to protect human population and preserve its biodiversity.

**T.O.2.2B-2**

**A NOVEL METHOD TO RAPIDLY ASSESS OCCUPATIONAL EXPOSURE TO MERCURY IN ARTISANAL AND SMALL-SCALE GOLD MINING (ASGM) USING NANO-GOLD COLOURIMETRY: FIELD AND LABORATORY TESTING**

**BLACK MOHER, Paleah**

Artisanal and small-scale gold mining (ASGM) is a crucial economic activity for millions of people throughout the globe, however it is associated with significant health concerns and high mercury exposure. Currently there are no inexpensive and rapid methods to assess occupational Hg0 exposure as all commercial monitors require power and/or laboratory analysis. These barriers have greatly limited the availability of data on mercury exposure in rural and remote locations throughout the world. A novel method is proposed that would provide rapid on-site information without the need for any specialized equipment or laboratory analysis. The direct reduction of gold into a porous nanostructure disk or membrane creates a colourometric indicator in its surface plasmon resonance when an Au-Hg amalgam is formed, which can be quantified by the analysis of pictures obtained with a cell phone camera. Laboratory and field proof of concept testing demonstrate linear changes in viscosity and color with increasing Hg0 exposure. Initial field testing was conducted at an ASGM site in Burkina Faso by placing disks alongside commercially available passive monitors during an open-pan burn event the miners conducted on-site. A subsequent field test was performed in Indonesia using a much cheaper and simpler membrane construction. The commercially available monitors have been validated by the US’s Occupational Safety and Health Administration (OSHA) and are widely used in several industries, although to our knowledge this was the first time they were used in ASGM. We found that occupational exposure was high with a time weighted average (TWA) exposure of 7026 ± 6857 µg/m3 for burners. Most (82%) of the people present at the burn exceeded OSHA’s Permissible Exposure Limit (PEL) of 100 µg/m3, and 11% exceeded the level considered to be Immediately Dangerous to Life and Health (IDLH) of 10,000 µg/m3. A relatively good correlation was obtained between the commercial monitors and the disks, suggesting that the disk sampler is effectively sensitive in field conditions and that the color change can be used as a qualitative indicator of mercury exposure. The membranes also showed excellent response. Further work is required to validate this method. This novel technology may provide a reliable and economical method to monitor real-time mercury exposure in rural and remote ASGM locations as well as in other industries where Hg0 exposure is suspected.

**T.O.2.2B-3**

**DETERMINANTS OF HEALTH AMONG ARTISANAL SMALL-SCALE GOLD MINERS USING MERCURY FOR GOLD EXTRACTION IN KADOMA, ZIMBABWE**

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Background: Artisanal small-scale gold (ASG) miners use simple methods including the application of mercury to extract gold from ore resulting in environmental contamination and human exposure of workers themselves and people nearby. More than 500,000 ASG miners are assumed to be active in Zimbabwe.

Objective: To identify and discuss main determinants of health among ASG miners using mercury for gold extraction in Kadoma, Zimbabwe.

Methods: The determinants of health among ASG miners using mercury for gold extraction were surveyed in a two-week field project in Kadoma, Zimbabwe. Methods included individual interviews (quantitative/qualitative), qualitative group interviews, observations and informal conversation. Thematic analysis was used to encode qualitative interviews. Quantitative data was analysed using descriptive statistics. Notes of observations and informal talks were used to confirm or contradict information collected during the interviews.

Results: 83 adult miners, 2 nurses and 2 health officials participated in the project. The miner population is growing with a slow but increasing involvement of particularly women. Korokozas (“miners without rules”) is another expanding group. The general health situation of miners was described as poor. Lifestyle factors were dominated by high alcohol consumption (one quarter drinks alcohol daily) and cigarette smoking (34%). Living conditions differ considerably. Some sleep under very primitive, unhealthy conditions near the mines while others live in villages. Most miners had good social and community networks while they are organized in small groups at fixed mines supported by the local mining association. Beyond, Korokozas build only loose bonds with other miners. Working conditions are hazardous, including the use of mercury. Amalgamation is done by the miners. Amalgam burning is nearly always attended or entirely executed by the mine owners to avoid theft. The use of personal protection equipment (PPE) is mixed but in general poor. 30-40% of miners answered to use PPE like respirator (39%), ear plug (30%), eye protection (30%) or dust masks (34%), while this was not confirmed due to observations of the researcher team. The location of ASG mines in remote areas leads to a difficult access to health care. Their income varies from month to month. Superior determinants of health are heavy rainfalls.

Conclusion: Important determinants of health were identified to describe the situation of ASG miners. Opportunities to design appropriate interventions for safeguarding miners’ health were revealed.

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DIETARY COUNSELING ON RISKS AND BENEFITS OF FISH CONSUMPTION AND MERCURY TESTING IN REPRODUCTIVE AGE WOMEN IN A HEALTH CLINIC SETTING

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Consumption of fish low in mercury should be encouraged in reproductive age women because benefits of fish consumption for the fetus, including improved eye and brain development, outweigh risks if fish that are low in mercury are eaten. The Fish are Important for Superior Health Project was designed to intervene with reproductive age women to reduce mercury exposure in an area where elevated exposure in infants has been found.

At a clinic visit, 499 women answered detailed questions on fish consumed in the past year and donated blood for mercury and docosahexaenoic acid (DHA) measurements. A nurse delivered information on risk and benefits of eating fish and tailored advice on fish consumption based on the information reported by the participant in the survey. Laboratory results were reported to participants through letters from the clinic. After six months, all 15 women with blood mercury levels above the level equivalent to the EPA RfD (5.8 µg/L), and 30 with blood mercury below 5.8 µg/L completed a follow-up visit identical to their initial clinic visit. Longitudinal models tested changes in measures of mercury, DHA and fish intake and adjusted for season of assessment, usual fish portion size and omega-3 fatty acid supplement use.

At the 6 month follow up, we found a decline in blood mercury and in consumption of fish species with moderate Hg contamination (>0.22 ppm) that was significantly greater in participants with elevated mercury levels at the initial visit. No change in consumption of low mercury fish or plasma DHA levels was observed in either participant group. This investigation demonstrated the feasibility of administrating a tailored mercury reduction intervention to reproductive age women in a health clinic setting to reduce intake of fish with moderate levels of mercury while maintaining beneficial intake of fish with low levels of mercury.

HUMAN EXPOSURE TO MERCURY AND DIETARY RISK ASSESSMENT IN CYPRUS: BENEFITS OF CROSS-BORDER EUROPEAN HARMONIZATION AND COOPERATION.

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Cyprus, a Mediterranean member state (MS) of the European Union (EU), ratified the Minamata Convention on 17/12/2018. The country has been active in the efforts to harmonize and promote human biomonitoring in Europe as a policy-support tool since 2004 and currently serves as ‘leader for mercury and its organic compounds’ in the European Human Biomonitoring Initiative (HBM4EU, https://www.hbm4eu.eu/). Cyprus was one of 17 European countries to implement harmonized, quality-assured assessment of total mercury (Hg) in scalp hair of mother-child pairs (DEMOCPHES project, 2010-2012). This hands-on experience facilitated valuable national capacity building, which may be used in the effectiveness-evaluation of the Minamata convention. The results provided an indication of the mercury body burden of Cypriots, as follows: (a) mothers (N=60, 27-45 years old): geometric mean (GM) = 0.463 µg/g hair, range: 0.100 – 3.060 µg/g; P95 = 2.065 µg/g; (b) children (N=60, 6-11 years old): GM = 0.326 µg/g hair, range: <LOQ (0.01 µg/g) – 2.640 µg/g, P95 = 1.385 µg/g. Only 1 (adult) participant exceeded the FAO/WHO health-guidance value of 2.3 µg/g. The found GMs were above the European GMs (0.225 µg/g (0.216 – 0.234) for mothers; 0.145 µg/g (0.139 – 0.151)) for children), but considerably lower than those found in other participating Southern European countries, and were higher in those who consumed more fish. The dietary risk associated with fish consumption in adolescents was estimated using the ImproRisk model (http://www.improrisk.com/) of the Cyprus State General Laboratory (CY-SGL), which combines ‘food categorization into miners (n= 30) and non-miners (n = 50). ASGM is an additional livelihood source in these villages, involving men as miners, and women in gold amalgam processing which generate monthly income as IDR 272.000 to IDR 2.000.000. Mercury was used in gold amalgam processing, ranges from 2 to 4 ounces to produce 0.8 to 4 grams of gold per month, so the average use of mercury was ranging from 260 -520 kg per month. Preliminary total mercury analysis was conducted for hair samples of 20 respondents (7 male and 13 female), with an age range of 9 month to 60 years old. The highest concentration of T-Hg (17 ppm) was found in a woman who works in gold processing. The concentration of mercury that exceeds the WHO standard was also found on the 9-month-old baby (4.2 ppm). The high level of total mercury in the respondents apparently are associated with the exposure time of mercury to the community, since location of the gold amalgam processing’s site is at the residential area. Furthermore, the level of knowledge of the villagers about the impact of mercury on the environment and health is still low. Another reason is that the villagers are still hesitated to change the use of mercury in gold ore processing to other technologies. This research recommends that the government should alter solutions by providing other jobs which emerge higher income than gold mining; developing social forestry program; conduct further health examination on people with high mercury level; and increase public knowledge of the dangers of mercury on the environment and public health.

Keywords: ASGM, mercury, perception, socio-economic characteristics and Sukabumi.

MERCURY POLLUTION IN ARTISANAL AND SMALL-SCALE GOLD MINING IN SUKABUMI, INDONESIA: KNOWLEDGE, PERCEPTIONS AND HEALTH IMPLICATION

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Artisanal and small-scale gold mining (ASGM) are the largest source of mercury pollution in Indonesia, spread widely in 33 provinces. In West Java Province, ASGM is found in Bogor, Cianjur and Sukabumi Regencies. The aims of this research were to describe the socio-economic characteristics, level of knowledge and community perceptions towards mercury use and to evaluate the total mercury (T-Hg) level in human hair in Cicadas, Sukarame and Kertajaya Villages, Sukabumi Regency. The total gold miners in the three villages are 1,500 households (25.77% from total 5,044 households), ASGM has been practiced since the Dutch colonial era in Kertajaya, meanwhile, in Lebak Nangka it was started since the 1970s and the 1990s in Sukarame. Respondents were chosen by using stratified random sampling based on occupation,
3.6C Mercury Emissions Reductions – A Challenge to Industry

T.O.3.6C-1

MERCURY BALANCE DURING THE COOKING PROCESS AND ITS DETERMINATION IN COKE OVEN GAS

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In 1993, a total of 308 million tons of coke were produced worldwide. By 2017 the global coke production increased to an estimated 644 million tons. In Poland, the coking industry consumes about 12 million Mg of bituminous coals each year. To determine mercury content in bituminous coals delivered to Polish coke plants eighty-two samples from 9 mines were analyzed. The average mercury content varied from 28 to 183 μg/kg. The mercury balance results for bituminous coal coking shows that mercury is transferred to: coal tar (75%), coke (6%), sulfur (2%) and coke oven gas (3%). Balance data shows that almost 14% of mercury is emitted to the atmosphere during the process of firing the coke. Thereby the mercury migration behavior and Hg species transformation in coke oven gas is of great importance for environmental protection and occupational health. The developed method was validated according to the Eurachem recommendation and was applied to determine mercury in the clean coke oven gas. The coke oven gas sampling was performed in a coking plant in Poland. The average concentration of mercury in the clean coke oven gas was 3.2±0.3 μg/m³N (k=2) for n=18.

T.O.3.6C-2

MIGRATION AND IDENTIFICATION OF MERCURY SPECIES IN A TYPICAL WET FLUE GAS DESULFURIZATION SYSTEM

CHANG, Lin; ZHAO, Yongchun; ZHANG, Junying

Environmental problem concerning Hg pollution has attracted worldwide attention. A wet flue gas desulfurization (WFGD) system is generally equipped in a coal fired power plant which is utilized for SO2 control and is beneficial for Hg removal. The adsorbed Hg accumulates in the WFGD system and transported to gypsum which is considered as a multipurpose by-product in downstream industry. This study investigates the Hg migration behavior and Hg species transformation in the gypsum production process of a WFGD system. The temperature programmed decomposition (TPD) technique was applied for the identification of Hg species in the solid fraction of samples which were obtained from field scale WFGD system. The results indicated that the Hg concentration of solid fraction in desulfurization tower was 0.574 mg/kg while the liquid fraction was 0.054 μg/L. Most Hg was transported to effluent treatment process resulting in about 11.8% of Hg in desulfurization tower transported to gypsum in which the concentration of Hg in gypsum was 0.194 mg/kg. The Hg-TPD results indicated that the HgS was predominately form in gypsum which accounted for 77.77% of total Hg where black HgS and red HgS shared 51.98% and 25.78% of total Hg, respectively. HgO production was prohibited in the desulfurization process where HgO might be dissolved in the acid environment. A small amount of HgCl2 was identified existed on gypsum.

Keywords: Hg species; gypsum; wet flue gas desulfurization

T.O.3.6C-3

MERCURY EMISSIONS FROM INDUSTRIAL SOURCES – MORE THAN 30 SECTORS ANALYSED TO FIND REAL SINKS

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In many industrial sectors, mercury is introduced via raw materials and fuels, released to air and to water bodies, as well as recovered or disposed of as waste. In a few sectors, such as waste incineration, input and output are relatively well known since mercury is regularly monitored. In other sectors, mercury input analysis and emission monitoring are rare. Therefore, there is no comprehensive picture of mercury input and output from industrial industries in Germany.

In some mercury-relevant industrial sectors, such as coal-fired power plants, waste incinerators, non-ferrous metals and the cement industry, mercury is partly removed from waste gas, ending-up in filter dust and ashes. However, this mercury-laden waste is re-used as secondary raw material, e.g. FGD gypsum from coal power plants is used in the gypsum industry.

With these recovery practices, mercury air emissions are reduced locally. But, mercury is still widely distributed with the products and, therefore, associated with new mercury emission potential. Real mercury sinks which absorb mercury permanently from the biosphere are only used in primary smelters of the non-ferrous metals industry and in waste incineration (underground disposal of calomel or filter dust). In a three-year research project led by the Öko-Institut, the German Federal Environment Agency (UBA) investigated the presence of mercury in all relevant industrial sectors of Germany. Mercury inputs and outputs within more than 30 sectors were analysed and quantified where data was available. Besides coal-fired power plants, waste incinerators, cement plants and the non-ferrous metals industry, the research covered: steel works; the manufacture of lime, glass, gypsum and bricks; waste treatment; the chemical industry; pulp and paper production, as well as industrial boilers.

Information sources comprised research reports, presentations, publications, emission measurements and analyses of the mercury content of the input and output of the plants. Numerous measurements were made by the researchers, which were supplemented by measurements arranged by industry associations.

Mercury reduction techniques for mercury are described in the project report. The authors investigated whether techniques proven in some industries are also applicable to other industry sectors. Economic aspects were taken into account. Specific efforts were made to identify techniques that removed mercury from material use and deposited into sinks that ensure the pollutant is removed from the biosphere as permanently as possible.

Based on its findings, the study proposes a mercury reduction strategy for German industries.
EMPOWERING THE ARTISANAL AND SMALL-SCALE GOLD MINERS AND ENGAGING THE GOVERNMENT AT SUB-NATIONAL LEVELS THROUGH FORMALIZATION IN ORDER TO REDUCE MERCURY IMPACTS TO THE ENVIRONMENT

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Artisanal and small-scale gold mining (ASGM) in Indonesia is conducted in 152 regencies/municipalities in 31 provinces throughout Indonesia (MOEMR, 2015). This sector is estimated to produce 65 – 130 tons of gold (Ballfokus, 2012). Mercury is still widely used in ASGM in Indonesia and releases 195 tons of mercury (57.5% of total release) annually (GEF GOLD ISMIA, 2019).

In 2014, Pure Earth conducted a study that focused on the implementation of the Decree of Minister of Environment and Forestry No. 23 Year 2008 about the technical guidelines to prevent environmental pollution and/or damages due to ASM. The study found ways in which the regulation might adapt to the Minamata Convention on Mercury and build upon recent progress in national policies, regulations, and conditions in the field. Thus, some inputs were made to encourage miners to formalize and steps were put in place to minimize the environmental impacts of ASGM:

1. To allow ASG to work within a designated area (Wilayah Pertambangan Rakyat/WPR);
2. To simplify the procedure of obtaining an environmental permit which serves as a recommendation to apply for mining permit;
3. To encourage people to work in groups, such as cooperatives or village corporations, which will buy gold produced by its members;
4. To encourage people to use mercury;
5. To provide eco-labelling for gold produced using environmentally friendly techniques and waste management; and
6. To make ASGM responsible for post-mining rehabilitation.

In supporting ASGM, inputs were also made to engage the government at sub-national levels to create local capacity building on the management of ASGM. The government at sub-national levels are also expected to conduct regular monitoring, write reports, and enforce regulations with necessary penalties.

It is a challenge to advocate such inputs in order to legitimize an informal sector and miners would be faced with responsibilities regarding the environment. Formalization will empower miners as it would give access to technical assistance for non mercury techniques, financial resources to acquire necessary technology, and official government support. In the end, formalization is expected to reduce mercury emissions at the source and consequently limit the environmental and human exposure from mercury contaminated land. This plan implies that miners act as responsible parties and engage in the rehabilitation of contaminated land with the assistance from the government.

CHALLENGES AND DRIVERS FOR THE CONVERSION AND DECOMMISSIONING OF CHLOR-ALKALI PLANTS

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Mercury has been used a catalyst in the production of chlorine and caustic soda for over a century. Although the use of mercury in chlor-alkali plants has reduced significantly in recent years, many plants in Asia, Latin America, Russia and Africa still use mercury in their production. Chlor-alkali plants are thus a significant source of mercury supply and releases to the environment.

The Minamata Convention on mercury came into force on 16 August 2017 and mandates that parties must phase out mercury use in chlor-alkali production by 2025. The Chlor Alkali sector partnership area of the Global Mercury Partnership works to identify mercury cell chlor-alkali plants globally and support efforts at conversion and decommissioning.

This paper explores the requirements of the Convention, the regional variations in closure of chlor-alkali facilities, highlights the related challenges and examines key drivers for conversion or decommissioning. The major challenges found include lack of sufficient financing for conversion, market risks, technical and financial constraints in the management of mercury wastes and the age of the plant. Major drivers found include regulatory pressure, access to finance for expansion and energy efficiency improvements and presence of active industrial associations.

The following conclusions and recommendations were made:

• Regulatory pressure at the national or regional level plays a significant role in encouraging conversion.
• Bundling of financial resources from various sources can help facilities to acquire funding that covers all costs including site conversion, decommissioning and waste management.
• The extent to which clear guidelines or practical options for the management of mercury wastes from decommissioned plants (including protocols for selection of appropriate waste stabilization and storage methods), impact on conversion decisions should be explored.
• Long-term assessment, management and monitoring of contaminated sites needs to be taken into account by the respective governments.

EMISSION AND SPATIAL DISTRIBUTION OF MERCURY IN SOLID WASTE LANDFILL IN SOUTH KOREA

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Landfill is regarded as one of important emission sources of atmospheric mercury (Hg), which is associated with environmental and potential health risks. This study presents the Hg concentrations in landfills along with air-soil Hg exchange fluxes depending on the types of waste (e.g., household waste: 4, hazardous waste: 6). Hg levels in landfill gas, soil, leachate, groundwater, effluent water, and air and Hg fluxes are clearly higher in hazardous waste landfill than in municipal waste landfill. It was found that the landfill gas contained 24-255 ng m-3 of Hg in hazardous waste landfill and 18-45 ng m-3 of Hg in municipal waste landfill. The air-soil Hg fluxes were 65-382 ng m-2 h-1 in hazardous waste landfill and 9.6-59 ng m-2 h-1 in municipal waste landfill. The air-soil surface Hg exchange fluxes increased when solar radiation reached the soil surface, possibly because reducible Hg was abundant at the soil surface. Overall, the cover soil surface is the leading source for Hg emission (99.6 %), followed by effluent water (0.3%) and landfill gas (0.07%). The results suggested that considerable amount of Hg are probably transported from the landfill to nearby environmental media. In addition, strategies for controlling landfill Hg emissions are considered, including reducing the Hg load in landfill and in situ controls.
1.9 Mercury cycling in terrestrial ecosystems

W.O.1.9-1

INCREASED METHYLATION OF Hg(II) IN HILLSLOPE SOILS AFTER FOREST HARVEST – AN IMPORTANT CONTRIBUTOR TO BOREAL SURFACE WATER METHYL MERCURY LOAD

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Boreal coniferous forests cover 8.7 million km², corresponding to 30% of the global forest area. Forestry is the predominant land-use throughout the Boreal zone and currently about two-thirds of the forest area is managed. Effects of Boreal forest harvest on inorganic mercury (Hg(I)) and methyl mercury (MeHg) soil pools and their export by stream runoff were quantified by comparing 10 reference watersheds (REFs) covered by >80-years-old Norway spruce forests with 10 similar watersheds (CCs) subjected to clear-cutting 2 years prior to sampling. While clear-cutting did not change the Hg soil storage, MeHg pools in the organic topsoil increased six times (p<0.004). The largest increase (11 times, p<0.003) occurred in concert with significant increases in soil water content at intermediate hillslope positions 20-38 m from stream, outside the immediate stream riparian zone. Incubation experiments demonstrated that soils with enhanced soil pools of MeHg after clear-cutting also showed significantly enhanced methylation potential as compared with similarly positioned soils in reference stands. Metabolic inhibitors revealed methanogens and sulfate reducing bacteria as responsible methylators. When recalculated to cover 100% of the watershed, clear-cutting increased the annual MeHg stream export 3.8 times (p<0.047) in undulating terrain positioned above the supraglacial marine limit (ML). In flatter terrain, below the ML, annual export of MeHg did not differ between REFs and CCs, likely because of a larger contribution of MeHg exported from peaty soils and small wetlands. We estimate that peatlands and forest soils contribute with 37% and 56% of the MeHg loadings to Boreal stream waters in Sweden, respectively, with forest harvest adding another 7%. In the Boreal zone as a whole, peatlands and forest soils are estimated to contribute with 53% and 47% of MeHg stream water loadings, respectively. The expected rapid increase in harvest and disturbance of Boreal forests urges for inclusion of land-use effects in mercury biogeochemical cycling models at different scales.

W.O.1.9-2

METHYL- AND TOTAL MERCURY EXPORT DYNAMICS FROM AN EXPERIMENTAL PEATLAND AFTER ENDING ENHANCED ATMOSPHERIC SULFATE ADDITIONS

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(4)Science Museum of Minnesota

Atmospheric deposition of sulfate has been linked to enhanced mercury methylation in peatlands; however, following legislative amendments in the early 1990’s in the U.S. and Canada, atmospheric SO42- deposition has significantly declined. In-situ peatland biogeochemical processes linking sulfur, mercury biogeochemistry, and hydrology are relatively well understood, but there remains little information on methylmercury (MeHg) or total mercury (THg) export from peatland-dominated watersheds as sulfate deposition declines. Here, we present results from a multi-year, ecosystem-scale experiment at the Marcell Experimental Forest wherein sulfate deposition was increased and then brought back to current natural deposition levels over two sequences. The response in MeHg and THg export dynamics were monitored in the surface water outlet through the entirety of the experiment. Between 2005 – 2008, experimental sulfate inputs were ceased in half of the experimentally manipulated peatland area furthest from the outlet but no distinguishable effect on THg and MeHg export was observed (p > 0.1). This suggests the majority of MeHg detected was likely produced within the remaining active sulfate input region nearest to the peatland outlet. Within one year of ceasing all experimental sulfate inputs (2009 – 2011), the annual MeHg as a percentage of THg export (p < 0.001) and average monthly flow-weighted MeHg (p = 0.03) significantly decreased. THg export remained consistent once the experimental loading ceased (p > 0.1). The export of MeHg, THg, and sulfate were all governed by the exponential transmissivity profile in the peatland (p < 0.001), where the largest solute fluxes occurred as the water table approached the surface. This study clearly illustrates the rapid (within one year) decrease in MeHg export following large decreases in sulfate deposition, which may have contributed to decreasing MeHg levels in the region following stricter controls on sulfur dioxide emissions in the early 1990’s.

W.O.1.9-3

MERCURY REMOBILIZATION FROM POLLUTED TOP-SOILS IN SEMI-ARID AREAS AFFECTED BY WILDFIRES

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Anthropogenic activities play an important role in the distribution and cycling of mercury (Hg). This research is focused on organic-rich top-soils highly polluted by the Tsumeb copper smelter, which processes Hg-rich concentrates (up to 20.0 ppm, bound mainly in sulphides) in the northern part of semi-arid Namibia. Total Hg concentrations in top-soils near the smelter attained 7.6 ppm. To understand the potential remobilization of Hg from polluted topsoil samples during wildfires, laboratory thermodesorption experiments in the temperature range 75-670 °C have been performed. In oxygen-rich atmosphere the Hg release occurred at temperatures higher than 100 °C and exhibited a sharp peak at 340 °C also supported by TG-DTA measurements, which indicated a massive mass loss at the same temperature. This observation indicates a local increase of temperature during the residual biomass burning, which causes the complete Hg release. To eliminate the effect of spontaneous burning and uncontrollable temperature increase during thermodesorption, the same experiments were performed under nitrogen atmosphere; the obtained results were identical with those obtained under the oxygen-rich conditions. This behaviour means that all the Hg can be mobilized under the low temperature conditions (ca. 350 °C), corresponds well to the mean bushfire temperatures. Moreover, these results confirm that Hg was mainly released from the topsoil organic matter and not from wind-blown concentrate particles adhering to the biomass surfaces (Hg release from concentrate peaked around 500 °C). We combined the knowledge of the spatial distribution of Hg in topsoil a biomass samples around the Tsumeb smelter with our experimental results and calculated that the amount of Hg, which is potentially remobilizable by a single wildfire in the most Hg rich hotspot (14 km²), could reach 125 g/ha. This study was supported by the Czech Science Foundation projects (GAČR 19-18513S; GAČR 19-08066S), student project from the Granting Agency of the Charles University (GAUK 1598218) and Center for Geosphere Dynamics (UNCE/SCI/006).
Effects of biomass removal post-timber harvesting on mercury export from hillslopes

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Mercury mobilization due to upland forestry practices can be complicated for numerous reasons. For instance, the removal or lack-there-of, of biomass after harvest has led to differential patterns in methyl-mercury (MeHg) and total mercury (THg) dynamics within harvested hillslopes depending on changes in hydrology, biogeochemistry, and ecology. These changes consistently affect down-gradient ecosystems, such as wetlands and riparian areas. Wetlands and riparian areas are thought to be biogeochemical hotspots within a landscape, yet, there is little information on how upland forestry practices may affect these hotspots. Thus, the primary objective of this study was to determine the effect on mercury dynamics from harvested hillslopes with and without biomass removal, and the associated effects on down-gradient wetlands. Using a before-after comparison design, three adjacent hillslopes at the USDA Forest Service’s Marcell Experimental Forest in northern Minnesota were monitored from 2010 to 2014 during the hydrologically active seasons (snowmelt to freeze-up) for runoff, THg, MeHg, DOC, sulphate, and pH. Harvesting of the two hillslopes occurred between December 2011 and March of 2012 and the biomass removed from one of the hillslopes (Biomass-Removed), while the second had the residual biomass left on the site (Biomass-Left). The third site was left as a reference site (Reference). The annual runoff ratios were significantly greater at Biomass-Removed relative to Reference (p = 0.01) post-harvesting, while no difference was observed between Biomass-Left and Reference (p > 0.1) post-harvesting. THg concentrations were significantly greater post-harvest at Biomass-Removed but no difference at Biomass-Left was observed, except for within the snowmelt period. Lower DOC and no change in sulfate concentrations were observed in the runoff from both harvested sites. However, the changes in hydrology in the Biomass-Removed treatment resulted in larger total loads of all solutes post-harvesting, yet no statistical changes in hydrology in the Biomass-Left treatment resulted in increased redox potential, resulting in limited sulfate reduction and the subsequent decrease in methylmercury production. This study clearly indicates that total mercury concentrations remained similar to pre-harvest levels, while total loads increased due to changes in the hydrology. Interestingly, the likely changes in redox conditions within the wetland due to the forestry practices decreased the wetlands role as a methylmercury hotspot.

The interplay between land-atmosphere exchange and soil dynamics of mercury in a Swiss subalpine forest

HUANG, Jen-How; OSTERWALDER, Stefan; MEUSBURGER, Katrin; RINKLEBE, Jörg; FENG, Xinbin; ALEWELL, Christine

Forest-atmosphere exchange of mercury (Hg) is largely undefined and knowledge about its interplay with Hg in forest soils limited. To investigate Hg fluxes in a coniferous forest ecosystem, we perform multiple-level gaseous elemental mercury (Hg(0)) concentration measurements on a tall tower and determine Hg in wet precipitation, litterfall and soil porewater at the research site Davos-Seehornwald in Switzerland. The tall tower gradient measurements were initialised in October 2018 and show that Hg0 concentrations at 8 different heights (1.8, 4, 7, 10, 15, 20, 25, 35 m) averaged at 1.07, 1.08, 1.08, 1.10, 1.10, 1.10, 1.11 ng m−3, respectively. These preliminary results indicate that the subalpine forest is neither a significant sink nor source for atmospheric Hg during the dormant season. The Hg concentration in bulk precipitation, throughfall and forest floor percolates all ranged between 23 and 72 ng L−1, reflecting little Hg dry deposition on the needle surface and negligible retention of Hg in the forest floor. In the forest soils (Podzol, FAQ classification), the Hg concentration peaked in the forest floor (263-317 µg kg−1) and Bh horizon (subsoil with organic matter accumulation, 64-83 µg kg−1). Moreover, the concentrations of organic matter and crystalline Fe and Al (hydr)oxide bound Hg decreased in E (eluvial horizon) but increased in B horizons in comparison with Ah horizon (topsoil with organic matter accumulation). This corresponds well with the eluviation from the upper soil layer and translocation of organo-metallic complexes into the subsoil. Along the soil profile, the averaged Hg concentration in soil porewater increased from 15 ng L−1 at 15 cm depth to 81 ng L−1 at 50 cm depth. At 80 cm depth, the porewater Hg concentration averaged at 5-4 ng L−1. The Bh horizon has the largest Hg soil storage (~100 mg Hg m−3) and may currently serve as a source of Hg to the deeper horizons. The soils at 0-15 and 50-80 cm depth are effective sinks of Hg released from the forest floor and from the Bb horizon. Our preliminary results highlight that Hg dynamics in the forest soils are strongly coupled with the podsolization process. Together with the upcoming investigations in the growing season, our research will improve the understanding on remobilisation of previously deposited Hg in soils to water bodies and the atmosphere.
1.2C Biogeochemical cycling of mercury in the aquatic ecosystems

W.O.1.2C-1

GROWTH AND DORMANCY EFFECTS ON METHYL-MERCURY ACCUMULATION IN PROFUNDALE INVERTEBRATES OF A NORTHEAST-TEMPERATE LAKE

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Benthic invertebrates are a key trophic link in the dietary transfer of methylmercury to fish. In addition to providing information on methylmercury exposure to fish, benthic invertebrates are commonly used as bioindicators to evaluate ecosystem processes that affect mercury accumulation near the base of the aquatic food chain. Here we report new findings on the role of growth and dormancy in controlling mercury bioaccumulation in a genus of aquatic insect, Chironomus (Diptera, Chironomidae), which is globally distributed in freshwater ecosystems. A study was conducted to characterize environmental and biological processes controlling the seasonal variation of methylmercury bioaccumulation in the profund benthic invertebrate. The chironomid Chironomus spp. was intensively sampled over a full 2-year period (36 dates from May 2016 to 2018) in a 21 m deep basin of small north-temperate lake near Ottawa, Canada. The study lake was thermally stratified from May to October and ice-covered from December to April. Chironomid densities and size distributions were measured on each sampling date to characterize life cycle dynamics, and approximately 100 samples were analyzed for methylmercury concentration, carbon and nitrogen stable isotopes to assess diet, and RNA/DNA content as a proxy for growth rate. Surface water, sediment porewater, and water-column selenium were also analyzed for methylmercury concentrations to characterize the mercury exposure regime. Large seasonal variation in chironomid methylmercury concentration was observed each year. Peak concentrations of 8.31 ng/g dry weight were observed in late spring and again in late fall/early winter. In summer/early fall and again in late winter, chironomid methylmercury concentrations dropped an order of magnitude to <2 ng/g for a duration of up to two months. Unexpectedly, minimum methylmercury concentrations in chironomids occurred during summer periods of anoxia in the hypolimnion or in late winter, when food availability was likely low. In contrast, their peak concentrations occurred during periods of growth when median larval body weights increased. Diet and ambient methylmercury concentrations did not explain the seasonal variation. Periods of dormancy and growth had the greatest influence on seasonal patterns of methylmercury bioaccumulation in the profund benthic chironomids. These findings suggest that future shifts in hypolimnetic oxygen regimes of small thermally-stratified lakes, driven by climate or eutrophication, will likely impact the seasonal dynamics of methylmercury bioaccumulation in profund benthic chironomids.

Mercury content in bottom sediments of water bodies of Central Vietnam varies widely - from trace amounts to 0.263 mg/kg. The highest median concentrations were found in sediments of lakes and reservoirs (0.61 and 0.065 mg/kg, respectively), the lowest in rivers and ponds sediments. Despite the difference of almost 2 times between the median mercury concentrations, the levels are not statistically significantly dependent from the type of water body (H(4, n=64) = 5.1, p=0.27).

No connection was found between the geographical location of the reservoir and the mercury content. Sediments of reservoirs located on the coastal plain on the mercury content have no significant differences from sediments of reservoirs of mountain areas of the studied region. Similarly, there is no significant correlation between latitudinal changes – mercury content does not differ significantly in the North-South direction.

The mercury content is statistically significantly dependent from sediment type (H(4, n=64)=27.7, p <0.001). In gravel and sand, the median mercury content is minimal at 0.007 and 0.008 mg/kg, respectively. The lowest maximum concentrations of mercury compared with other types of sediments in the bottom sediments with a predominance of clay and silt particles median values significantly higher (p<0.05) and reach a maximum in loamy sand (0.122 mg/kg). A significant, positive correlation (R=0.76-0.93, p<0.05) between mercury and organic matter concentration was found in all types of sediments except of loamy sand.

In the surveyed sediments, the mercury content is determined by the grain distribution. The geographical location and type of water body do not have a significant impact on mercury levels. Based on the overall low level of mercury in the sediments of water bodies in Central Vietnam, there are no anthropogenic sources. The revealed regularities of mercury accumulation depending on the properties of bottom sediments are similar to the reservoirs of temperate latitudes experiencing a weak anthropogenic load.

W.O.1.2C-3

POTENTIALLY TOXIC VERSUS PHYSIOLOGICALLY REQUIRED – MERCURY AND POLYUNSATURATED FATTY ACIDS AT THE BASE OF FOOD WEBS IN CHINESE RESERVOIRS AND SWEDISH LAKES

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The trophic transfer of potentially toxic mercury (Hg) and physiologically required polyunsaturated fatty acids (PUFA) varies across different aquatic food webs.

In this study, we compared total mercury (THg), methylmercury (MeHg), and PUFA in organisms at the base of food webs in Chinese Reservoirs and Swedish lakes. We found that MeHg content in phyto- and zooplankton as well as zoobenthos were generally higher in Chinese Reservoirs; THg content in zoobenthos was also higher in Chinese Reservoirs, while THg content in phyto- and zooplankton was higher in Swedish lakes. Total and the long-chain omega-3 PUFA eicosapentaenoic (EPA, 20:5n–3) and docosahexaenoic acids (DHA, 22:6n–3) in phyto- and zooplankton were higher in Chinese Reservoirs; however, total PUFA and DHA+EPA contents in zoobenthos were higher in Swedish lakes. Using fatty acids as diet source biomarkers, zooplankton in Chinese reservoirs and zoobenthos in Swedish lakes retained mainly algal and bacterial food sources, while zoobenthos in Chinese reservoirs and zooplankton in Swedish lakes contained also terrestrial food sources. The results were inconsistent with previous studies arguing that eutrophication of Chinese Reservoirs would decrease the Hg content at the base aquatic food webs due to the algal dilution, and reduce the dietary supply of highly required PUFA because of chang-

W.O.1.2C-2

MERCURY IN BOTTOM SEDIMENTS OF DIFFERENT WATER BODIES IN CENTRAL VIETNAM

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The mercury content in bottom sediments of different water bodies (rivers, reservoirs, abandoned open casts, ponds and lakes) in Central Vietnam was studied. Five types represent the examined sediments: gravel, sand, loamy sand, sandy loam, silt loam.

Mercury content in bottom sediments of water bodies of Central Vietnam varies widely - from trace amounts to 0.263 mg/kg. The highest median concentrations were found in sediments of lakes and reservoirs (0.61 and 0.065 mg/kg, respectively), the lowest in rivers and ponds sediments. Despite the difference of almost 2 times between the median mercury concentrations, the levels are not statistically significantly dependent from the type of water body (H(4, n=64) = 5.1, p=0.27).

No connection was found between the geographical location of the reservoir and the mercury content. Sediments of reservoirs located on the coastal plain on the mercury content have no significant differences from sediments of reservoirs of mountain areas of the studied region. Similarly, there is no significant correlation between latitudinal changes – mercury content does not differ significantly in the North-South direction.

The mercury content is statistically significantly dependent from sediment type (H(4, n=64)=27.7, p <0.001). In gravel and sand, the median mercury content is minimal at 0.007 and 0.008 mg/kg, respectively. The lowest maximum concentrations of mercury compared with other types of sediments in the bottom sediments with a predominance of clay and silt particles median values significantly higher (p<0.05) and reach a maximum in loamy sand (0.122 mg/kg). A significant, positive correlation (R=0.76-0.93, p<0.05) between mercury and organic matter concentration was found in all types of sediments except of loamy sand.

In the surveyed sediments, the mercury content is determined by the grain distribution. The geographical location and type of water body do not have a significant impact on mercury levels. Based on the overall low level of mercury in the sediments of water bodies in Central Vietnam, there are no anthropogenic sources. The revealed regularities of mercury accumulation depending on the properties of bottom sediments are similar to the reservoirs of temperate latitudes experiencing a weak anthropogenic load.
es in phytoplankton taxonomy. Our findings showed that THg in phyto- and zooplankton was more likely affected by biotic factors (PUFA profile), while THg and MeHg in zoobenthos were more likely closely related to abiotic factors (water chemistry), yet none of abiotic or biotic factors can fully explain the spatial variation of MeHg and MeHg% in phyto-and zooplankton.

W.O.1.2C-4

ATMOSPHERIC AND HYDROLOGIC TRANSPORT AND TRANSFORMATION OF MERCURY FROM ARTISANAL GOLD MINING IN THE PERUVIAN AMAZON

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Artisanal and small-scale gold mining (ASGM) is estimated to be the primary anthropogenic source of mercury (Hg) emissions globally. Yet, there is a gap in our understanding of the local transport and fate of this elemental mercury. ASGM is particularly prevalent in the Madre de Dios region of the Peruvian Amazon and occurs predominantly along two tributaries to the Madre de Dios River. In this study, we measured atmospheric deposition and hydrologic transport of Hg along a 200 km reach of the Madre de Dios River, including upstream and downstream of ASGM areas. Specifically, we measured total Hg and methylmercury (MeHg) in throughfall, bulk precipitation, and canopy foliage, as well as its storage in surficial soil (0-5 cm). We found that throughfall and canopy foliage Hg concentrations were highest near ASGM sites and decreased with distance from ASGM (throughfall THg range: 7.9-60 ng/L; foliage THg range 19-39 ng/g). However, concentrations of Hg in bulk precipitation did not vary with distance from ASGM (THg range: 1.5-9.1 ng/L). These results suggest that differences in atmospheric deposition with distance from ASGM is driven by dry deposition and foliar uptake, rather than wet deposition. Similarly, total Hg concentrations in surficial soils were highest near ASGM and declined with distance from ASGM and were higher under the canopy than in clearings (THg range: 0.027-580 ug/g). These patterns in atmospheric deposition were consistent during both dry and wet season sampling, but concentrations of Hg in throughfall and bulk precipitation in the dry season were lower than concentrations in the wet season. We also measured total Hg and MeHg in river water and sediment along the Madre de Dios River and its tributaries. We found that the highest river water and sediment concentrations were found in ASGM-impacted tributaries and along the mainstem draining these ASGM-impacted tributaries (sediment THg range: 3.3-59.6 ug/g; river water THg range: 0.35-46.9 ng/L). These results show the atmospheric and hydrologic pathways of Hg transport from ASGM and hotspots on the landscape for Hg methylation.

W.O.1.2C-6

THE EFFECT OF COMPLEX LIFE HISTORIES ON HG ACCUMULATION AND EXPOSURE IN LINKED AQUATIC-TERRESTRIAL FOOD WEBS

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Many animals such as insects and amphibians have complex life histories that involve metamorphosis from an aquatic to a terrestrial life stage. Aquatic systems tend to concentrate contaminants such as mercury (Hg), so animals that accumulate Hg during their aquatic life stage are potential vectors of Hg transport to terrestrial ecosystems. Some amphibians are particularly interesting for assessing mercury flux from one system to the next because they feed on algae as tadpoles, do not feed during the period of metamorphosis, feed on aquatic and terrestrial insects as adults, and then do not feed at all during hibernation which can last 7-8 months at high elevations. We measured total Hg (THg), methylmercury (MeHg), and isotopic composition (δ13C, δ15N) in chorus frogs (Pseudacris maculata) at two subalpine ponds (2775 and 2960 m elevation) in the Rocky Mountains in Colorado, USA. We sampled various life stages including spawning adults (‘starved’ adults just emerging from hibernation), eggs, tadpoles, metamorphs (recently emerged the aquatic environment), and mid-summer adults that remained and fed around ponds after spawning. We found large differences in MeHg concentrations and percent MeHg among life stages as a function of maternal transfer to eggs, diet switching, and catabolism during metamorphosis and hibernation. Starved spawning adults had the highest mean MeHg concentration (274 ng/g dry mass) of any life stage. Maternal transfer of mercury to eggs was minimal (22 ng/g) and remained low in tadpoles (36 ng/g) but roughly doubled at the metamorph stage (71 ng/g). This large increase was accompanied by a 53% loss of body mass during metamorphosis. Adults that remained around ponds during summer had concentrations roughly half (146 ng/g) that of the starved, spawning adults. The percent of MeHg and isotopic signatures also showed similar pronounced step changes across life history. Percent MeHg was high (~85%) for both adult life stages and remained high in eggs (52%) due to maternal transfer. After hatching,
this percentage declined to only 23% in tadpoles and then doubled to 50% during metamorphosis. Isotopic signatures also changed substantially and abruptly between egg, tadpole, and metamorph life stages. Our findings show that key transition periods in animals with complex life histories are an important consideration in understanding environmental exposures to contaminants. Further, factors such as catabolism can dramatically alter the typical trajectory of trophic transfer and accumulation of contaminants such as mercury.

1.3D Regional and local scale stable isotope studies in mercury biogeochemical cycling and bioaccumulation

W.O.1.3D-1

METHYLMERCURY PHOTODEGRADATION PATHWAYS AND ISOTOPIC FRACTIONATION IN THE WATER COLUMN OF LAKE TITICACA (BOLIVIAN ALTIPLANO)

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Within the project LA PACHAMAMA we investigated the biogeochemical cycling of Hg in the high altitude hydrosystem of Lake Titicaca, combining integrated ecological approaches with the determination of the molecular speciation and isotopic composition of Hg. The originality of this project lies into the fact that most of the experiments were conducted in situ within aquatic ecosystems displaying unique biogeochemical features such as high altitude, significant productivity, intense UV radiations and low oxygenated waters that stimulate significantly both the production and degradation of MeHg, as well as the fractionation of Hg isotopes (MDF/MIF). In situ experiments were conducted in 2014 during the late wet and dry seasons to evaluate both the methylation, demethylation and reduction potentials in the water column using isotopically enriched Hg tracers and measurements by GC-ICP-MS. The vertical distribution of biogeochemical parameters, including organic matter, algae distribution and sunlight spectral parameters were recorded for each station. In parallel, the fractionation of stable Hg isotope was followed during kinetic experiments after addition of natural MMHg, using compound specific isotopic analysis at trace level (CSIA) by GC-MC-ICP-MS. Various representative sites and conditions were recorded for each station. In parallel, the δ199Hg values in plankton in the lake with lower DOC concentration during the highly stratified mid to late summer period prior to fall mixing. plankton Hg MIF was used to estimate photo-demethylation, which is the most relevant parameter supporting that the main source of Hg to the plankton is from atmospheric precipitation supporting that the main source of Hg to the plankton is from atmospheric deposition. The plankton from both lakes displayed a seasonal trend in Hg MIF with values increasing from early spring to late summer and then decreasing to winter. This seasonal trend was driven by the seasonal cycle in UV radiation and also lake dynamics that affect how long MMHg was in the upper mixed layer. The seasonal trend in plankton Hg MIF was used to estimate photo-demethylation, which ranged from 15-40% with higher photo-demethylation observed during the highly stratified mid to late summer period prior to fall mixing.

W.O.1.3D-2

QUANTIFYING THE SEASONAL CYCLE OF METHYLMERCURY PHOTODEGRADATION IN FRESHWATER ECOSYSTEMS USING MERCURY ISOTOPIC FRACTIONATION PRESERVED IN PLANKTON

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Mercury (Hg) is a globally distributed pollutant that bioaccumulates in aquatic food webs. Mercury enters terrestrial and aquatic ecosystems dominantly in its inorganic form. Within these ecosystems, Hg can be transformed into methylmercury (MMHg), the form of Hg that bioaccumulates. Various MMHg sources and sinks in aqueous environments determine the MMHg burden in aquatic organisms, and quantifying them is necessary for understanding how MMHg in food webs will change with changing inputs and/or environmental parameters. In freshwater systems, MMHg photodegradation is an important pathway for the removal of MMHg from surface waters. A rapidly growing tool to study Hg is the stable Hg isotope system, which is already being used to successfully trace sources and quantify transformations of Hg. For example, photo-demethylation leads to large mass independent fractionation (MIF) of Hg isotopes, and numerous studies have used Hg MIF preserved in fish and biological samples to estimate photo-demethylation in surface waters. However, these exciting applications are limited by controlled studies that explore how Hg MIF in biota vary with respect to many environmental variables. This study measured Hg isotopes in freshwater plankton bi-weekly from two mid-latitude lakes with different amounts of DOC and sunlight penetration during the full spring to fall period. All the plankton exhibited large positive odd MIF and small positive even MIF. The positive δ199Hg in plankton mostly reflects the isotopic composition of MMHg that has undergone photodegradation in surface waters prior to its incorporation into aquatic biota. The even MIF signatures in the plankton samples are similar to the even Hg MIF in atmospheric precipitation supporting that the main source of Hg to the plankton is from atmospheric deposition. The plankton from both lakes displayed a seasonal trend in Hg MIF with values increasing from early spring to late summer and then decreasing to winter. This seasonal trend was driven by the seasonal cycle in UV radiation and also lake dynamics that affect how long MMHg was in the upper mixed layer. The seasonal trend in plankton Hg MIF was used to estimate photo-demethylation, which ranged from 15-40% with higher photo-demethylation observed during the highly stratified mid to late summer period prior to fall mixing.

W.O.1.3D-3

USING MERCURY STABLE ISOTOPE RATIOS TO TRACE THE BIOACCUMULATION OF MEHg IN THE LOWER FOOD WEB OF LAKE ERIE

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In aquatic ecosystems, the use of mercury (Hg) stable isotopes to identify Hg sources has typically focused on the identification of point and non-point sources in sediments, with the assumption that sediments were primary source of bioaccumulative methylmercury (MeHg). We measured Hg stable isotopes in the suspended particulate matter (SPM),
water, planktonic material of Lake Erie, and from surrounding watershed inputs to better understand the relative availability of contrasting Hg sources for bioaccumulation. Tracers for mass dependent and independent isotopic fractionation suggest contrasting Hg source portfolios for SPM and filtered water in both inflowing rivers and open water. Riverine SPM resembled terrestrial soils, and western Lake Erie sediments, while open lake SPM, primarily comprised of planktonic material, resembled atmospheric Hg with isotopic signatures linked to the percent of MeHg in planktonic material. This allowed calculation of δ202Hg and Δ199Hg for the source inorganic Hg and epilimnetic MeHg, useful for determining dynamics associated with recently deposited Hg. Large Δ200Hg in filter passing water and in planktonic material highlights the importance of recently deposited Hg from atmospheric precipitation. These results decouple Hg sources to the lower trophic epilimnetic food web from Hg to the sediments, highlighting the relative importance of atmospheric and watershed-sourced Hg to biota.

W.O.1.3D-4

RELATIONSHIP BETWEEN METHYL MERCURY CON-TAMINATION AND PROPORTION OF AQUATIC AND TERRESTRIAL PREY IN DIETS OF SEVEN TAXA OF SHORELINE SPIDERS

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Recent studies have demonstrated that terrestrial organisms such as shoreline spiders can be contaminated with methyl mercury (MeHg) if they consume prey from aquatic food webs. The present study had two objectives: 1) determine concentrations of MeHg in shoreline spiders including one taxon of orb weaver and six taxa of hunting spiders, and 2) assess the relationship between MeHg contamination and the proportion of aquatic and terrestrial prey in spider diets using stable isotopes of nitrogen and carbon. We collected shoreline spiders, emergent aquatic insects and terrestrial insects from in and around 10 experimental ponds at the Eagle Mountain Fish Hatchery in Fort Worth, Texas, USA. Mean MeHg concentrations in spiders ranged from 59.3 to 200 ng/g (dry weight) in striped lynx spiders and fishing spiders, respectively and were significantly different among spider taxa. Average MeHg concentrations (mean±SE) in aquatic and terrestrial insects were 63.0 ± 1.38 ng/g and 3.46 ± 0.69 ng/g, respectively. To examine the proportion of aquatic and terrestrial prey in spider diets, we used a stable isotope mixing model based on δ15N and δ13C. The mixing model suggested that the proportion of aquatic prey in spider diets varied from 0.45 to 0.75 for striped lynx spiders and fishing spiders, respectively. The concentration of MeHg in spider taxa increased as a function of the proportion of aquatic prey in their diet. Taxonomic differences in spider diet and contamination levels must be taken into account when using shoreline spiders as biosentinels in contaminant monitoring studies.

W.O.1.3D-5

MERCURY ISOTOPE FRACTIONATIONS IN DIFFER-ENT FORM OF MERCURY IN PADDY ECOSYSTEMS AND ENVIRONMENTAL IMPLICATIONS

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Rice consumption is the main pathway of methylmercury (MeHg) exposure for residents that rice as the stable food in inland areas of Southwestern China. However, the mechanism of MeHg bioaccumu-lation in rice grain is still unclear. Stable isotope is a powerful tool to track the sources and processes of migration and transformation of Hg in the environment. In this study, new methods were applied to extract MeHg from soils and rice plant tissues as well as total mercury (THg) for Hg isotope analysis, which aimed to understand the pattern of MeHg isotope fractionation in paddy ecosystem during whole rice growing seasons. We calculated Hg isotope values in inorganic mercury (IHg) according to its proportion of THg. The results suggested that MeHg and IHg in rice plants showed different characters of mass dependent fractionation and mass independent fractionation. In rice plants, the δ202Hg values in MeHg showed no fractionation in roots, stalks, leaves, and grains, and gradually decreased with the growing season of rice. However, the δ202Hg values in IHg of stalks were the mixing of signal in roots and leaves. In paddy ecosystem, the Δ199Hg values showed that irrigation water was the original source of MeHg to soil and rice plants, but IHg in rice plant simultaneously affected by the irrigation water and atmosphere. Our study spatially and temporally demonstrated the sources of MeHg and IHg in rice plant by Hg stable isotope approach, which can help us to better understand the mech-anism of bioaccumulation of MeHg and IHg in rice plant and to provide scientific advice for risk controls.

Keywords: MeHg, IHg, stable mercury isotope, paddy ecosystem, rice growing season.

W.O.1.3D-6

MERCURY ISOTOPE VARIATIONS IN CHINESE BOHAI SEA FOOD WEB AND THEIR IMPLICATIONS FOR MERCURY SOURCES AND CYCLING

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Mercury (Hg) concentrations in upper ocean have reached up to ~2.5 times of pre-anthropogenic level.[1] Because inorganic Hg (IHg) can be transformed into more toxic methylmercury (MeHg) in sediments and water columns, elevated Hg in seawater is expected to promote MeHg production in the oceans.[2] Oceanic MeHg could be uptaken by low trophic-level organisms and bio-magnified by several orders of magni-tude via predator-prey relations in marine food webs, posing threats to human health.[3] Comprehensive knowledge on sources and dynamics of Hg in marine food web including uptake pathways, internal distributions, excretion processes, in-vivo methylation/demethylation mechanisms, and trophic transfer is crucial to understand the impacts of anthropogenic Hg loadings to the oceans and to evaluate current and future efforts to reduce anthropogenic Hg emission. In this study, a large-scale food web samples were collected from a typical human-impacted marine ecosystem in China and analyzed for Hg speciation and isotope compositions, carbon and nitrogen isotope compositions, and lipid contents. The results showed that the trophic levels ranged from 0.97 to 5.48, with a mean value of 3.57. The food web had a large variation up to ~5% (~4.57 – 5.03%) in δ202Hg and mostly positive values in Δ199Hg (~0.01–1.21‰). The Δ199Hg/Δ201Hg ratio is 1.15 ± 0.06, indicating that the Bohai Sea biota were likely imparted by odd-isotope mass-independent fractionation (MIF) signatures of both photo-reduced IHg and photo-demethylated MeHg. The trophic transfer along coastal food web exhibited an enrichment in heavier and odd Hg isotopes, which is attributed to a preferential transfer of MeHg with higher δ202Hg and Δ199Hg rather than in-vivo Hg isotope fractionation. Interestingly, we found for the first time significantly negative δ200Hg (~0.36 – 0.08‰) and positive δ204Hg (~0.05 – 0.82‰) anomalies in some biota, with a δ200Hg/δ204Hg ratio of ~0.50 ± 0.02. These signatures were quite similar to those of atmospheric Hg0, suggesting that atmospheric Hg0 was a potential source of bio-accumulated Hg in coastal areas.
2.1 Bioaccumulation and biomagnification in food as a source of Hg exposure.

W.O.2.1-1

BIOMAGNIFICATION OF MERCURY IN SANDY BEACHES OFF THE COAST OF THE STATE OF RIO DE JANEIRO, BRAZIL

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Mercury (Hg) is able to biomagnify through the food chain, especially in its organic form (methylmercury). However, few studies about biomagnification focused on sandy beaches food web, although the huge importance of this coastal ecosystem to human activities and to ecological equilibrium. Furthermore, Guanabara Bay sandy beaches (located at the external part of the Bay) suffer the influence of several anthropogenic activities that includes Hg sources. Therefore, this work aimed to evaluate the process of biomagnification at three sandy beaches from Guanabara Bay (Adão, Itaipu and Forte do Rio Branco beaches) using fish species that occupy different trophic levels, captured by beach seining net. Muscles were removed, lyophilized and homogenized. The total mercury (THg) was performed by atomic absorption spectrometry and the methylmercury (MeHg), by atomic fluorescence spectrometer (AFS) coupled to a gas chromatographer (GC). To determine the trophic level and to identify the food source origin, it was analyzed the elemental (C and N) and isotopic (δ13C and δ15N) compositions. The biomagnification factor (BMF) was estimated using the anti-log of the slope of a log-linear regression (MBF = 10^a) between the MeHg and HgT and the trophic level calculated by δ15N. All Hg concentrations were bellow the legal criterion for human consumption (0.5 µg g⁻¹) and the MeHg was responsible for almost 100 % of THg. The isotopic signatures of δ13C and δ15N varied from -12.2 to -6.4 % and 6.6 - 14.4%, respectively. The C/N ratio (2.9 - 4.1) and δ13C (-12.2 to -6.4 %) were used in the analysis of the food web. Mercury (Hg) is able to biomagnify through the food chain, especially in its organic form (methylmercury). However, few studies about biomagnification focused on sandy beaches food web, although the huge importance of this coastal ecosystem to human activities and to ecological equilibrium. Furthermore, Guanabara Bay sandy beaches (located at the external part of the Bay) suffer the influence of several anthropogenic activities that includes Hg sources. Therefore, this work aimed to evaluate the process of biomagnification at three sandy beaches from Guanabara Bay (Adão, Itaipu and Forte do Rio Branco beaches) using fish species that occupy different trophic levels, captured by beach seining net. Muscles were removed, lyophilized and homogenized. The total mercury (THg) was performed by atomic absorption spectrometry and the methylmercury (MeHg), by atomic fluorescence spectrometer (AFS) coupled to a gas chromatographer (GC). To determine the trophic level and to identify the food source origin, it was analyzed the elemental (C and N) and isotopic (δ13C and δ15N) compositions. The biomagnification factor (BMF) was estimated using the anti-log of the slope of a log-linear regression (MBF = 10^a) between the MeHg and HgT and the trophic level calculated by δ15N. All Hg concentrations were bellow the legal criterion for human consumption (0.5 µg g⁻¹) and the MeHg was responsible for almost 100 % of THg. The isotopic signatures of δ13C and δ15N varied from -12.2 to -6.4 % and 6.6 - 14.4%, respectively. The C/N ratio (2.9 - 4.1) and δ13C (-12.2 to -6.4 %) were used in the analysis of the food web.

W.O.2.1-2

DIFFERENCES IN MERCURY AND METHYLMERCURY BIOACCUMULATION BETWEEN KEY BIVALVE SPECIES AND ATLANTIC SILVERSIDES FROM LONG ISLAND SOUND

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A multitude of factors influence the bioaccumulation of both mercury (Hg) and methylmercury (MeHg), including both environmental and biological factors. For this reason, different species within the same ecosystem can have different patterns in Hg and MeHg bioaccumulation. This can be reflected in both the mean concentrations measured in each species and in the relationships, or lack thereof, observed between Hg concentration and size of the organism. While Hg and MeHg relationships with various biological factors in pelagic species are well studied, Hg and MeHg data for benthic species, such as bivalves, is limited. Bivalves are important components of many coastal food webs, and thus an important link in the trophic transfer of contaminants. In this study, we collected four bivalve species that ranged in size: northern quahogs (Mercenaria mercenaria), soft-shell clams (Mya arenaria), eastern oysters (Crassostrea virginica), and ribbed mussels (Geukensia demissa) along with one forage fish species, Atlantic silversides (Menidia menidia) throughout the summer of 2016 from the same Long Island Sound embayment. Mumford Cove. Environmental samples included seawater, small phytoplankton-representative seston (3-20 µm), and surface sediments. We measured both total Hg and MeHg for all samples. Atlantic silversides were separated based on sex with individuals too young for sex determination considered as juveniles. Overall, the average THg concentration for adult silversides was 0.36 ± 0.16 (mean ± SD) µg/g dry weight while it was 0.17 ± 0.03 µg/g in juvenile silversides. The percentage of THg that was MeHg (%MeHg) was above 90% for both adults and juvenile silversides. The THg concentrations in the quahogs, oysters, and ribbed mussels were 0.25 ± 0.10 µg/g, 0.26 ± 0.07 µg/g, and 0.26 ± 0.04 µg/g, respectively, showing that inter-species differences had no baring on the concentrations of accumulated THg. The %MeHg for all bivalve species ranged from 10-80%. While a significant positive relationship between size and THg concentration was observed for the silversides (p=0.05), a similar relationship was not observed in any of the bivalve species. Rather, a significant negative relationship between size and MeHg concentration was observed in the northern quahogs (p=0.034). In the presentation, we will discuss factors and processes behind the observed patterns in our data.

W.O.2.1-3

MERCURY BIOACCUMULATION, TOXIC EFFECTS AND MERCURY ISOTOPE FRACTIONATION IN RATS FED WITH METHYLMERCURY POLLUTED RICE

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Recent evidence indicated that methylmercury (MeHg) contaminated rice can be a significant source of MeHg human exposure, but the health implications are not known. The objective of this study was to study the kinetics, speciation, and effects of MeHg contaminated rice using a rat model. Five groups of adult Sprague-Dawley rats (n=10 in each group) were fed control rice, low (10 ng/g MeHg) and high (25 ng/g MeHg) MeHg contaminated rice. Two groups of the positive control were fed control rice spiked with the same levels of MeHg-Cl. There were significant differences in the accumulation of THg and MeHg among different groups and different organs. THg and MeHg concentrations in the kidney were the highest among the organs examined. Exposure to rice containing 25 ng/g MeHg decreased antioxidant...
We measured total mercury (Hg) in 625 Greenland halibut fillets (Reinhardtius hippoglossoides) collected from the Norwegian Sea from 2006-2015. Hg concentrations averaged 0.17 mg/kg (range = 0.002 - 0.95 mg/kg) on a wet weight basis. Hg speciation analyses conducted on Greenland Halibut baseline study samples (n = 224) showed that methyl Hg comprised > 91% of the total Hg in skinless and boneless fillet tissue. Our length normalized fish data showed that total Hg biaccumulation in fillet tissue decreased by approximately 50% over a ten year period from 2006-2015. Results from a Bayesian predictive, information theoretic model showed that total Hg concentrations were driven by a regime of conditions rather than by a single variable. This regime of conditions included a model supported by the following trends 1) Hg decreasing with time (year of study sampling), 2) Hg increasing with fish length (cm), 3) Hg increasing with higher trophic positions (δ15N) and 4) Hg increasing with a more benthic diet (δ13C). This investigation will likely serve as an important model for the effectiveness evaluation of the relevant biomonitoring articles of the United Nations Minamata Convention on Mercury (UN-MCM) for the following reasons. First, this study utilizes reproducible data and reliable information from an existing, long-term research and biomonitoring program with analyses conducted at an accredited laboratory. Secondly, our study considers the importance of food web dynamics and trophic shifts as important drivers of global environmental change and marine apex predator Hg exposure regimes. Additionally, our sampling approach and continued efforts will allow for temporal assessments of circumpolar fish mercury exposure over time scales relevant to the initiation and effectiveness evaluation of the UN-MCM.

META-ANALYSIS OF MERCURY CONCENTRATION IN FORAGE FISH ACROSS NORTHEAST USA ESTUARIES

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Multiple studies have indicated the importance of water column methylmercury (MeHg) concentration in predicting estuarine fish tissue concentrations, however, fewer studies have examined the role of environmental variables such as land use in concurrently driving mercury (Hg) bioaccumulation. In the current study, a meta-analysis was conducted to examine variability and potential drivers of bioaccumulation across the range of sites and landscapes. Forage fish (Fundulus heteroclitus and Menidia menidia) were collected from 2012 to 2016 in estuaries spanning the Northeast coast of the United States, from Maryland to Maine. The collection sites encompassed both unimpacted and contaminated sites, in both rural and developed landscapes. This resulted in a gradient of land uses, as well as large variation in Hg and MeHg biotic and abiotic concentrations. Fundulus were collected from 39 sites (mean MeHg range 14 - 850 ppb DW) and Menidia from 31 sites (mean THg range 28 - 1380 ppb DW). Sediment mean MeHg concentration ranged from 0 - 63 ppb DW, particulate MeHg from 0.1 - 36 ppb DW, and dissolved MeHg from 0 - 1.1 ng/L across sites for both species combined. Tissue concentrations were length normalized and standardized by site prior to statistical analysis. Initial analysis indicates species-specific differences in patterns of influence on tissue concentration. Abiotic sediment and water concentrations of both MeHg and total Hg had the strongest relationship with fish tissue Hg concentrations, with sediment concentrations decreasing in importance with the removal of contaminated sites from the model, particularly for Menidia. For both species, land use variables were weakly predictive of tissue concentrations, with the exception of percent forest. Unlike in lakes and rivers, the presence of forest in the watershed was negatively related to tissue concentrations. High levels of development had a greater positive influence on Menidia than on Fundulus tissue concentrations. Overall, environmental Hg and MeHg concentrations in sediment and water were more predictive of fish Hg bioaccumulation than land use associations.

THE MERCURY TEN YEAR CHALLENGE: RAPID TEMPORAL DECLINE OF METHYLMERcury IN CIRCUMPOLAR GREENLAND HALIBUT

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We measured total mercury (Hg) in 625 Greenland halibut fillets (Reinhardtius hippoglossoides) collected from the Norwegian Sea from 2006-2015. Hg concentrations averaged 0.17 mg/kg (range = 0.002 - 0.95 mg/kg) on a wet weight basis. Hg speciation analyses conducted on Greenland Halibut baseline study samples (n = 224) showed that methyl Hg comprised > 91% of the total Hg in skinless and boneless fillet tissue. Our length normalized fish data showed that total Hg biaccumulation in fillet tissue decreased by approximately 50% over a ten year period from 2006-2015. Results from a Bayesian predictive, information theoretic model showed that total Hg concentrations were driven by a regime of conditions rather than by a single variable. This regime of conditions included a model supported by the following trends 1) Hg decreasing with time (year of study sampling), 2) Hg increasing with fish length (cm), 3) Hg increasing with higher trophic positions (δ15N) and 4) Hg increasing with a more benthic diet (δ13C). This investigation will likely serve as an important model for the effectiveness evaluation of the relevant biomonitoring articles of the United Nations Minamata Convention on Mercury (UN-MCM) for the following reasons. First, this study utilizes reproducible data and reliable information from an existing, long-term research and biomonitoring program with analyses conducted at an accredited laboratory. Secondly, our study considers the importance of food web dynamics and trophic shifts as important drivers of global environmental change and marine apex predator Hg exposure regimes. Additionally, our sampling approach and continued efforts will allow for temporal assessments of circumpolar fish mercury exposure over time scales relevant to the initiation and effectiveness evaluation of the UN-MCM.

TRACING THE BIOACCUMULATION PATHWAYS AND METHYLATION/DEMETHYLATION OF MERCURY IN RICE PLANT USING MULTI-ISOTOPE TECHNIQUE

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Rice has been highlighted in recent literatures as a bioaccumulator plant species of methylmercury (MeHg). Cultivation of paddy rice for human consumption is a dominant agricultural activity throughout the world. The rice consumption could be the main pathway of MeHg exposure to human in Hg contaminated area. Therefore, the influence of MeHg contaminated rice on human health threat should receive considerable attention. However, the understanding of the bioaccumulation pathways of inorganic Hg (I>Hg) and MeHg in tissues of rice plants is limited; the methylation/demethylation of Hg in rice plant is still un-known. Field experimental pots were carefully designed based on the multi-isotope technique (Me198Hg and 200Hg2+) to trace the bioaccumulation pathways and methylation/demethylation of mercury in rice plant. Concentrations and distributions of isotopic I>Hg and MeHg both in tissues of rice plant and corresponding soil samples during a full rice growing season were determined. Our results showed that both the Hg in soil and air were the potential sources of I>Hg to tissues of rice plant. Specially, the contribution of I>Hg to root and stalk through soil pathway is much higher than those to the other parts of rice plant; on the opposite, I>Hg concentrations in leaf and seed was predominantly restricted to Hg concentration in air. Differently, MeHg in paddy soil is a potential source to tissues of rice plant. More important, we observed obviously demethylation of MeHg in stalk and leaf during the rice growing seasons; however, no discernable Hg methylation was observed in tissues of rice plant during the rice growing periods. Current study become a great breakthrough in the mechanism of accumulation of mercury species in rice plant and supplied the new theory foundation for understanding the interaction between Hg and plant in the supergene environment.
3.1 Legacy mercury contamination and solutions for remediation

W.O.3.1-1

EVALUATING THE EFFECTIVENESS OF BANK MANAGEMENT EFFORTS IN REDUCING Hg LEACHING INTO STREAMS

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River banks serve as mercury (Hg) repositories in contaminated streams while posing continual risk to ecological health. Mercury accumulated in banks have tendency to be released back into the streams via erosion and groundwater-surface water interactions during episodic storm events. Therefore, tackling the impacts of contaminated banks represent a crucial part in effective stream restoration. This presentation discusses the results of a case study in South River, Virginia, that implemented bank stabilization efforts through application of sand and armoring to minimize erosion, and a sand-biochar mix layer to reduce soluble and non-particle Hg release. The effectiveness of the bank management efforts was evaluated by pre and post-stabilization measurements of non-particulate total Hg (THg) release from the bank using diffusive gradient in thin-film (DGT) passive sampling devices. Sampling was performed at the base of the bank during baseline flow (July 2015 and August 2017 for pre and post-stabilization, respectively) and during bank drainage after a storm event (October 2015 and October 2018 for pre and post-stabilization, respectively) that is most likely to leach highest concentration of Hg from the bank. The pre-stabilization DGT measurements taken at two different time periods of July and October 2015 showed relatively high THg (pore-water values ranging from ~15 to 10,000 ng L⁻¹). The comparative post-stabilization THg pore-water values were orders of magnitude lower with values ranging from ~10 to 130 ng L⁻¹ even during the bank drainage condition. Dialysis samplers were used to estimate drainage velocities and define fluxes using a novel technique and showed substantially reduced fluxes after stabilization. In summary, the DGT sampling show that the bank management efforts were effective in substantially reducing the non-particulate THg concentrations at all bank locations when compared to the measurements obtained in the pre-stabilization sampling and is a promising strategy for mitigating risks in such Hg contaminated bank systems.

W.O.3.1-2

NOVEL APPROACHES TO THE INVESTIGATION AND REMEDIATION OF MERCURY IN THE ENVIRONMENT

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The overall aim of this project is to develop and apply novel approaches to the investigation and remediation of mercury in the environment. Here we present findings from a two-part initial study investigating: (1) Hg concentration and its chemical speciation in contaminated sediment; and (2) the impact of three iron-based nanoparticle treatments on Hg, and additional geochemical and geomicrobiological parameters, in long-term microcosm experiments. The chemical speciation of mercury in contaminated canal bed sediment from the Weaver Navigation (Runcorn, UK) was investigated using a sequential extraction procedure (SEP) in combination with inductively coupled plasma – mass spectrometry (ICP-MS), and x-ray absorption spectroscopy (XAS). A total Hg extraction procedure established that the Hg concentration in the sediment is ~86 ± 1 mg/kg (dry wt.). Additional analytical techniques were employed to assist in other aspects of sediment characterisation. Mineralogical analysis identified that the bulk of the sediment contained calcite, halite and brucite, which are key components of solid waste from mercury-cell chlor-alkali plants. SEPs revealed that the mercury appears to be recalcitrant in the sediment as ~97% requires strong acids to be extracted, suggesting that it is predominantly strongly complexed or mineral bound, and therefore relatively immobile and less bioavailable. XAS data was able to reveal more detailed Hg compound specific information, XANES linear combination fitting suggested that the major portion is metacinnabar (β-HgS). Additional experimental work investigating the impact of three iron-based nanoparticle treatments (biomagnetite, NanoFER and Carbo-Iron) on residual Hg in sediment and added soluble HgCl₂ are currently in progress (commenced June 2018). Long term anaerobic microcosms were setup in 120 mL serum bottles containing sediment and artificial groundwater to simulate environmental conditions at the sediment-water interface. Microcosms were monitored over a one-year period to determine changes in: (1) sediment and pore-water chemistry (and mineralogy); (2) the chemical speciation of mercury; and (3) the microbial community. Monitoring samples were taken by degassed needle and syringe, aliquots of each sample were allocated for various analytical techniques, detailed here: ion chromatography (IC) (aqueous phase anions), ICP-MS (aqueous phase Hg), ferrozine assay (bioavailable solid phase Fe), XAS (solid phase Hg speciation), transmission electron microscopy (TEM) (solid phase high resolution imaging) and 16S rDNA (sequencing of microbial communities in solid phase). This research work is part of an EPSRC CASE funded studentship and will provide scientific information that could assist in the development of new in situ remediation treatments.

W.O.3.1-3

MERCURY – ENVIRONMENTAL RISK ASSESSMENT AND REMEDIATION APPROACH.

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Due to its toxicity, mercury is constantly withdrawn from products in Europe. Thanks to international action resulted in 2013 in the Minamata Convention on Mercury, a legally binding international agreement aimed at tackling mercury pollution. Unfortunately, the times of the communist regime in Poland have left a significant, toxic trace in the environment – post-industrial soil pollution, including mercury. The region of Upper Silesia is one of the most polluted areas in Poland. There, in one of the cities, Arcadis carried out research on groundwater and soil which showed quite large exceedances of not only mercury but cadmium and other metals, Chlorinated Hydrocarbons, BTEX, Cyanides, Chlorobenzene, Bromobenzene and PAH (locally occur). Mercury, the subject of this presentation, was detected in two parts of the studied area. The first part of which managed to perform ex-situ remediation, and in the second part, further research and work is being carried out due to the complicated technical situation. The area was subjected to numerous investigation phases including GPR survey drilling of boreholes in connection with sampling of soil, groundwater and soil gas, as well as using high resolution characterisation tools such as Membrane Interface Probe (MIP), used for detecting VOC, mainly CHC in this case). Mercury concentrations occurred at various depths, mainly in embankment. The highest concentration measured in a soil sample was 780 mg/kg. Modeling of the human health and environmental risk assessment also has been performed. The model was prepared using the RBCA Tool Kit and US EPA Intrusion modules. The modelling (elemental mercury) is challenging due to lack of local guidelines as regards choice of the model, input parameters, calculated target levels. Modeling has shown that the most critical routes for the identified receptors will be: Site workers and off-site groundwater. Certainly, the possibility of direct exposure through skin contact, inhalation of dust or accidental intake
of contaminated soil should also be considered. On the example of a project from Upper Silesia, the detailed description of the process of works related to remediation of sites contaminated with mercury and the principles of occupational health and safety associated with them will be presented in a comprehensive manner.

W.O.3.1.4

SCIENCE-BASED REMEDY DRIVERS FOR A LARGE ES-TUARY SITE, HACKENSACK MEADOWLANDS, USA

BRUSOCK, Peter; MARTIN, Todd; DE HAVEN, Peter; HIMMEL-HEBER, David; TOMCHUK, Douglas

(1)The ELM Group, Inc.
(2)Integral Consulting, Inc.
(3)Geosyntec Consultants, Inc.
(4)USEPA

A rigorous, science-based study conducted in a process where initial results feed the analysis going forward can provide a sound and objective basis for selecting a remedy for large, complex contamination sites. This paper presents a summary of the scientific elements of a comprehensive study of Berry's Creek, a mercury-contaminated urban estuary in the Mid-Atlantic United States. It presents how the understanding derived from a progression of studies provided the scientific basis for a framework to support the visioning of a remedial process that will reduce risks while reducing the potential that remedial actions will compromise the water-marsh stability or its resilience.

The site characterization took place over 10 years in an iterative manner, streamlined with frequent work sessions with varied stakeholders, to address study questions established to focus the characterization process. Initial phases focused on detailed study of the inter-related physical dynamics and trends in chemical conditions. Multiple field methods adapted for the site-specific conditions (e.g. sub-bottom profile imaging, high-resolution cores with radioisotope dating) were used to develop an initial Conceptual Site Model (CSM) that integrated information from field surveys of aquatic life and marsh receptors. Based on this CSM and updated study questions, additional phases of site characterization were scoped to develop detailed understanding of the biologically active zones, food web (e.g. isotope studies, organic matter CSM), biogeochemistry (e.g. voltammetry, metals sequential extraction) and uptake rates of methylmercury in receptor tissues. These studies supported further refinement of study questions and the CSM leading to the design of studies to understand the reasons for the observed low biouptake of mercury (methylmercury) given relatively high sediment concentrations of total mercury. Explanations related to the detritus-based food web, mercury sequestration, suppression of methylation via metabolic pumping of oxygen from Phragmites root mats, and elevated demethylation were explored and supported by site-specific data, including treatability studies. The dynamics of methylation and methylmercury transport within the water-marsh system were evaluated with optics-based surface water studies to understand the movement of methyl mercury into and out of marshes, and the role that the elevated levels of suspended particulates within the system has on methylmercury fate and transport.

This paper will present how these multiple lines of evidence were used to establish the dominant factors influencing mercury biogeochemistry relationships and a site-specific CSM that served as a framework to manage uncertainties in a phased adaptive remedy to reduce risks in a prioritized manner.

W.O.3.1.5

REVIEW OF RECENT ADVANCES IN MERCURY RE-SEARCH: ASSESSMENT AND REMEDIATION OF MER-CURY CONTAMINATED SITES.

ECKLEY, Chris; GILMOUR, Cindy; JANSSEN, Sarah; LUXTON, Todd; RANDALL, Paul; WHALIN, Lindsay

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Areas where mercury (Hg) has been utilized as part of anthropogenic activities (either industrial or artisanal) can contain Hg concentrations that are elevated above what would be expected from atmospheric and geologic sources. There are many different anthropogenic activities that have created Hg contaminated sites, with some of the major sources being: Hg mining, manufacturing, gold and silver mining, and caustic soda production. While much of the global concern regarding Hg pollution is related to its widespread contamination of remote systems through atmospheric deposition and subsequent biogeochemical cycles resulting in elevated concentration in biota, there are unique opportunities to assess and remediate spatially discrete, but highly contaminated, areas of Hg pollution. This presentation focuses on the results of a recent literature review and synthesis project aimed at summarizing the recent advances regarding the assessment and remediation of Hg contaminated sites. This effort is one part of a forthcoming special issue of Science of the Total Environment with over 15 papers providing a review of advances in Hg research and understanding the Hg biogeochemical cycle. Contaminated site assessment activities include the determination of the geographic extent of the contamination, understanding the sources of Hg contamination, identifying major pathways of release and exposure, and estimating the mobile and bioavailable forms of Hg at a site. All of these aspects of Hg contaminated site assessment have evolved in recent years due to improvements in XRF instrumentation, stable isotope fractionation studies, flux measurements, and analytical methods that estimate lability (sequential extractions, EXAFS, etc). In addition, approaches and techniques for the remediation of Hg contaminated sites have also seen many advancements in recent years due to the increased use and availability of soil and sediment amendments such as biochar and activated carbon. There have also been other advances in remediation techniques related to site removals, capping, pump and treatment techniques, among others. Overall, this presentation provides a summary and synthesis of the current understanding of the important topics related to the assessment and remediation of Hg contaminated sites.

W.O.3.1.6

ASSESSING THE RELATIVE SUCCESS OF MULTIPLE INTERVENTIONS AT ONONDAGA LAKE TO REDUCE MERCURY BIOACCUMULATION

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(1)Anchor QEA
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Mercury concentrations in fish in Onondaga Lake (Syracuse New York, USA) have declined over the past 10 years contemporaneous with a combination of interventions by Honeywell and Onondaga County to, respectively, reduce contaminant concentrations and improve water quality. For mercury, interventions involved control of inputs to the lake via groundwater and tributaries, dredging and capping of contaminated nearshore sediment, and redox control of lake water to prevent methylmercury release from profundal sediment. These interventions along with natural recovery in profundal sediment have addressed the major external and internal sources of mercury and methylmercury identified in the mercury mass balance model first reported at ICMGP in 1994. Redox control by nitrate injection to the hypolimnion supplements nitrate discharged from the Onondaga County Metropolitan Sewage Treatment Plant which supplies 20 percent of annual water flow to the lake and underwent significant upgrades to limit phosphorus and ammonia discharges. Now, the lake is experiencing less eutrophication and improvements in diversity and abundance of fish and plant communities. Methylmercury concentrations in water and zooplankton are similar to concentrations in lakes lacking point source mercury contamination.
4.3 Linking Science and Policy for the implementation of the Minamata Convention

W.O.4.3-1

REVIEW OF RECENT ADVANCES IN MERCURY RESEARCH: MAJOR FACTORS CONTROLLING TERRITORY CYCLING

BISHOP, Kevin1; SHANLEY, Jamie2; RICASSI, Ami3; OSTERWALDER, Stefan4; ZHU, Wei4; EKLÖF, Karin5; MITCHELL, Carl6; MENG, Bo7; DE WIT, Helleen8; WEBSTER, Jack9; SCHUSTER, Paul2

1)Swedish University of Agricultural Sciences
2)US Geological Survey
3)Univ. of Virginia
4)Univ. of Basel
5)Univ. of Toronto
6)CAS State Key Laboratory of Environmental Geochemistry
7)Norwegian Institute of Water Research
8)California State University, Chico

This presentation summarizes advances during the past decade in understanding the terrestrial Hg cycle. We start by examining three “gateways” to/from the terrestrial cycle, 1) terrestrial exchange with the atmosphere, 2) surface water outputs, and 3) the utilization of vegetation for food by both people and wildlife. Different aspects of how human activity alters terrestrial Hg cycling are then examined: climate change (including melting permafrost, and fires), atmospheric deposition of sulfur on wetlands, and forest landscape management, (including, wetland alteration, and the spread of beaver.) The role of progress in our ability to measure different aspects of the cycle will be noted throughout. The paper will conclude with a reflection on how these advances in the understanding of terrestrial Hg cycling bear on the work of the Minamata convention in regard to both the global Hg cycle, and bioaccumulation of Hg derived from the terrestrial Hg cycle.

W.O.4.3-2

MERCURY EMISSIONS FROM SATELLITE ELECTRIC PROPULSION SYSTEMS: A NEW SOURCE THAT COULD AFFECT THE EFFECTIVENESS OF THE MINAMATA CONVENTION

PIRrone, Nicola1; Fourier, Daniel H.2; de Simone, Francesco1; Sunderland, Elise M.3; Hedgcock, Ian M.1

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A new generation of satellites for earth observation and telecommunications are being designed and built with off the shelf components. This is driving down costs and permitting the launch of satellite swarms with greater spatial and temporal coverage than before. In orbit maneuvering is commonly achieved using ion thrusters, for which one of the cheapest and most easily stored propellants is mercury. Mercury released in Low Earth Orbit (LEO) will either escape the earth’s gravitational field or fall back to earth. Our model simulations suggest that the Hg entering at roughly the altitude of the turbopause (0.01 h Pa 80 km) will fully diffuse within the troposphere in about 6 years, and is a concern for people. The concern is greater (almost 80 %) deposited over the oceans, independently of the initial Hg release conditions considered. It is interesting from a policy point of view, that although released over a larger time window, Hg deposited resulting from satellite emissions are potentially greater than the annual terrestrial anthropogenic emissions (considering the 2035 maximum feasible reduction emission scenario), especially over the oceans. Understanding the potential scale of the future impact of this novel potential mercury source in a post-Minamata Convention world is necessary in order to limit continuing ecosystem exposure to mercury contamination.

W.O.4.3-3

OVERCOMING TECHNICAL AND QUALITY ASSURANCE CHALLENGES FOR THE WIDESPREAD USE OF A MERCURY PASSIVE AIR SAMPLER (MERPAS) METHOD FOR MINAMATA CONVENTION MONITORING

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Researchers at the University of Toronto have developed and published multiple peer-reviewed papers on the use of a mercury passive air sampler (MerPAS) method for high-accuracy and precise air mercury determinations at the ppqv level (150 ppqv = 1.3 ng/m3). It is now taken for granted that measurements at this level are routine using the automated, continuous, CVAFS-based, Tekran 2537X Gaseous Mercury Air Monitor and associated speciation modules. At these levels, which are one thousand and one million times lower than typical ambient NOx and O3, respectively, it is not surprising that maintaining continuous and accurate automated gaseous air mercury measurements can be more challenging and costly than anticipated. While high-resolution, automated air mercury speciation measurements have, and still are, demonstratively valuable to quantify atmospheric mercury cycling, the Minimata Convention on Mercury has created an opening for low-tech, lower cost and more widespread ambient air mercury monitoring to complement the current global instrument-based networks. For continuous and low-cost passive air sampling methods have to be applied with an understanding of the trade-offs in sensitivity and resolution. Furthermore, there are many technical challenges for converting a research-based method, with a high level of experienced oversight, and offering the sampler and method to a wide range of applications and multitude of end-user types. Applications are nearly limitless and include spatial mapping and gradient studies of polluted sites, fence-line monitoring, urban air networks and indoor monitoring of residences and workplaces for human exposure, such as artisanal gold mining communities. Questions answered by this presentation include: 1) What packaging and preventative measures work for use and storage of samplers in high air mercury environments to prevent contamination? 2) How will the use of the MerPAS sampler affect the reproducibility of the carbon preparation? 3) Is the analysis of the sample straightforward and transferable to a routine laboratory and 4) What sampler configurations and sample times work best for indoor air monitoring and highly contaminated sites.
EXPERIENCES WITH HALOGEN-BASED MERCURY OXIDATION IN COAL AND WASTE COMBUSTION

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In USA lots of coal-fired power plants are served with bromides and/or iodides – e.g. in form of pre-combustion bromide addition (onto the coal) or in form of high-temperature bromide injection into the fire-box (boiler bromide addition) – as invented by Prof. Vosteen and filed for patent by BAYER AG/CURRENTA GmbH & Co. OHG in 2002 and demonstrated large scale already in 2005 by US EPRI at the Lunminic Monticello Power Station, Unit 3 under a license of Vosteen Consulting GmbH. In total there are today more than 100 GWel of coal-fired US power plants – which is about 1/3 of the total coal-based US-power generation capacity – using bromide and iodide this way as a mercury oxidizer to achieve compliance with the stringent Mercury and Air Toxics Standards regulations (US MATS rules). In Europe about 20 incinerators of hazardous wastes and sewage sludges are served with Prof. Vosteen’s BEMO-technology (Bromine Enhanced Mercury Oxidation) since 2004. German and Polish lignites partially are fairly different from US-american lignites (moisture content, sulfur content, ash content, ash composition). To transfer the halogen-based mercury oxidation technology onto lignite-fired plants still is a challenge. The paper will report about recent experiences with halogen-based mercury oxidation tests in coal and waste combustion in Germany and the Czech Republic, applying both bromide and iodide onto the coal. The European Patent EP 1 386 655 B1 of Prof. Vosteen covers both bromide and iodide addition at plants with wet and/or dry APC.

COMPREHENSIVE MERCURY MONITORING IN AQUATIC AND TERRESTRIAL SAMPLES FROM THE GERMAN ENVIRONMENTAL SPECIMEN BANK: MATRIX COMPARISONS, SPATIAL COMPARISONS AND TEMPORAL TRENDS OVER THREE DECADES

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Mercury (Hg) is a naturally occurring, ubiquitous metal that has broad anthropogenic uses. It is applied in everyday products and is released to the atmosphere, soil and water from a variety of sources. The Minamata Convention on Mercury is a global treaty to protect human health and the environment from the adverse effects of Hg. It was agreed in 2013 and entered into force in 2017. The Convention aims at controlling the anthropogenic releases of Hg by phasing-out mining and certain uses. To verify the success of the Convention a monitoring of Hg in environmental matrices should be performed. Hg is also a priority substance under the Water Framework Directive (WFD). To this end an environmental quality standard (EQS; 20 µg/kg fresh weight) in fish was derived which should protect both human health (fish as food) and wild life (secondary poisoning of predators). The WFD demands a good chemical status of waters by 2027 (i.e. fish levels below EQS). Moreover, a trend monitoring is required. Since Hg is measured regularly in all samples that are archived in the German Environmental Specimen Bank (ESB), the monitoring data can support the implementation of these regulations. Time series of Hg concentrations in ESB samples are available for up to three decades. Samples cover different trophic levels in representative coastal, limnetic and terrestrial ecosystems. For some sample types also methylmercury concentrations are available, revealing, e.g., temporally varying fractions of methylmercury in mussels. The aggregated Hg data allow a comprehensive evaluation regarding: spatial comparisons – how variable are the Hg levels throughout Germany (e.g., at near-natural forest sites and for trees near conurbations?); matrix comparisons – are the Hg levels increasing towards sample types representing higher trophic levels (e.g., for the coastal sites from mussels to fish samples?); and temporal trends - are there similar concentration changes of Hg levels in all matrices/all regions? The data are discussed with view on the Minamata Convention and WFD aims on reducing Hg burdens. Most time series show for the recent 10 year period decreases of Hg levels of a few percent per year although not all trends are significant. However, although freshwater fish levels of Hg are decreasing nearly all ESB fish samples are still exceeding the WFD EQS for Hg.
ADVANCES IN CHEMICAL SPECIATION OF MERCURY COMPOUNDS USING HIGH ENERGY RESOLUTION FLUORESCENCE DETECTED X-RAY ABSORPTION SPECTROSCOPY (HERFD-XAS)

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Knowledge on the chemical forms of mercury is critically important in understanding the chemical rationale for its activity and can help explain many aspects of global mercury cycling. Furthermore, the mechanisms of toxicity – target, activity, severity, etc., heavily depend on the chemical form of mercury compounds. Therefore, to reliably identify the chemical structure of various mercury compounds is essential to navigate the strategic efforts of environmental remediation and the design of optimal sequestering agents. The global deposition of mercury can exist in a number of chemical forms and the biogeochemical cycling of mercury involves a range of biotic and abiotic sample types – air, biological organisms, soil, and water. Using newly available advanced synchrotron techniques, distinguishing various chemical species of mercury using hard X-ray methods is achievable with the considerable advantage of having no requirements for pre-treating the sample. We will present results that highlight the exquisite chemical sensitivity given using High Energy Resolution Fluorescence Detected X-ray Absorption Spectroscopy (HERFD-XAS). This advanced technique utilizes sophisticated crystal analyzers which provide superior energy resolution that directly improves the chemical sensitivity using X-ray spectroscopy. HERFD-XAS results provide chemical information on the oxidation state and coordination environment of mercury compounds. Advancements include the chemical analysis of a range of sample types down to the low nano-molar range. Among the results collected from our laboratory using HERFD-XAS, we will present results displaying the elaborate spectroscopy with distinct spectral features capable of discerning isostructural compounds of mercury. Additionally, we probe the chemical components within mammalian and natural biological tissue samples to reveal the accumulation patterns of specific mercury species. The methods of HERFD-XAS as well as the advantages and limitations afforded will be discussed. These new advancements in X-ray methods provide richer spectroscopy, allowing for the direct chemical characterization in a range of sample types which will have a profound impact on the analysis of mercury species in the fields of health and environmental sciences.

APPLICATION OF MEHg STABLE ISOTOPES IN THE FOX RIVER, WI, USA TO UNDERSTAND BIOACCUMULATION IN A CONTAMINATED FRESHWATER ESTATE

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The Lower Green Bay and Fox River in northeastern WI, USA is one of fourteen ongoing Areas of Concern (AOCs) in the Laurentian Great Lakes region, due to legacy contamination of polychlorinated biphenyls and mercury (Hg) from past industrial activity. Many beneficial use impairments are listed for the river system, including those related to sediment and water quality, and contaminants in sport fish. The major Hg source in the Fox River is that sequestered in sediments, which at times, have exceeded 6 mg kg-1.

Our study focuses on the availability of legacy Hg in contaminated sediments for bioaccumulation. Bulk total Hg (HgT) measurements of contaminated sediments, analyzed across a 60 km spatial scale of the river system, have a homogenous isotopic composition (δ202Hg -0.56 ± 0.05 %) which complicates source tracking efforts and masks nuances in bioavailable Hg pools. In systems like the Fox, traditional Hg measurements are inadequate to resolve source apportionment questions, however by tracking subtle changes in the ratios of methylmercury (MeHg) isotopes, we can begin to assess bioaccumulation and the relative contributions of legacy Hg to aquatic food webs.

In our study, we apply the measurement of MeHg isotopes to sediment, benthic invertebrates, plankton, and lower trophic level fish to assess the preservation of legacy-derived MeHg in the lower Fox River food web. Surface sediments in the Fox River tend to be < 1% MeHg, similar to other highly contaminated systems, and average isotopic measurements are enriched in comparison to HgT measurements (δ202HgMeHg 0.01 ± 0.16 %). This value is almost identical to HgT isotope measurements in smallmouth bass and perch (>87% MeHg) after photochemical correction, indicating the potential bioaccumulation of sediment-derived MeHg.

Additional measurements of plankton will elucidate potential water column sources of MeHg to fish while invertebrate samples can be used to examine the preservation of the sediment MeHg sources in the lower food web. These results support the need for future examinations of MeHg isotopes in contaminated systems, as they provide a more suitable comparison of the Hg isotopic composition of sediment and benthic matrices which will be vital in predicting bioaccumulation from source-specific pools of Hg. This information is important for resource managers in AOCs tasked with the responsibility of identifying and remediating Hg source hotspots that potentially influence bioaccumulation.

INNOVATIVE ANALYTICAL METHODOLOGIES BASED ON A THIOL-CONTAINING IONIC LIQUID TO FACILITATE HG DETECTION IN NATURAL WATERS

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There is a need for simple and efficient techniques facilitate mercury monitoring to obtain reliable and significant data concerning contamination in aquatic environments.

In this context, chemically functionalized membranes can play an important role, and polymer inclusion membranes (PIMs) are one of the most promising functionalized membranes existing nowadays. PIMs consist of a polymer, which provides mechanical strength, the carrier, which is the responsible of the extraction process, and sometimes also a plasticizer can be used to provide elasticity. The stability, versatility and easy manufacturing show PIMs as a useful separation technique to be taken into account.

In this work we have studied how PIMs can solve different analytical difficulties in the analysis and/or monitoring of mercury (Hg). For that, PIMs have been prepared fixing cellulose triacetate (CTA) as polymer and the ionic liquid trioctylmethylammonium thiocyanate (TOMATS) as extractant. A PIM with a composition 50% CTA+50% TOMATS was shown to be an effective sorbent to extract Hg from different natural waters without any effect of water matrix. Moreover, Hg collected in PIMs was analysed by means of an Energy Dispersive X-ray fluorescence (EDXR) spectrometer allowing the determination of Hg at low µg L-1 levels.

The methodology used is simple, reliable and has an advantage in terms of accuracy with a LOD of 0.2 µg L-1. Besides, taking into account the problems associated with preservation and storage of aqueous sam
ples for ambient-level Hg, we also explored the use of this PIM as a suitable material to preserve the metal until the appropriate analysis is done. It was found that the concentration of Hg extracted in PIMs did not change over time (after 6 months). This finding can lead to the development of suitable sorbents that can be used to preserve sample information of natural waters with Hg [1]. We have also used a special device to incorporate a PIM and to contain a small reservoir of a 10-3 M cysteine solution where Hg is released after membrane transport. From our studies, it has been seen that the addition of the plasticizer nitrophenyloctyl ether (NPPOE) to the PIM, allowed the selective transport and preconcentration of Hg from several natural waters such as river and sea water without any previous treatment (pH adjustment or salinity control). This important result shows this new PIMs-based device as a promising tool to perform Hg monitoring. [1] G. Elias, E. Margul, S. Díez, C. Fontás, Anal. Chem. 2018, 90, 4756–4763.

**R.O.1.6A-4**

**TRACE MERCURY DETECTION IN WATER: NEW ELECTROCHEMICAL SENSOR BASED ON GOLD NANO-PARTICLES MODIFIED ELECTRODE**

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According to the UNEP 2013 Global Mercury Assessment, mercury emissions in the aquatic media have been rising since the mid-19th century, and are expected to be higher in 2050. Facing this global threatening trend, rigorous monitoring must be kept all over the world in order to comply with the threshold value set by the WHO. 1 μg L–1 for drinking water. Once in the water, mercury is converted to a more toxic form: methylmercury (MeHg), which has the potential to cause serious damage to the human cardiovascular system. Spectroscopic techniques like Cold Vapor Atomic Fluorescence Spectroscopy (CV-AFS) are routinely used directly on Hg(II) bioavailability. Spectroscopic techniques like Cold Vapor Atomic Fluorescence Spectroscopy (CV-AFS) are routinely used for trace mercury determination. Although they offer good sensitivity and selectivity, they involve complex procedures and expensive material, which limit their use for on-site analysis. In this context, our group focused on electrochemical sensors as a promising alternative for in-situ Hg(II) trace analysis, for their manifold advantages; cheap devices with simple and quick procedure, low energy consuming and portability. Herein we present a new method to design and optimize an electrochemical sensor based on Glassy Carbon (GC) electrode functionalization with Gold Nanoparticles (AuNPs), chosen for their strong affinity for mercury and their high effective surface which allows good sensitivity suitable for trace Hg(II) determination. In order to enhance the sensor stability, the AuNPs were bonded to the electrode surface using an organic film, grafted by diazonium salts reduction using Constant Potential Electrolysis (CPE). Then, AuNPs were directly electrodeposited by CPE, from a gold precursor (HAuCl4). Field Emission Gun Scanning Electron Microscopy showed small homogeneous AuNPs with 27±3 nm average diameter and 158 NPs/µm2 density when the CPE was carried out during 300 seconds. The deposits were then activated by Cyclic Voltammetry in H2SO4 in order to rearrange the crystallographic plans of AuNPs, to homogenize the surface, and to calculate the sensitive Electroactive Surface Area. The electrochemical response of the sensor towards different amounts of Hg(II) in 0.1 M HCl solution, was evaluated by Square Wave Anodic Stripping Voltammetry (SWASV). The procedure consists in Hg(II) preconcentration at the electrode surface followed by the preconcentrated Hg(II) oxidation in Hg(III). Under optimized conditions, the sensor showed a linear range from 1 to 10 nM and allowed to reach concentrations at the picomolar level. The stability was studied after several weeks storage at 22°C, in air, HCl, and phosphate buffer. Finally, Hg(II) detection assays were conducted in natural water samples and compared to reference method results (CV-AFS).

**R.O.1.6A-5**

**DIRECT DETECTION OF GASEOUS OXIDIZED MERCURY BY CHEMICAL IONIZATION MASS SPECTROMETRY**

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Mercury is a persistent environmental pollutant, entering the atmosphere mostly in its elemental form and leaving in its various oxidized forms. We know little about the molecular identity of gaseous oxidized mercury (GOM) and this limitation hinders our ability to evaluate the fate of mercury in the environment. This presentation will cover our recent work on the development of an analytical technique for molecular analysis of GOM and the illustration of its application for direct detection of HgX2 and HgXY molecules in the gas phase (where X and Y are inorganic anions). The technique is based on the chemical ionization mass spectrometry (ID-CIMS), where gas-phase molecules react in a drift tube at a few Torr pressure with an appropriate reagent ion to form well-defined product ions, which are detected by a mass spectrometer. To choose reagent ions, we were guided by quantum chemical calculations. We found that a GOM like HgC12 can react quantitatively with many different reagent ions, including SF6–, CO3–, CO2O2–, and HNO3(NO3–), but the latter one will be most useful for the atmospheric detection because it is least susceptible to interference from the air matrix. The current detection limit of the low-pressure CIMS for HgC12 is about 1 part per trillion, using a 1-minute integration time. By utilizing the ambient pressure chemical ionization, this limit can be improved to below 10 parts per quadrillion for direct detection of GOM in the atmosphere.

**R.O.1.6A-6**

**DEVELOPMENT OF AN AUTOMATED METHOD FOR MEASUREMENT OF GASEOUS OXIDIZED MERCURY**

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Given that the only currently available system for measurement of gaseous oxidized mercury (GOM), the Tekran 2537/1130/1135 system, uses KCl-coated denuders that do not accurately quantify GOM concentrations, a method for quantification is needed. In addition, the Tekran system method for measurement of particulate bound mercury (PBM) suffers from artifacts. Recent work has demonstrated that catalytic ion exchange membranes (CEM) are a useful tool for measuring reactive mercury concentrations in air. Reactive Hg includes both PBM and GOM. Here we report on the development of a method that allows for quantifying reactive mercury concentrations at 20 min resolution. This resolution is better than for the Tekran system that has a resolution of 1 to 2 hours. This method involves the use of membranes and a pyrolyzer linked to a Tekran 2537. To develop this method, comparisons were made with the University of Nevada, Reno Reactive Mercury Active System (UNRRMAS_2.0) and a Tekran 2537/1130 system for measurements of gaseous elemental mercury (GEM) and GOM. Preliminary results indicate that the new system – currently called the UNR Automated Reactive Mercury System (UNRARMS) – allows for measurement of GOM at 20 min resolution and that system configuration is important to achieve comparable results between the UNRRMAS_2.0 and UNRARMS systems.
R.O.1.1C-1

ATMOSPHERIC MERCURY MODEL EVALUATION VS. REALISTIC LIMITS OF DETERMINISTIC PREDICTIONS: WHAT IS SUCCESS?

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A typical exercise in the evaluation of atmospheric mercury models is to compare model-predicted concentrations against concentrations measured at specific monitoring sites. In some cases, reasonably good results can be obtained for long-term averages, especially at locations remote from strong emissions sources. However, in the nearfield region (e.g., <100 km) downwind of any significant mercury emissions source, it can be difficult to accurately model the time series of concentrations at any given location, and in particular, to accurately predict the timing and magnitude of significant “plume hits” from nearby sources. This problem can make it very challenging to interpret trends in measurement data. If temporal trends are seen at a given measurement site, it is difficult to assess the extent to which these trends may be due to changes in local and regional emissions sources. This has implications for the evaluation of the Minamata Convention. Ultimately, one of the ways that the Convention will be evaluated will be an assessment of trends in ambient mercury concentrations. But the lack of deterministic ability of models limits our ability to interpret what caused those changes. In this study, we have used the NOAA HYSLIP atmospheric fate and transport model to conduct extensive numerical experiments ground-truthed against ambient measurements. With this methodology, we have investigated key factors that limit the deterministic ability to predicting downwind plume hits. Measurements of speciated mercury and other pollutants at NOAA’s long-term atmospheric monitoring sites near Moss Point, Mississippi (USA) and Beltsville, Maryland (USA) are used to evaluate model results. Uncertainties in emissions, atmospheric chemistry, atmospheric phase partitioning, meteorological parameters (e.g., three-dimensional fields of wind speed, wind direction, and turbulence), plume rise, mixing, and dispersion can all play a role in limiting the ability of a model to accurately predict downwind concentrations. By using many years of hourly data in the analysis, this “big data” approach has yielded important insights that were not apparent from previous studies focusing on a few short-term episodes. This study provides useful information about the relative importance of different physical and chemical uncertainties in affecting model accuracy and important insights into the realistic limits of model success. It is a component of a larger effort at the NOAA Air Resources Laboratory investigating boundary layer transport and mixing processes using tracers of opportunity such as sulfur dioxide, mercury, and other pollutants.

R.O.1.1C-2

QUANTIFYING THE DOWNWARD TREND OF AIR MERCURY IN URBAN CHINA DUE TO REDUCTION OF ANTHROPOGENIC MERCURY EMISSIONS USING A GENERALIZED ADDITIVE MODEL

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Atmospheric mercury is one of the major air pollutants attracting international concern, especially in China where anthropogenic emissions were in high level in this region. The rapidly changing atmospheric mercury emission would have impacts on total gaseous mercury (TGM) in regional scale. Here we investigate TGM concentration from April 2015 to December 2018 to examine the long-term trend and dominant factors of TGM in urban Beijing. The TGM concentrations decrease from 4.61±1.77 ng m⁻³ in 2015 to 2.67±0.97 ng m⁻³ in 2018, with a decreasing trend (Sen’s slope) of -0.44 ng m⁻³ yr⁻¹. The decreasing trend is more pronounced in winter (-0.79 ng m⁻³ yr⁻¹) than in other seasons (-0.50 ~ -0.39 ng m⁻³ yr⁻¹). The CO concentrations also show biggest decline in winter (-0.87 ppm yr⁻¹) comparing to other season (-0.16 ~ -0.06 ppm yr⁻¹), which reflects the synergistic effect of strict anthropogenic emission control policy on TGM during winter. A statistical model named Generalized Additive Model (GAM) is used as a function of meteorological factors to estimate the influence of meteorological condition and emission on TGM. The statistical model represents 47.9% of the variance for the TGM data from 2015 to 2018. The residuals decrease from 0.72 ng m⁻³ in 2015 to -0.45 ng m⁻³ in 2018, which suggests that the decline of anthropogenic emission contribute to 62% of the total decreasing trend due to co-benefit of strict air control policy since 2013.

R.O.1.1C-3

ATMOSPHERIC MERCURY TRENDS IN WESTERN CANADA ARE ON THE RISE

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Total gaseous mercury (TGM) has been measured across Canada at various locations since 1995. Canada is a net recipient of anthropogenic mercury and; thus, long term monitoring and investigation into the transport of mercury into Canada is a government priority. Annual mean concentrations levels from 11 locations in Canada, over various years, range from 1.24 to 3.23 ng m⁻³ with an average of 1.55 ± 0.54 ng m⁻³. The highest concentrations were observed at Flin Flon, Manitoba where a large copper smelter operated for over 40 years and closed in 2010. Not including this location, TGM concentrations in Canadian air range from 1.24 to 1.53 ng m⁻³ (average 1.38 ±0.01 ng m⁻³). This average is significantly lower than those published in 2007 where the country saw an average of 1.58 ng m⁻³. Annual trend analyses of the TGM concentration levels have been published and range from -4.2 to +1.4 % y⁻¹. The trends observed at most locations in Canada reflect the decreases that have been shown at other northern hemisphere background locations. Rates of decline are higher at some sites (more urban or industrially influenced) than others (coastal or Arctic influenced). However, there is a striking difference from what is observed in 2 western Canadian locations than all others in Canada. At Little Fox Lake, Yukon and Whistler, British Columbia an annual average trend of +1.4 and +1.3% y⁻¹, respectively, have been observed. At Little Fox Lake, monthly trends from 2007-2016 are increasing for each month of the year. At Whistler, monthly trends from 2008-2015 are increasing for 7 months, decreasing for 3 months and not significant for 2 months. These increasing trends contrast trends reported for TGM in North America and Asia. In this paper, the understanding of why trends are observed in western Canada are on the rise and whether this trend may continue into the future will be presented.
ATMOSPHERIC METHYLMERCURY: FROM THE OCEAN TO FOG TO BIOACCUMULATION IN COASTAL TERRESTRIAL APEX PREDATORS IN CALIFORNIA USA

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Coastal upwelling of ocean water can result in a sea-air flux of the potent yet highly reactive neurotoxin dimethylmercury. Marine stratus clouds are commonly present over the Pacific Ocean off the coast of California during the seasons when upwelling is active (spring and summer). These clouds act as an efficient absorber of dimethylmercury and also of airborne monomethylmercury that may arise from sea spray. As these clouds advect onto land and deposit water as fog drip, they can transfer significant quantities of methylmercury to terrestrial ecosystems. This talk will describe the research that has been conducted since 2011 to quantify methylmercury in fog and marine stratus clouds, and its possible sources and sinks. An investigation of the mercury burdens in the coastal terrestrial food web will also be presented. These results show that methylmercury concentrations in the California mountain lion, mule deer, and lichen (a deer food) are significantly elevated in samples taken from a fog-inundated coastal forest area versus inland areas with no fog. This suggests that while fog drip is a small portion of the hydrologic inputs, the methylmercury it contains may play a disproportionate role in bioaccumulation of mercury in coastal terrestrial food webs.

MEASUREMENT AND UNDERSTANDING GOM CONCENTRATIONS AND CHEMISTRY FROM SITES IN UTAH, HAWAII, MARYLAND, AND NEVADA, USA.

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From November 2017 to February 2019, the improved University of Nevada-Reno Reactive Mercury Active System (UNRRMASC_2.0) was deployed in Nevada, Utah, Colorado, Maryland, and Hawaii, USA, to test performance and demonstrate robustness and application at a variety of sites. Each of the selected field sites presented a unique opportunity to test the application of the system in locations with different atmospheric chemistry and pollutants, as well as meteorological conditions. The site at Horsepool, Utah is surrounded by oil development activity, with high ozone concentrations and winter inversions. The Maua Loa Observatory on Hawaii is at high elevation and is impacted by the free troposphere. Additionally, we had the opportunity to measure reactive mercury (RM) during the May 2018 Mount Kilauea volcanic eruption. The rural site in Maryland over power plants. The location in Nevada is directly adjacent to a major interstate highway and is exposed to significant mobile source pollution. RM concentrations and chemistry were measured at each location using the UNRRMASC_2.0 at 1-to-week resolution, along with measurement of Tekran Hg concentrations (2537 and/or 1130). Ancillary data collected included ozone, relative humidity, nitrate, and more. Ancillary data were correlated with total RM and Tekran measurements. RM chemistry, as determined by thermal desorption, demonstrated unique profiles and chemistry for each site and changing patterns over space and time. Back trajectories were compiled using NOAA’s HYSPLIT model to determine likely sources of atmospheric Hg at each site per sampling period. The UNRRMASC_2.0 collected more GOM than the Tekran 1130 system during the same time periods and previous years. The UNRRMASC_2.0 system provides an effective method for measuring RM concentrations and chemistry at a variety of field sites.

A NEW PROJECTION OF HISTORICAL ANTHROPOGENIC EMISSIONS OF MERCURY

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An order-of-magnitude projection of historical emissions of mercury due to human industrial activity from 1500 to 1900 is presented, based on the following sets of input: 1) the historical production curve of mercury 2) the losses of mercury during the smelting of cinnabar ore at the main mining sites of Almadén (Spain), Idria (Slovenia), Huanacavaca (Peru) and California (USA) as deduced from historical records 3) the consumption of mercury during the refining of silver and gold, based on historical tax and official sources 4) the conversion of mercury into calomel (mercuric chloride) during the refining of silver ores 5) alternate markets for mercury in the 19c (vermilion, fulminate). The methodology integrates historical production data, the chemistry and physics of silver and gold refining, the reports from historic first-hand observers on emissions from refining and recycling equipment and processes, and a cross-checking of projections within the overall mass balance of production and consumption. It takes into account the major swings observed in the 19c, from the use of mercury for silver refining to smelting, from placer gold to stamp milling to cyanide, and the impact of Russia, Australasia and South Africa as well as Mexico and the U.S.A. as major bullion refining centres. The projection breaks down emissions into mercury sequestered in solid calomel, liquid mercury to the soil and waterways, and direct air emissions of mercury. Smelting of cinnabar ores contributes the majority of direct air emissions of mercury, the refining of gold and silver are secondary sources, and the profile of these three magnitudes is different and their sum lower than what has been proposed under the ‘high’ mining scenario. The methodology avoids the anachronism of equating modern artisanal gold refining practice with historical refining of silver, incorporates the chemical reactions inherent to silver refining with mercury, takes into account the sizeable contribution from the smelting of cinnabar ores, evaluates the impact of gold and silver produced as a by-product of the refining of each other, and is global in geographical scope. Further interpretation of the results will require new research into the lifecycle of calomel in the soil, on the characteristics of the historic depositional footprint of mercury as a function of industrial infrastructure, and the time-lag between immediate and long-term re-emissions of mercury to the environment around smelting and refining sites.

1.7C Sources and cycling of mercury in freshwater ecosystems and oceans

MULTIPLE REGRESSION ANALYSIS AS TOOL TO STUDY INORGANIC MERCURY AND METHYMERCURY BEHAVIOUR IN CONTAMINATED COSTAL ENVIRONMENT

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The Laranjo Bay, situated in the Aveiro Lagoon (Portugal), is among the most contaminated coastal areas with Hg coming from a single upstream source. The export fluxes of inorganic mercury (Hg) and methylmercury (MeHg) from the Laranjo Bay to the rest of the Aveiro Lagoon were estimated to be much higher than the input fluxes from the Hg source and from the main freshwater discharge to the bay. Therefore, resuspension of contaminated sediments was crucial for the
transport of both Hg species. However, there was an enrichment of suspended particles with MeHg, which prompted further investigation of both surface sediments and water.

The concentrations of particulate IHg (IHgPART) in the water depended on the distance to the contamination source and on dilution with downstream particles. Similar processes were evidenced for particulate MeHg (MeHgPART), however, its concentrations increased for particles rich in phaeophytin (Pha). The concentrations of filtered Hg species (MeHgDISS, IHgDISS) increased with Pha concentrations in the water. Multiple regression models are able to depict MeHgPART, IHgDISS and MeHgDISS concentrations with salinity and Pha concentrations exhibiting additive statistical effects and allowing separation of possible addition and removal processes during estuarine mixing. A link between phytoplankton/algae and consumers’ grazing pressure in the contaminated area can be involved to increase concentrations of IHg-DISS and MeHgPART. These processes could lead to suspended particles enriched with MeHg and to the enhancement of IHg and MeHg availability in surface waters and higher transfer to the food web.

Different behaviour of IHg and MeHg in surface sediments was observed based upon multiple regression analysis, including geochemical characteristics of the sediments (fine fraction, concentrations of organic matter and metals) and non-Euclidean distances between sampling points. This data treatment method was valid over the entire concentration range of IHg and MeHg, allowing robust quantitative evaluation with respect to extrapolation. For IHg, there was statistical separation of the dispersion away from the contamination source and of Al concentration in the sediments. The MeHg concentrations followed those of IHg at high concentrations. The geochemical variables, such as concentrations of Ca (marine influence proxy), Mn and organic matter, were necessary to describe the behaviour of MeHg across the whole concentration range. The models for MeHg demonstrated that, close to the mouth of the lagoon, net production of MeHg was higher. In future, multiple regression analysis could be applied to separate environmental processes in contaminated sediments and water.

R.O.1.7C-2

HG POLLUTION IN THE VENICE LAGOON: INTEGRATING MODELING AND OBSERVATIONS TO EXPLORE PAST DYNAMICS AND FUTURE SCENARIOS

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Since 1936, significant amounts of Hg and other pollutants were dumped into the Venice Lagoon (Mediterranean Sea) from an industrial site, which included a chlor-alkali and a zinc smelting plant. Several studies carried out since the late 1970s have assessed pollutants levels and ecological risk, highlighting a critical concern for Hg levels in the lagoon. Due to the persistence of Hg in the environment, the legacy Hg from historical pollution is expected to continue to affect the area in the long run. Moreover, the shallowness of the Venice Lagoon water and the high nutrient load from watershed can trigger seasonal hypoxia and anoxia that favor Hg methylation in the water, increasing the vulnerability of the ecosystem.

In this work, we estimate time-variable industrial emissions of Hg to the lagoon, based on available information about industrial production and technology-dependent emissions factors, as well as the time-variable loading of Hg species from diffuse sources (river, atmospheric deposition, urban wastes). We use estimated Hg inputs to drive a biogeochemical box model and simulate the evolution of Hg species dynamics in the Venice Lagoon for 200 years (1900 – 2100), using observations from previous field investigations as constraints. Future trends of Hg atmospheric deposition are extrapolated from global models to explore alternative scenarios. Given the intense benthic-pelagic coupling in the shallow lagoon, simulations also take into account the changes in anthropogenic activities that have affected sediment dynamics over years, influencing the fate of Hg species in the lagoon.

The model reproduces the observed accumulation of Hg in sediment during the high Hg emissions period and the subsequent redistribution of Hg among boxes due to the erosion and transport of surface sediments. We provide the budget for the lagoon in its present state and possible evolutions of the system under different scenarios of emissions and atmospheric deposition (‘zero emissions’, ‘Hg control’, ‘current trend’, ‘constant emissions’, ‘business as usual’). We estimated about 58 kg/y of Hg and 0.2 kg/y of MeHg exported from the lagoon to the Mediterranean Sea, and about 3 kg/y of Hg0 emitted to the atmosphere for 2019; thus the lagoon accounts for about 2% of Hg input to the Mediterranean Basin. Modeled Hg concentrations in the Venice Lagoon show a general decreasing trend, the rate of which is affected by the atmospheric deposition scenarios.

R.O.1.7C-3

EXAMINING TOTAL MERCURY AND METHYLMERCURY LEVELS ALONG A SALINITY GRADIENT IN A COASTAL WETLAND ECOSYSTEM IN SOUTH CAROLINA, USA

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Sea level rise is gradually leading to salinization of many low-lying coastal wetlands worldwide, such as coastal region throughout the southeastern United States. Salinization can cause degradation of healthy freshwater coastal wetlands (e.g., extensive tree mortality), which can be followed by the development of salt marsh with grass as dominant vegetation. In this study, we examined total mercury (THg) and methylmercury (MeHg) along a salinity gradient in a coastal wetland ecosystem located near Winyah Bay, South Carolina. Specifically, we performed seasonal sampling of surface and subsurface water, sediment, and aquatic biota (e.g., crayfish and dragonfly larvae), analyzed all samples for THg and MeHg, as well dissolved organic carbon (DOC) for water samples. Our initial data on surface water showed that on average degraded wetland (with elevated salinity) had higher aqueous (filtered) levels of THg (~2.5 ng/L) and MeHg (~0.24 ng/L) than both healthy freshwater wetland (THg: 1.8 ng/L and MeHg: 0.12 ng/L) and salt marsh (THg: 1.5 ng/L and MeHg: 0.12 ng/L). However, such differences in THg and MeHg levels could not be explained by differences observed in their DOC levels, as healthy freshwater wetland had the highest DOC levels (23.9 mg/L) as opposed to those in degraded wetland (16.3 mg/L) and salt marsh (8.2 mg/L). Seasonal sampling and sample analyses are still underway, and a complete dataset for one year will be presented and discussed. Thus, our work implies that changes of low-lying freshwater coastal wetlands may have important consequences on Hg biogeochemical cycling, which may ultimately affect the food web uptake of toxic MeHg.

R.O.1.7C-4

BEHAVIOR OF METHYLMERCURY AND TOTAL MERCURY AFTER RESUSPENSION OF CONTAMINATED SEDIMENTS FROM GUANABARA BAY, BRAZIL

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In this study, we examined the behavior of MeHg and total mercury (THg) following resuspension of contaminated sediments from Guanabara Bay, Brazil. We used a multi-box model to simulate the behavior of these elements in the lagoon. We collected water samples from different depths and distances from the shore, and measured THg and MeHg concentrations. The model was able to reproduce the observed behavior of these elements, indicating that resuspension can significantly affect the distribution of Hg in the ecosystem.
The resuspension of contaminated sediments in the water column has been pointed as an important source of dissolved contaminants in historically contaminated estuaries. In southeastern Brazil, dredging activities are made with certain frequency at Guanabara Bay (Rio de Janeiro State), due to harbor activities in port of Rio de Janeiro, where the flow of cargo and cruise ships is intense. While the northwestern / western region of the Bay is recognized as the most impacted of the system, because it receives effluents of Metropolitan Region of Rio de Janeiro State, including a chlor-alkali plant located in the Acari River (affluent of Meriti River). The aim of this study was to assess possible changes on the geochemical behavior of mercury caused by sediment resuspension in two areas of a hypereutrophic estuary (Guanabara bay, Brazil). For the resuspension experiments, approximately 7.5 g of wet sediment was weighted in a 125 mL Erlenmeyer and 100 mL of unfiltered water was added, carried out in six time intervals: 30 min (T1), 1h (T2), 3h (T3), 6h (T4), 12h (T5) and 24h (T6). The total mercury (THg) determination was performed using a portable multifunctional atomic absorption spectrometer coupled to a gas chromatograph (Merx- Brooks). The THg concentrations in Meriti River estuary (MR) before agitation were 13,076.9 ± 7,560 ng g⁻¹. After resuspension, the THg concentrations oscillated, ranging from 11,254.9 ± 8,962.8 ng g⁻¹ (30 min) to 14,375.4 ± 9,695.4 ng g⁻¹ (24 hours). In RJu, THg concentration before resuspension was 50.2 ± 27.9 ng g⁻¹. After resuspension, the concentrations had an increasing tendency, ranging from 87.7 ± 74.6 ng g⁻¹ (after 1 hour) to 166.0 ± 136.7 ng g⁻¹ (after 12 hours). MeHg concentrations in MR were 11 times higher than those found in Rio de Janeiro Harbor (RJu). However the percentage of MeHg is 46 times higher in RJu. The increase on the organic matter content at RJu after resuspension can be responsible by high MeHg percentages, affecting possibly the sediment’s toxicity. Other hypothesis is that the sulfides oxidation after resuspension could release the Hg inorganic ions and those were assimilated by bacteria and transformed into MeHg. The resuspension was able to induce changes on chemical form of Hg in sediment, mainly in RJu, increasing, potentially the bioavailability.

R.O.1.7C-5

MERCURY CYCLING IN A PORTUGUESE MESOTIDAL ECOSYSTEM, TAGUS ESTUARY: WATER COLUMN CHEMISTRY AND TRANSPORT.

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The data set emphasizes the importance of examining the complex site-to-site variation within a system, in order to understand estuary wide mercury (Hg) and methylmercury (MM-Hg) dynamics, and demonstrates that processes driving MM-Hg fate may be distinct in different regions of the same system. Tagus estuary is one of the largest estuaries in Europe with several longitudinal channels in the central bay. Sampling campaigns in North Channel (NC) and in adjacent areas were performed bimonthly during one year. Samples were collected covered different tide conditions, to better understand MM-Hg and Hg transport and fate in the water column. Also a tidal cycle of 13 hours was made with samples collected hourly. Mercury, MM-Hg, organic carbon in both dissolved and particulate fractions, salinity and other interpretative parameters were determined.

Tidal induced resuspension processes produced large temporal variations in particulate and dissolved Hg and MM-Hg in the water column. Highest concentrations of particulate and dissolved MM-Hg were observed in NC in bottom waters and in the warmest months. The MM-Hg distribution coefficients between particulate and dissolved fractions were mainly influenced by particulate matter and dissolved organic carbon. The values were slightly higher in summer than in winter and in NC. Overall results established that the tidal effect is a main driver on the transport and fate of Hg and MM-Hg from NC to outer estuarine areas, evidenced by the export of the Hg species from NC to the upstream station in high tide and to the downstream one in low tide. Furthermore, the low hydrodynamic conditions of NC, with a very narrow width, low depth and large water residence time, favored the retention of Hg species and consequently their in situ physico-chemical transformations. The natural methylation processes in the sediments are important sources of MM-Hg in the water column of Tagus estuary, but the potential influence of phytoplankton biomass is likewise significant, especially in the middle and lower estuarine zones, where an increment of MM-Hg was observed with increasing chlorophyll a concentrations. Besides, the % of particulate MM-Hg exhibited an increase with the potentially active biomass, suggesting the preferential uptake or sorption of MM-Hg by living phytoplankton species.

Consequently, NC may be considered a source of Hg and MM-Hg to the outer estuary however, also the south shore of the estuary seems to have a considerable contribution of Hg to the water column probably due to additional anthropogenic sources from industrial activities.

R.O.1.7C-6

LIGNIN BIOMARKERS AS TRACERS OF MERCURY SOURCES IN SHELF AND CONTINENTAL SLOPE, CAMPOS BASIN-RJ BRAZIL

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The TOM (terrestrial organic matter) plays a major role in the transport of contaminants from the watershed to the global marine systems. In this context, contaminants as mercury (Hg) can be transported to the ocean, considering that the biogeochemical cycling is closely linked to the organic matter (OM). The measurement of spatial and temporal variations of Hg isotope ratios in sediments may enable source identification and tracking of environmental processes. Our objective is to characterize the role of TOM in the transfer of Hg to Campos Basin RJ-Brazil, considering two areas continental shelf and in 9 transects (25-3000m water depth), in particular the relationship between the Hg and the lignin as an organic geochemical tracer in surface sediments (0-2cm) during the transport from continent to the ocean. We establish also the mercury isotope ratios of three transects. The values of organic carbon (OC), δ13C, lignin yields and THg in surface sediments varied from 0.06% to 1.98%, -27.6 to -21.2 ‰, 48 to 1289 µg/100mg OC and 1.64 to 51.60 ng g⁻¹. Distinct differences in Hg isotope ratio signatures were observed, suggesting that the two regions were impacted by different sources of Hg. The shelf showed more negative δ202Hg and δ199Hg values ranging from -0.59 to -2.19% and from -0.76 to 0.08%, respectively. In contrast, the slope exhibited δ202Hg values from -0.29 to -1.82% and δ199Hg values from -0.23 to 0.09%. Isotope ratios observed in the shelf region (D an I transects) are similar to Hg ratios commonly associated with plants and vegetation and very comparable to those detected in the estuary and adjoining mangrove forest, which suggests that Hg exported from rivers may be the dominating source of Hg in near coastal regions along the northern part of the shelf. The positive correlation between total Hg and lignin in shelf region may indicate that the TOM through the proxy lignin can be an important geochemical support for the Hg in the transport from land to the continental shelf. On the other hand, the slope region displayed a negative or lack of correlation between both variables. These findings stress the need to take action to properly managing watersheds in the sense of limiting massive remobilization of fresh soil organic matter after logging or agriculture practices in order to limit terrigenous mercury inputs to Campos Basin.
1.2D Biogeochemical cycling of mercury in the aquatic ecosystems

**R.O.1.2D-1**

INTER- AND INTRA-SPECIES DIFFERENCES IN EGG MERCURY CONCENTRATIONS IN FOUR SEABIRD SPECIES IN ATLANTIC CANADA AND ASSOCIATIONS WITH STABLE SULPHUR, NITROGEN, AND CARBON ISOTOPE RATIOS

BURGESS, Neill

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The eggs of four seabird species have been used in Atlantic Canada as biomarkers of contaminant trends in marine ecosystems since the 1970s. The four seabirds were selected to monitor contaminants in different marine food webs: i) inshore – double-crested cormorant (Phalacrocorax auritus) and herring gull (Larus argentatus), ii) on the continental shelf – Atlantic puffin (Fratercula arctica), and iii) beyond the continental shelf – Leach’s storm-petrel (Oceanodroma leucorhoa = Hydrobatides leucorhous). In this study, we assessed the differences in egg mercury (Hg) concentrations between the four seabird species and between breeding colonies within species in 2016. We also examined the associations between Hg concentrations and stable sulphur (δ34S), nitrogen (δ15N), and carbon (δ13C) isotopes ratios in seabird eggs, across the four species and within species. In 2016, we collected 15 eggs from each species at each breeding colony -- at 3 sites for cormorants, 5 sites for gulls, 4 sites for puffins, and 2 sites for storm-petrels across Atlantic Canada. Analysis of covariance (ANCOVA) of Hg and isotope data from all four species combined revealed significant differences between species in log-transformed egg Hg concentrations and significant associations between egg Hg and stable sulphur, carbon, and nitrogen isotope ratios. Geometric means of egg Hg concentrations were significantly different among all four species: Leach’s storm-petrels > double-crested cormorants > Atlantic puffins > herring gulls. Spatial differences in geometric means of egg Hg levels (between breeding colonies) within species were found for all four seabird species. However, associations between egg Hg concentrations and stable isotopes ratios within species were inconsistent across the four seabirds. These associations were strongest in herring gulls (δ34S, δ15N & δ13C) and Leach’s storm-petrels (δ34S), less so in double-crested cormorants (δ15N & δ13C), and absent in Atlantic puffins. These associations suggest that variation in egg Hg concentrations is driven by differences in diet in herring gulls and storm-petrels, less so in cormorants, and very little in puffins. While trophic level had some influence on egg Hg concentrations, the seabird with the highest egg Hg levels (Leach’s storm-petrel) did not feed at the highest trophic level. Rather, their elevated egg Hg levels were strongly associated with δ34S, suggesting that Hg methylation by sulphate-reducing bacteria may be enhanced in their mesopelagic food webs.

**R.O.1.2D-2**

MERCURY CONTAMINATION IN AQUATIC SYSTEMS IN THE BRAZILIAN EASTERN AMAZON

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Mercury (Hg) contamination is a long-standing environmental and social problem, notably in the Amazon. Human activities have increased the global circulation of Hg and the artisanal small-scale gold mining sector is the main source of Hg emissions in Latin America. In the Amazon, traditional communities and indigenous people are highly exposed to Hg compounds due to the high consumption of mercury-contaminated fish. To our knowledge, this is the first study comparing levels of Hg contamination between estuary and inland areas in the Amazon. Between August 2017 and May 2018, samples from 428 fish from 45 different species were collected in five zones within and around protected areas in the Amapá state – Eastern Amazon, including three estuarine and two inland water areas. Total-mercury analysis was carried out using Cold Vapor Atomic Fluorescence Spectrometry. The threshold adopted as health safety limit for fish consumption was 0.5 µg.g⁻¹ (World Health Organization). Two-sample Kolmogorov-Smirnov test was used to compare the median results from estuary and inland areas. The association between fish contamination and zones was confirmed by logistic regression using odds ratio. All measures showed 95% confidence intervals. The median of Hg contamination for fish sampled in inland areas was 0.580 µg.g⁻¹ in carnivorous specimens (n=131), 0.045 µg.g⁻¹ in herbivorous (n=15), and 0.680 µg.g⁻¹ in omnivorous (n=33). While in estuarine areas, the median Hg level was 0.165 µg.g⁻¹ for carnivorous (n=194), 0.019 µg.g⁻¹ for herbivorous (n=5), 0.290 µg.g⁻¹ for omnivorous (n=15) and 0.044 µg.g⁻¹ for detritivorous (n=35). Surprisingly, the median of Hg levels between carnivorous and omnivorous species had no statistical differences in both aquatic systems (p-value=0.222, and p-value=0.240; respectively). The prevalence of Hg contamination was 28.7% for all samples, while in estuaries it was 5.2%, and in inland areas it was 61.5% (p-value<0.001). Therefore, chances of a fish sample presenting Hg levels ≥ 0.5 µg.g⁻¹ in inland areas was 29 times higher (95%CI 15.3-54.6) than in estuarine areas. Our study suggests the existence of regional patterns regarding Hg levels related to differences and dynamics between inland and estuarine areas. Even in remote legally protected areas in the Eastern Amazon, high levels of mercury were found in different species and trophic levels of fish, evidencing higher risk of Hg contamination for fish consumers from inland waters in the Amazon.

**R.O.1.2D-3**

ACCUMULATING MERCURY AND METHYLMERCURY BURDENS IN WATERSHEDS IMPACTED BY OIL SANDS POLLUTION

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(4) University of Michigan
(5) University of Waterloo

Bitumen mining and upgrading in Northeastern Alberta, Canada releases toxic pollutants into the atmosphere, including mercury (Hg) and methylmercury (MeHg). This Hg and MeHg is then deposited to the surrounding landscape: however, the fate of these contaminants remains unknown. Here we compare snowpack chemistry with high-frequency measurements of river water quality across six watersheds (five impacted by oil sands development and one unimpacted) and spanning three hydrologic years (2012–2014). Snowpack Hg and MeHg loads scaled with watershed size, but area normalized snowpack loads were highest near oil sands operations. Snowpacks samples collected near industry also had a unique Hg stable isotopic composition relative to snowpack samples collected further away. River water Hg concentrations and loads tracked discharge and tended to be higher downstream of mining operations, while MeHg concentrations and loads increased through the summer, reflecting peak summer MeHg production rates. Except in the reference watershed, snowpack Hg and MeHg loads equaled or exceeded the amount of Hg and MeHg exported during freshet, and in some cases, the entire hydrologic year. This suggests landscapes across the oil sands region, which are dominated by wetlands and other shallow-water systems, are accumulating Hg and MeHg. The loading of Hg and MeHg...
to these environments will ultimately increase MeHg burdens across the region and particularly within downstream environments. Finally, Hg stable isotopes are being used to potentially fingerprint the input of industry-derived Hg to the aquatic ecosystem.

R.O.1.2D-4

THE FENNOSCANDIAN FISH MERCURY DATABASE: SPATIAL PATTERNS AND TEMPORAL TRENDS IN RELATION TO SOURCES, DEPOSITION, LAKE MORPHOMETRY AND CATCHMENT PROPERTIES

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Mercury (Hg) contamination in freshwater fish is a severe environmental problem throughout the world, including Fennoscandia (Norway, Sweden, Finland, and Russian Murmansk area). The Fennoscandian database demonstrate consistent declines of Hg in freshwater fish from boreal and subarctic Fennoscandia, covering large temporal (1965-2015) and spatial (55°-70°N) gradients. The database contains 54560 fish entries (n: pike>>perch>>brown trout>>roach>>Arctic char) from 3132 lakes. 74% of the lakes did not meet the 0.5 ppm limit to protect human health. However, after 2000 only 25% of the lakes exceeded this level, indicating improved environmental status.

Fish Hg were related to predominant sources of Hg for the lakes, i.e. local point industrial sources (point source lakes) and long-range atmospherically transported Hg (LRTAP lakes, referring to the Convention on Long-Range Transboundary Air Pollution, CLRTAP). In point source lakes, pike and perch Hg concentrations were significantly higher between 1965 and 1990 (0.69±0.10 and 0.47±0.12 ppm, respectively) compared to values after 1995 (0.55±0.14 and 0.21±0.03 ppm, respectively), likely an effect of implemented reduction measures. In LRTAP lakes, consistent Hg declines (3-7%/y) per year) were found for perch and pike in boreal and subarctic Fennoscandia, indicating common environmental controls for these regions. Fish Hg in LRTAP lakes showed minimal declines with latitude, suggesting that drivers affected by temperature, such as for example slower growth, counteracted Hg loading and may elevate biomagnification in food webs. The lakes in the Fennoscandian fish database span large differences in lake (<0.2 – 1900 km2) and catchment areas (<10 – >15000 km2), and we modelled effects of catchment morphology on spatial patterns and temporal trends of fish Hg concentrations. Variables added to the models included catchment parameters (area, land-use types, human population density), deposition (Hg and sulphur), lake (area, depth, elevation) and climate (air temperature, precipitation). We show robust tests of hypotheses on effects of these drivers on fish Hg patterns and trends. Since absence of data from the same lakes over time leads to confusin- ing temporal patterns drawn from spatial variation, we investigated a subset of lakes (n=25) in more detail. The lakes, located along a north-south gradient in Fennoscandia, have been subject to varying degree of burning and climate warming, enabling us to test hypotheses on factors driving Hg levels in fish. Temporal trends were identified using a covariance analysis, where explanatory variables included season, year, fish morphology and stable isotopes (δ15N and δ13C).

R.O.1.2D-6

PERiphyton and fish MERCURY in the Florida Everglades

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Mercury (Hg) is recognized as one of the major water quality concerns in the Florida Everglades. Elevated Hg has been frequently detected in fish, birds, and other animals of the Everglades since 1980s, promoting the long-term Hg studies in this system. However, there is still a lack of knowledge on the long-term variation in fish Hg in this ecosystem and its controlling factors. The changes in Hg atmospheric deposition and the alteration in ecosystem properties are deemed to be the two most important reasons for the temporal variations in fish Hg concentrations. The ecosystem of the Everglades has been greatly changed since the launch of the Comprehensive Everglades Restoration Plan (CERP) in 2000. In this study, the variation in mosquitofish Hg concentrations in the past twenty years was investigated using the EPA RE-MAP data from 1995-2014. A dramatic decline in mosquitofish Hg was observed from 1995 to 2014. The decreasing rate in dry season (~7%/y) was higher than that in wet season (~4%/y). By analyzing the Mercury Deposition Network (MDN) data from 1996 to 2015, negligible change was observed on the wet deposition of Hg in the Everglades. Previous studies also showed a relative constant concentration of GEM in Florida in recent years. These results suggest that the emission of Hg into the Everglades should be stable in the past twenty years. This opinion was further supported by the minor changes in water and sediment THg concentrations in the Everglades from 1995 to 2014. Therefore,
the decrease in mosquitofish Hg should not be due to the change in the atmospheric deposition of Hg in the Everglades. MeHg is the major form of Hg specie in mosquitofish. No significant change in MeHg was detected in the sediment of the Everglades; however, MeHg in the water and periphyton decreased dramatically during this period. The decrease in periphyton and water MeHg could be an explanation for the decrease in mosquitofish Hg. Phosphorus and sulfate in water showed a significant decreasing trend in the Everglades in the past twenty years, attributed to the implementation of the CERP project. Phosphorus is expected to significantly affect the biomass and composition of periphyton while sulfate is one of the necessary reactants for Hg methylation. The decrease in both substances in Everglades water may inhibit the production of MeHg by periphyton, subsequently causing the decrease in mosquitofish Hg in the Everglades.

2.8A Ecotoxicology and risk assessment of mercury exposure to fish and wildlife

SHORT- AND LONG-TERM EFFECTS OF ENVIRONMENTAL MERCURY EXPOSURE ON THREE-SPIINED STICKLEBACK (GASTEROSTEUS ACULEATUS) POPULATIONS

DELAHAUT, Vyshal; CALBOLI, Federico; VOLCKAERT, Filip; DE BOECK, Gudrun

A multitude of anthropogenic activities have left a legacy of mercury pollution in the region of Flanders (Belgium). As a consequence, mercury levels in certain aquatic habitats are currently still exceeding environmentally safe limits. The three-spine stickleback is a well-known model species in environmental monitoring and evolutionary biology. It is a fish species that is inhabiting most of the low-land rivers in Flanders, which makes it a promising sentinel species for environmental monitoring and risk assessment. The overall goal of our research is to identify how stickleback populations, being exposed for multiple generations to elevated Hg-levels, developed strategies to increase their success of survival. In a first study we identified 21 stickleback populations distributed all over the Scheldt- and Meuse basin. The degree of mercury exposure was characterized, and each population was genotyped by sequencing. The results were combined in a genome wide association study (GWAS), in order to identify single nucleotide polymorphisms (SNPs) that potentially have played a role in adaptation to mercury. In a second study, invertebrate samples were taking at 3 unpolluted and 3 polluted locations. Additionally, a suite of biochemical and organismal endpoints was tested to identify biomarkers that correlate robustly with environmental mercury contamination. A wide variation of mercury accumulation was observed between the 21 distinct stickleback population, ranging from 18.4 ± 2.3 ng/g DW to 374.2 ± 45.5 ng/g DW and there was a significant correlation between length and Hg-level in the muscle tissue. Hepatic enzyme activities and metabolites related to oxidative stress pathways were elevated in those populations which are continuously being exposed to higher mercury levels in their diet. The GWAS resulted in 2 SNPs that were significantly associated with increased mercury levels measured in the fish. No genes were annotated at the exact position of these SNPs in the genome. However, potentially relevant causal genes were found down- and upstream of the particular locus. Additionally, alignments with genomes of other species did result in sequences of known genes. It is currently being investigated whether this is of any significance or not, and what the role of the mutation might be.

MERCURY LEVELS IN BIRDS FROM LAS ORQUIDEAS NATIONAL NATURAL PARK, COLOMBIA

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(1)University of Cartagena
(2)LAS ORQUIDEAS NATIONAL PARK

Mercury (Hg) is a toxic heavy metal widely found in wildlife. The importance of Hg resides in its capacity for accumulation and biomagnification generating adverse effects on many species. Artisanal gold mining activities release substantial quantities of this metal, contaminating different matrices such as water, soil, plants and animals, among others. To evaluate the impact of gold mining carried out near Las Orquideas National Natural Park (Colombia), 37 bird species were collected in two sites within the Park, at the municipalities of Abriaquí and Frontino, measuring total Hg levels (T-Hg) in feathers. The mean concentration of T-Hg in bird feathers from sampling sites was 0.84 ± 0.05 μg/g fw. Differences between species were found according to diet habits of the birds. Total Hg levels were greater on insectivorous (1.00 ± 0.08 μg/g fw), followed by nectarivorous (0.73 ± 0.07 μg/g fw) and frugivorous (0.57 ± 0.09 μg/g fw) species. These Hg levels were greater than those found in feathers from Penelope perspicax (0.53 ± 0.03 μg/g fw), a frugivorous species living at the Otún Quimbaya Fauna and Flora Sanctuary, a forest without known gold mining. These data suggest birds in the Las Orquideas National Park are bioaccumulating Hg, perhaps not only from gold mining, with concentrations dependent on trophic guild. The effects of Hg exposure in studied birds are not known, and additional research must be conducted to characterize possible negative outcomes from Hg exposure in these organisms. Unicartagena (2017-2019), Colciencias, 647-2014.

FACTORS INFLUENCING HG EXPOSURE IN TWO SUBANTARCTIC SYMPATRIC SEABIRDS, THE GIANT PETRELS

BUSTAMANTE, Paco; THOMAS, Perronno; JÉRÔME, Fort; CHRIS-TOPHE, Barraud; KARINE, Delord; CHEREL, Yves

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As they integrate Hg, feathers of seabirds constitute a relevant tissue to monitor contamination of marine environment at large spatial scales. It is now clearly established that high trophic level species display the highest concentrations as a consequence of Hg bioamplification, diet and foraging habitat playing a major role in the exposure. However, very little is known about the factor influencing Hg exposure in very similar species like the Northern and Southern giant petrels. Indeed, these two species are sympatric breeders in the subantarctic area. They are very close both morphologically and ecologically but show foraging segregation between males and females within each species and also among species. Here, we examined the significance of various factors (species, sex, feeding habitats [513C] and trophic level [815N]) on Hg concentrations in the feathers of Northern and Southern giant petrels breeding at the Southern Indian Ocean French Territories (Crozet and Kerguelen Archipelagos). 4 feathers were analysed per birds with 15 Northern and 14 southern giant petrels (9:6 and 8:6 males and females, respectively) from Crozet and 18 Northern giant petrels (8:10 males and females) from Kerguelen. At Crozet, mean Hg concentrations varied widely (10-fold) in each species between individuals, from 4.08 to 32.86 μg/g-1 and 4.46 to 43.26 μg/g-1 with means ± SD of 14.03 ± 6.81 μg/g-1 to 14.47 ± 7.48 μg/g-1 in the Southern and the Northern giant petrels, respectively. At Kerguelen, Hg concentrations in the Northern giant petrel range from 7.99 to 51.93 μg/g-1 with a mean ± SD of 18.86 ± 5.35 μg/g-1. No significant difference due to sex
was found. In both species, Hg concentrations decreased with increasing latitude (using δ13C as a proxy) and they increased with trophic level (using δ15N as a proxy) as a consequence of Hg biomagnification along the food webs. The present study shows that ecological segregation observed during the reproduction period between males and females and between each species is not reflected by Hg feather concentrations, suggesting such a segregation is limited during this period.

R.O.2.8A-4

SPATIAL PATTERNS OF EXPOSURE TO MERCURY IN BOREAL SONGBIRDS: COMBINING FEATHER MERCURY AND STABLE ISOTOPE (Δ2H) MEASUREMENTS.

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Migratory songbirds breeding in the Canadian boreal forests are exposed to both naturally occurring and anthropogenic Hg sources. Several species are in decline and recent concern over links between Hg burden and migratory success have focused attention on Hg exposure. However, a large proportion of breeding areas are remote and without easy access, making direct Hg measurement in individuals difficult. We assayed feathers for total Hg concentration near breeding sites. We assayed feathers for total Hg concentration at four CMMN stations that were grown on or adjacent to breeding locations, suggesting such a segregation is limited during this period.

R.O.2.8A-5

THE INFLUENCE OF ENVIRONMENTAL AND BIOLOGICAL FACTORS ON METHYLMERCURY BIOMAGNIFICATION IN AQUATIC ECOSYSTEMS.

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The majority of fish consumption advisories in the US and Canada are due in part to high methylmercury contamination of fish, resulting in over a million river miles under advisory. Methylmercury incorporation into fish muscle tissue is largely the result of biomagnification, and has been the subject of considerable study in recent decades. The majority of research on methylmercury biomagnification has been conducted in lakes and large river systems, whereas small stream environments are understudied. Examining mercury biomagnification in these small, dynamic systems is ideal for understanding mercury dynamics in aquatic food webs. Previous investigations of the Red Deer River, Canada, have demonstrated mercury levels in the water which often exceed chronic and acute guidelines for the protection of aquatic life. However, many environmental factors, in addition to diet and age, can influence methylmercury biomagnification from the water column to consumer organs. In this study, we examine the influence of environmental factors such as primary productivity, stream pH, dissolved organic carbon and available dissolved methylmercury on fish mercury levels. Additionally, contaminant analysis is coupled with food web tracers (13C and 15N) to understand biomagnification. In 2017, fish and invertebrates were collected from four tributary streams in the Red Deer River watershed of Alberta, Canada. Fish muscle tissue was analyzed for total mercury, and otoliths were examined to estimate fish age. Stable carbon and nitrogen isotope analysis was conducted on both fish and invertebrate tissue to examine aquatic food web structure. Water quality data was accessed from long term river network monitoring stations managed by the government of Alberta. Both environmental and biological factors will be modelled to understand the primary drivers of mercury biomagnification in aquatic ecosystems. This study provides a unique opportunity to combine data from long-term environmental monitoring, metal biological analysis to inform our understanding of methylmercury biomagnification. The results of this study will provide an important contribution to our knowledge of bioaccumulation dynamics in aquatic ecosystems.

R.O.2.8A-6

TOXICOLOGICAL AND HISTOLOGICAL EFFECTS OF MERCURY CYANIDE AND SODIUM CYANIDE IN ZEBRA-FISH (DANIO RERIO).

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Mercury amalgamation is carried out by 16 to 20 million artisanal and small-scale gold miners in more than 70 countries. Worldwide miners take their ores to be processed by centers using amalgamation where they must leave their Hg-contaminated tailings as payment for the services. These tailings are then processed by cyanidation by the owners of the processing centers. Mercury-cyanide is formed and dumped into the local drainages as well as large amounts of free cyanide. However, data on cyanide-mercury interaction and the formation/dissociation of the mercury cyanide complex (Hg(CN)2) are very scarce. In this work, we investigated the impact of free cyanide and the bioavailability of mercury to zebra-fish (Danio rerio) when added as Hg(CN)2. In aquariums with pure mercury cyanide or sodium cyanide ranging from 0.05 mg/L to 0.60 mg/L, we found a LD50 of 0.24 mg/L for NaCN and a LD50 of 0.14 mg/L for Hg(CN)2. In the Hg(CN)2 experiment, free cyanide levels ranged from 0.05 mg/L to 0.228 mg/L, a significant increase compared to the control (0.002 mg/L). Fish exposed to Hg(CN)2 showed total mercury levels in muscle ranging from 7.9 ppm to 11 ppm, significantly higher than the controls (0.2 ppm). Our results indicate that Hg(CN)2 is readily dissociated and presents higher toxicity than NaCN to D. rerio. Data on THg in kidney, MeHg in muscle and kidney and on the histological effects of both cyanides on D. rerio tissues will also be presented.

3.2 Treatment of Hg Containing Wastes

R.O.3.2.1

SOURCES AND TREATMENT OF MERCURY WASTES FROM THE GAS INDUSTRY.

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For political reasons, mercury from the oil and gas industry is not mentioned in the Minamata Convention. However, this industry remains a major source of mercury waste and emissions, and it is time to shine a spotlight on the quantities of waste generated, and the treatment methods currently used (or not) in the major gas fields. This is especially
important as major new gas fields with significant mercury (and radiative) contamination are coming online in western Australia. The nine countries (Indonesia, Malaysia, Thailand, Australia, Myanmar, Vietnam, Brunei, Cambodia, Qatar) responsible for over 90% of the mercury waste generated (primarily adsorbents/catalysts and sludges) are targeted. The quantities of mercury waste generated by each country are identified, as well as the countries’ current waste disposal practices, some of which are notably substandard. In other cases, contrary to the prescriptions of the Minamata Convention with regard to "by-product" mercury, some operators are recovering mercury from the gas wastes for resale on the open market. Not least, this research also relates to Article 3, para. 3(a), of the Minamata Convention, which states: “Countries need to report on stocks exceeding 50 metric tons (MT), and mercury supply-generating stocks exceeding 10 MT/yr.” Some gas companies are not currently aware that they should be reporting their mercury supply-generating stocks. The paper concludes with an overview of the existing methods for responsibly dealing with mercury (including radioactive mercury) wastes from the gas industry, which are ignored by some companies only because of the added cost. The diffusion of this information to an international audience will help to pressure industry to implement responsible waste management practices, and will also provide researchers with improved data for the calculation of mercury emissions linked to gas production.

R.O.3.2-3

METHYLMERCURY RETENTION IN A LOW-LEVEL RADIOACTIVE CEMENT-SLAG-FLY ASH WASTE FORM

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(1) Savannah River National Laboratory

Mercury is a contaminant of concern in Savannah River Site (SRS) high level waste (HLW). For five decades elemental mercury was used in the catalytic dissolution of aluminum cladding from the enriched-alloy uranium recovery process. Over 60,000 kg of mercury are now distributed in the SRS HLW tanks. The mercury speciation in the liquid waste streams resulting from conditioning HLW sludge for vitrification and in the decontaminated low activity sodium salt solution removed from the tanks was initially thought to be primarily ionic with a minor amount of elemental mercury. Recent sampling detected organic mercury, primarily methylmercury, Hg(CH3)+ (MeHg+), and a trace amount of ethylmercury (EtHg) in these streams in addition to the ionic and elemental forms. The objective of this work was to identify the fate of the organic mercury in saltstone, a waste form containing Portland cement, slag cement, and Class F fly ash. This information is to assure regulatory compliance for disposal and to identify opportunities to enhance the waste form performance. X-ray diffraction and scanning electron microscopy/energy dispersive x-ray analysis results indicate that the MeHg+ reacts with sulfide in the cementitious reagents to form nanoparticles of β-HgS, meta cinnabar. The slag component of the cementitious reagents is the source of the sulfide which releases during hydration. HgS nanoparticles suggest great affinity between Hg and S and rapid reaction kinetics. The metacinnabar solubility product and is very low, pKsp = 53. Consequently, β-HgS is not expected to be solubilized by the TCLP extraction fluid, saltstone pore solution, or leachate. Complete reaction of the MeHg+ with S2- was expected. However, results indicate that leachates contain trace amounts of MeHg+. Incomplete reaction of organic Hg in saltstone may be the result of: (1) unknown side reactions, (2) depletion of sulfide ions in the waste form, (3) inaccessibility of sulfide due to reaction rims around the slag particles, i.e., slow equilibrium kinetics, and/or (4) formation of other Hg phases which are more soluble.

Determination of the reaction pathway and fate of the methyl group is currently in progress. One of many possible reactions is shown in Equation 1. Methane, CH4, was detected in a concurrent study to evaluate thermolytic hydrogen generation rate of saltstone containing Tank 50 salt solution containing organic mercury (e.g., MeHg(OH)).

Equation 1: CH3Hg(OH) + S2- → HgS + CH4 + ½ O2

Where sulfide ion, S2-, is provided by hydration of the slag.

R.O.3.2-4

WHERE DID IT GO? AN ASSESSMENT OF MERCURY SOURCES AND SINKS IN ARTISANAL AND SMALL-SCALE GOLD MINING IN COLOMBIA

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Artisanal and small-scale gold mining (ASGM) represents approximately 72% of the mining sector in Colombia and produces up to 86% of the country’s gold (Ministerio de Minas y Energia, 2014). The ASGM sector in Colombia is generally characterized by a lack of long-term planning and rudimentary technology and releases large concentrations of mercury into the environment. In 2013, Colombia signed the Minamata Convention, and in July 2017, they implemented a ban on importing and using mercury; however, mercury use continues to be pervasive in ASGM operations. In light of the ban and the stricter controls on mercury, government officials are growing increasingly concerned that artisanal and small-scale miners will begin to “mine” their tailings for...
mercury so they can reuse it in mineral processing systems or sell it in illegal markets. Although the government has begun to identify potential ways to address this issue, there is little to no data on exactly how much mercury is being released into the environment and in what form (i.e. vapor, disposed of in water bodies). This paper reports on a study conducted at various ASM sites in the Antioquia department. Through mercury mass-balances, the sources and sinks of mercury throughout ASM are quantified. These data enable a more scientific understanding of mercury use and its disposal in ASM processing systems, and can inform future research and regulatory approaches aimed at addressing mercury emissions from ASM.

R.O.3.2-5

DEVELOPMENT OF STABILIZATION TECHNOLOGY FOR WASTE INCINERATION FACILITIES USING CHELATE

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Minamata Convention on mercury covers three types of mercury waste: mercury consisting waste, mercury containing waste and mercury contaminated waste. Mercury contaminated waste is generated as various types and forms from industrial facilities, which is fly ash generated from waste incineration facilities. Stabilization of fly ash contaminated by mercury was carried out using EDTA and Na2S. The evaluation for the stabilized products was conducted using a 5 step sequential extraction procedure (SEP). EDTA and Na2S are functioning as stabilized agents by showing more fraction of mercury extracting out in later steps of SEP. The best results were shown when both agents were used as stabilization materials. Both EDTA and Na2S were applied, the ratios leaching at by steps F1, F2 and F3 decreased and the ratio leaching at by steps F4 and F5 increased. From the results, it is considered to be safe enough that the unstable forms of mercury compound may be converted to stable form to be disposed in landfill.

R.O.3.2-6

CALCIUM ALGINATE-MESOPOROUS ACTIVATED CARBON COMPOSITE BEADS AS A NOVEL ADSORBENT FOR ELEMENTAL MERCURY FROM NATURAL GAS

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Mercury is one of the most harmful metals in nature, as a result of its high toxicity, high instability, and its potential bioaccumulation. It is well known that the elemental mercury is more difficult to capture due to its higher volatility, chemical inertness, and insolubility in water. Several methods have been used to remove Hg⁰ from the gas streams e.g. adsorption, oxidation-reduction, photochemical oxidation and chemical sedimentation methods. However, the adsorption has been considered as economically feasible technique for removal of the mercury from different matrices in the industry. In this work, high surface area mesoporous activated carbon-Calcium alginate (mAC–Ca–Alg) beads were successfully fabricated and then investigated as a novel adsorbent for Hg⁰ from natural gas. The formulation of sodium alginate and mAC in calcium chloride bath allowed the production of stiff and spherical mAC–Ca–Alg beads with good permeability (such merits are attainable only by the composite approach in comparison with alginate or mAC alone). The produced mAC–Ca–Alg composite beads (about 150 µm in diameter) were characterized by means of SEM, N₂-sorption analysis, TGA, XRD, and FTIR. The adsorption of elemental mercury was studied by using the mercury permeation device (model 450, VICI Metronics, USA) as the source of Hg⁰ vapor. Moreover, inlet and outlet Hg⁰ concentrations were measured by Mercury Analyzer (WA-4, Nippon instrument Co., Japan). The influence of various factors (such as flow rate, initial Hg⁰ concentrations and temperature) on the adsorption behavior was investigated. Maximum adsorption capacity was 894.3 µg/g at a flow rate 250 mL/min, temperature 25 °C and 500 µg/Nm³ as Hg⁰ concentration with breakthrough time (tb) and exhaustion time (te) of 6 and 25 h, respectively. The adsorption kinetics were studied with the Lagergren first- and pseudo-second-order kinetic models as well as the intraparticle diffusion model. The adsorption mechanisms on the systems Hg⁰–composite (AC–Ca–Alg) follow pseudo-second-order kinetics. Moreover, Yoon–Nelson and Thomas models best described the experimental Hg⁰ breakthrough curve model which R²> 0.95. The findings reveal the feasibility of AC-alginate beads composite to be used as a potential and low cost adsorbent for removing Hg⁰ from natural gas, by not only reducing the environmental problems associated with gaseous mercury emissions but also by making the process more economical and simply.

1.11A Methylation and demethylation of mercury – session to honor work of the late Dr. Mark Hines

R.O.1.11A-1

AN OVERVIEW OF OUR UNDERSTANDING OF HG METHYLATION AND MEHg DEMETHYLATION – PART 1

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This talk will provide a critical review of the processes and organisms that contribute to Hg methylation and methylmercury (MeHg) demethylation, and assess progress toward the goal of modeling these reactions in the environment. We will explore how the discovery of hgcAB, a gene pair that codes for microbial methylation, has advanced knowledge of the diversity of Hg-methylators, including unculturative putative methylators outside the Deltaproteobacteria, Firmicutes and Methanogens. Several molecular approaches are now available for detecting the gene copy number and diversity of hgcAB in natural samples, but all have caveats for use. Applying these techniques has allowed the community to begin to understand how the diversity of Hg-methylating organisms relates to site geochemistry. Unsurprisingly, the well-known terminal electron acceptors for methylators (Fe(III) and sulfate) often seem to control the distribution of hgcAB+ organisms. However, putative hgcAB+ organisms including Chloroflexi, Nitrospirae, Spirochaetes and Nitrospira are often captured in high densities in high-throughput sequencing. A challenge going forward will be to determine if, and to what extent these organisms contribute to MeHg production in the environment. The native function of hgcAB in microbial metabolism remains a mystery. We will also discuss the role of syntrophy in MeHg production, an interaction observed in early work by Richard Bartha’s group, and highlighted in Mark Hines’ last paper. Mark Hines contributed substantially to our understanding of demethylation, always highlighting the importance of the process to net MeHg production, and providing some of the earliest measurements. Methymercury degradation has traditionally been a difficult measurement to make and remains poorly understood. The mer operon is the best understood system. Different forms of this inducible detoxification process specify MeHg demethylation via degradation to methane and Hg(0). This reductive demethylation dominates in oxic environments with high Hg concentrations, where mer genes are readily detected. But rapid demethylation is also commonly observed in anaerobic environments. An early proposed mechanism for oxidative metabolism of the CH₃ group in MeHg by certain anaerobes was dubbed “oxidative demethylation,” but the mechanism has never been fully described.
METHYLMERCURY (MeHg) formation and degradation (or demethylation) are two competing processes controlling MeHg net production and bioaccumulation in natural environments. Demethylation can occur by many processes, including chemical, photochemical, and biological reactions in water and sediments, although exact mechanisms and environmental factors controlling MeHg degradation in nature are not fully understood. This presentation will provide a perspective of our current understanding of MeHg degradation in aquatic environments, with special emphasis on biologically and photochemically-mediated demethylation. For the former, despite their ubiquitous presence in the environment, certain strains of methanotrophs (methane-oxidizing bacteria) have only recently been recognized for their ability to degrade MeHg. Specifically, Alphaproteobacteria methanotrophs such as Methylosinus trichosporum OB3b and Methylcystis SB2 can degrade MeHg rapidly, whereas others such as the Gammaproteobacteria methanotrophs Methyllobacillus capsulatus Bath and Methylloethinium miyakonense can take up but not degrade MeHg. Unlike merB-mediated demethylation, methanotrophic demethylation can occur at picomolar to nanomolar Hg concentrations and under circumneutral pH conditions, indicating that methanotrophs likely play a critical role in controlling net MeHg production and toxicity in situ. Interestingly, degradation by methanotrophs is dependent on the production of methanobactin, a novel copper-binding compound synthesized by many but not all of these microbes, although the exact biochemical mechanism(s) of methanobactin-catalyzed demethylation remains an open question. Compared to methanotrophically-mediated demethylation, much more research has been carried out examining abiotic photochemical demethylation, although the mechanisms by which MeHg is degraded are also still debatable, particularly with respect to the roles of reactive oxygen species or free radicals and the involvement of complexing ligands such as naturally dissolved organic matter. Nonetheless, it has been reported that photochemical demethylation may account for as much as 80% of MeHg degradation in some freshwater lakes, but the rates and extent of photo-demethylation in marine and other aquatic ecosystems remain uncharacterized. Future studies with advanced molecular tools and multiplex proteogenomic approaches are warranted to further elucidate the chemical and biochemical mechanisms of biotic and abiotic demethylation, and thus to provide more accurate assessments of methanotrophic and photochemical demethylation in net MeHg production and bioaccumulation in the environment.
assessment in ecosystems and human health. Many studies have addressed Hg speciation and transformation in various ecosystems but it is still difficult to get a clear view of the cellular processes leading to MeHg production at the bacterial cell level. Our objective is to clarify these mechanisms at the cell level to progress in the understanding of Hg metabolic pathways. For that, we investigated the SRB strain Pseudodesulfovibrio hydrargryri BerOc1, able to methylate and demethylate Hg, and the Desulfovibrio alaskensis G20 SRB strain, only able to demethylate MeHg. Both strains were exposed in non sulfidogenic conditions to various concentrations of inorganic Hg (IHg) and MeHg (from 50 nM to 50 μM) and methylation and demethylation kinetics were investigated by Gas Chromatography-ICP-MS. Combining High Energy Resolution Fluorescence Detected - X-ray Absorption Near Edge Structure spectroscopy (HERFD-XANES) at the Hg LIII-edge and synchrotron nano-X-ray Fluorescence imaging (nano-XRF) we could speculate Hg with high sensitivity and locate Hg and other elements at the bacterial cell level during transformation kinetics. Results showed a maximum of cellular MeHg production at 3μM of IHg whereas IHg production by demethylation always increased by increasing spiked MeHg concentrations, suggesting a saturation of the Hg methylation process. HERFD-XANES identified a tetracoordinated βHgS form as dominant Hg species for both strains exposed to inorganic Hg while MeHg-cysteine was detected in BerOc1 for the lower IHg exposure in agreement with Hg methylation rates. During the demethylation process, various Hg- and MeHg-thiols were identified for both strains. Kinetics suggested an excretion of Hg from the cell and the formation of βHgS getting more crystalline with time and likely formed by biomolecules of the cells. Finally, these results highlighted the crucial role of S ligands in Hg biotransformation processes, even when bacteria are grown in non-sulfidogenic conditions.

R.O.1.11A-5

A MULTI-OMICS VIEW OF THE NATIVE BIOCHEMICAL FUNCTION OF HG METHYLATION PROTEINS IN DESULFOVIBRIO DESULFURICANS ND132

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The hgcAB gene pair encodes Hg methylation capability in anaerobic microorganisms spanning a diverse array of metabolic clades. Yet it is unclear what environmental conditions have resulted in the conservation of these genes in Bacterial and Archaeal genomes. Biomethylation of Hg does not provide any observed benefit to the cell, and deletion of hgcAB does not appear to hinder growth or produce any major phenotype. It is postulated that the native function of Hg methylation proteins (HgcAB) is not Hg methylation, but the methylation of an unknown metabolite(s). Hg methylation has been linked to one-carbon metabolism for acetyl-CoA and methionine biosynthesis, sometimes as part of the Wood-Ljundahl pathway, yet a specific biochemical pathway remains elusive. Here we take a systems biology approach to exploring the physiologic function of HgcAB using Desulfovibrio desulfuricans ND132 as a model organism. For this study, we compared growth and metabolite profiles of various D. desulfuricans ND132 gene deletion strains related to carbon and Hg cycling to the wild-type. Mutant strains (e.g., ΔhgcAB, ΔmetH, ΔcoBT, ΔhgcAΔT101A) that exhibited differences in Hg methylation capability compared to wild-type (e.g. 0–246%) were grown in defined media with various substrates (e.g. pyruvate, fumarate, lactate, sulfate, formate, acetate). Organic acid, anion, and metabolite concentrations were monitored throughout the growth of the cells to determine if changes in central metabolism coordinated to changes in MeHg generation between wild-type and mutant strains. Indeed, significant differences in substrate consumption, acetate and biomass production, and transcription of C1 metabolism genes were observed between the strains under fermentative and sulfate-reducing conditions. A genome-scale metabolic model of Desulfovibrio desulfuricans ND132 using multi-omics analyses indicates that deletion of hgcAB results in changes to carbon substrate utilization and compensatory gene regulation to compensate for the loss of HgcAB. Understanding this native contribution of HgcAB to cellular metabolism will help predict the environmental conditions and metabolic states that control distribution and activity of Hg-methylating bacteria.

R.O.1.11A-6

STABILITY OF DIMETHYLMERCURY IN THE PRESENCE OF REDUCED SULFUR AND UNDER VARYING TEMPERATURE AND pH CONDITIONS

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Methylated mercury in marine waters typically consists to 30-80% of dimethylmercury (DMHg), the rest being monomethylmercury (MMHg). MMHg is taken up and biomagnified in marine food webs, generating concentrations of Hg in fish and seafood potentially harmful to human and wildlife health. Even though marine seafood is the main exposure route of Hg for large populations worldwide, our understanding of the biogeochemical processes controlling amounts of MMHg available for biological uptake is limited. To address this knowledge gap, improved understanding of the role of dimethylmercury (DMHg) for the biogeochemical cycle of Hg is needed. First and foremost, since DMHg could be an important sink or source for the MMHg pool, there is a need to identify potential DMHg formation and degradation pathways. Currently recognized degradation pathways of DMHg in marine systems include photochemical demethylation (although this pathway has been debated). Degradation through protonolysis of the Hg-C bond by dissolved sulfide has also been suggested and supported by density functional theory calculations. However, experimental support for this pathway is currently missing. Here, we will present data from a series of experiments where the stability of DMHg in the presence of dissolved sulfide or a sulfide-mineral (FeS (s)) has been examined. Initial experiments suggest DMHg to be stable at Hg:S ratios up to 1:10^6. At higher ratios, however, reduced DMHg concentrations were observed. This corresponds to ratios of DMHg and sulfide expected in reducing micro-zones in marine snow in oxic waters. Additionally, we will present data from experiments where the stability of DMHg in the presence of sulfide has been examined under different temperature and pH conditions.

1.6B Advances in analytical methods for environmental speciation determination

R.O.1.6B-1

TESTING METHODS FOR QUANTIFICATION AND IDENTIFICATION OF REACTIVE MERCURY COMPOUNDS

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The accurate quantification and identification of reactive mercury (RM = gaseous oxidized mercury (GOM) + particulate bound mercury (PBM)) compounds has proven to be a challenging task. The industry standard – the Tekran 2537/1130/1135 – under-represents the concentration of GOM in ambient air and is incapable of determining GOM chemistry. In addition, there are artifacts associated with the PBM measurement. Recent studies have worked towards developing alternative methods to more accurately quantify RM in ambient air and apply GOM permeation systems to better understand measurements and reactions. In addition, our work has focused on determining the chemistry of GOM compounds collected on sorption surfaces (i.e., membranes). In this presentation, research focused on development of methods for ambient air RM measurements and laboratory permeation
systems will be discussed. A range of a surfaces have been tested for uptake of RM from actively-sampled ambient air and as a material for thermal desorption. The collection efficiency and capacity for uptake of GOM compounds has been tested in laboratory conditions. We also are quantifying transformations of GOM compounds and identifying resulting compounds within high-concentration permeation systems and on membranes exposed to ambient air. Despite demonstrated quantitative retention of GOM compounds on some membranes, we are testing whether long-term storage of the GOM-loaded membranes, along with other storage conditions, affects GOM retention. Preliminary results indicate that storage duration is critical, with increased storage resulting in decreased mercury concentrations. Lastly, we are studying systematic changes to the configurations of GOM permeation tubes. The tubes were constructed of PFA, were very small (permeation rates from elemental and oxidized mercury permeation tubes are used in the commercial Tekran 2537 analyzer as a calibration source, and oxidized mercury permeation tubes (HgBr_2, HgCl_2, and others) are used to calibrate atmospheric oxidized mercury instrumentation. In all of these cases, permeation rates have been determined by comparison against Tekran or other mercury analyzers, which are in turn verified by temperature-controlled mercury vapor injections. Until now, no method has existed to verify oxidized mercury permeation rates and speciation independent of the analyzers they are used to calibrate. We developed a method to gravimetrically determine total mercury permeation rates from elemental and oxidized mercury permeation tubes. The tubes were constructed of PFA, were very small (permeable area of ~5 mm^2), were kept warm (temperatures between 50 and 100°C were tested), and were weighed weekly on a Mettler Toledo microbalance. At permeation rates of about 30 pg sec^-1, mass loss regression lines had r^2 values >0.999. At permeation rates less than 5 pg sec^-1, mass loss regression lines had r^2 values <0.95.

We used our automated calibrator to inject permeated mercury compounds into a Tekran 2537/1130 mercury speciation system that sampled air scrubbed of mercury and oxidants. The Tekran system was calibrated via mercury vapor injections, and we used the Tekran equation with ambient air correction to determine the mercury concentrations. Gravimetrically-determined permeation rates from our elemental mercury, HgBr_2, and HgCl_2 permeation tubes were 7, 6, and 11% lower, respectively, than those determined from the total mass of mercury recovered by the Tekran system. This is within the uncertainty of Tekran 2537 measurements reported by others (3-20%).

Injection of HgBr_2 and HgCl_2 into the Tekran 2537/1130 mercury speciation system that sampled air scrubbed of mercury and oxidants yielded 91 and 87% oxidized mercury (determined as mercury captured on the denuder), with the balance captured as elemental mercury. We reported lower ratios of oxidized to elemental mercury in ambient air calibrations in a previous study, and this work confirms that those lower ratios were likely due to measurement bias, rather than poor calibrator performance. We are currently developing methods to routinely verify chemistry of permeated GOM compounds with a gas chromatograph-mass spectrometry system, which provides compound-specific speciation information and is entirely independent of Tekran measurement systems.

R.O.1.6B-2

INDEPENDENT VERIFICATION OF ELEMENTAL AND OXIDIZED MERCURY PERMEATION TUBE EMISSION RATES AND SPECIATION

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(2)University of Nevada, Reno

We are developing methods to verify the performance of elemental and oxidized mercury permeation tubes. Elemental mercury permeation tubes are used in the commercial Tekran 2537 analyzer as a calibration source, and oxidized mercury permeation tubes (HgBr_2, HgCl_2, and others) are used to calibrate atmospheric oxidized mercury instrumentation. In all of these cases, permeation rates have been determined by comparison against Tekran or other mercury analyzers, which are in turn verified by temperature-controlled mercury vapor injections. Until now, no method has existed to verify oxidized mercury permeation rates and speciation independent of the analyzers they are used to calibrate. We developed a method to gravimetrically determine total mercury permeation rates from elemental and oxidized mercury permeation tubes. The tubes were constructed of PFA, were very small (permeable area of ~5 mm^2), were kept warm (temperatures between 50 and 100°C were tested), and were weighed weekly on a Mettler Toledo microbalance. At permeation rates of about 30 pg sec^-1, mass loss regression lines had r^2 values >0.999. At permeation rates less than 5 pg sec^-1, mass loss regression lines had r^2 values <0.95.

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R.O.1.6B-3

A CONCEPTUAL MODEL FOR EVALUATING THE TRANSPORT OF HG(II) IN THE PRESENCE OF NATURAL ORGANIC MATTER THROUGH A DIFFUSIVE GRADIENT IN THIN-FILM (DGT) PASSIVE SAMPLER

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Diffusive gradient in thin-film devices (DGTs) are promising sampling techniques to measure porewater mercury (Hg) concentrations in soils and sediments. DGTs operate as kinetic samplers in which the porewater concentration can be related to the rate of diffusion through a thin-film. To better understand the role of colloidal Hg species, we evaluated the effects of a model natural organic matter (Suwannee River) on the transport of Hg(II) into a DGT. The presence of NOM significantly reduced the diffusivity of the Hg (II) species and the reduction was strongly dependent on the NOM to Hg(II) ratio. In parallel, a conceptual model was developed by incorporating partition coefficients of size-fractionated NOM to Hg(II) measured by ultrafiltration and estimating diffusion coefficients based upon the NOM molecular weight distribution. The conceptual model agreed with the experimental DGT results and was also consistent with reported values obtained from other studies. Overall, our study suggests that NOM-associated Hg(II) is measured by DGT but its contribution to the Hg porewater concentration decreases as the molecular weight or the concentration of NOM increases because of its influence on the Hg effective diffusivity. Furthermore, the model provides insight in interpreting the nature of the NOM-Hg association and is useful for understanding the speculation of Hg in the presence of organic colloids.

R.O.1.6B-4

COMPARABLE MEASUREMENT RESULTS FOR GLOBAL MERCURY MONITORING IN THE MARINE ENVIRONMENT

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The launch of the United Nations Environment Programme Global Legally Binding Treaty on mercury, lead to the establishment/strengthening of Mercury monitoring efforts of the countries in different environmental compartments, in order to assess environmental mercury contamination, as well as to control the efficiency of the control measures undertaken. Therefore, mercury monitoring will become an integral part of all marine monitoring programmes implemented at national and/or regional level around the world. Because of the difficulties related to the accurate analysis of mercury and its species in marine samples, the use of recommended analytical methods by the laboratories involved in this effort, as well as the strengthening of the quality assurance of their data, is a necessity for the effective use of the generated data for environmental assessments and decision making. To assist countries in the strengthening of their mercury data quality assurance, the Marine Environmental Studies Laboratory of IAEA is developing fit-for-purpose recommended analytical methods for mercury and methyl mercury in marine samples (sediment and biota), organises Inter-Laboratory Comparison (ILC) exercises and produces relevant matrix Certified Reference Materials to be used by laboratories involved in mercury monitoring in the marine environment. The recommended monitoring methods for mercury and methyl mercury, as well as the reference methods used for the reference measurements will be outlined in the presentation. More details on the recently produced marine CRMs for mercury and methylmercury mass fractions in marine sediment and biota samples will be also discussed.
IN SITU REACTIVE GASEOUS GERCURY UPTAKE ON RADIARO DIFFUSIVE BARRIER, CATION EXCHANGE MEMBRANE AND TEFLOM FILTER MEMBRANES DURING ATMOSPHERIC MERCURY DEPLETION EVENTS

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Inlet filter media were field tested for their scrubbing efficiencies of reactive gaseous mercury (RGM) using two parallel Tekran speciation systems during atmospheric mercury depletion events (AMDE) in Alert, NU, Canada during the spring of 2018 and 2019. Testing was performed by installing an inlet filter in place of the typical Tekran 1130 impactor and frit on one speciation system and comparing the RGM collected on the typical potassium chloride (KCl) coated annual denuder on the reference system. The filter media employed in the testing included a standard 47mm 0.2 μm Teflon filter, a 47mm 0.45μm cation exchange membrane (CEM), and a Radiello diffusive barrier (pore size: 0.25μm) which is used on commercially available mercury passive samplers (MerPAS). Control experiments with identical inlets and a blank filter holder were also performed. Springtime AMDEs provide a natural experimental setup of very high RGM concentrations (602pg/m3 maximum) with an overall mean RGM concentration was 101pg/m3 during the 2018 testing period. Results showed the RGM collected on the KCl coated annular denuder after passing through the Teflon, CEM and Radiello filters was 51, 8 and 6%, respectively when compared to the reference system. Results from the control study showed the two analyzers when setup with identical inlets had similar results (relative percentage difference: 5.9%), and that the empty filterpack took up 52% of the RGM relative to the reference system. Results from these studies show that there is little to no transmittance of RGM through the Radiello used in the MerPAS sampler and thus we conclude that this sampler collects only GEM and not RGM. Similarly, the CEM filter showed little to no transmittance of RGM through the filter. The Teflon filter results demonstrate that approximately half the RGM in the sampled air is permeating through the filter under elevated RGM concentration conditions. Thus Teflon filters alone represent an inefficient mechanism of RGM removal under high concentrations.

1.1D Atmospheric mercury cycling and transformations: Insights from measurements and models

AIR-SEA EXCHANGE OF MERCURY SPECIES IN THE NORTH AND TROPICAL PACIFIC OCEAN; EVIDENCE GAINED FROM THE GP15 GEOTRACES EXPEDITION

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Air-sea exchange of mercury (Hg) is an important process of the global Hg cycle, which affects the input and output of Hg from surface seawater, and prolongs the residence time of Hg in the biosphere. Previous studies in the South Pacific Ocean and during the US GEOTRACES Arctic expedition, have provided new insights into the factors controlling the cycling of Hg and methylated Hg across the air-sea interface. In this study, we aimed to improve this understanding of not only elemental Hg (Hg0) exchange, but also the exchange of methylated Hg (both methylmercury (CH3Hg) and dimethylmercury (CH32Hg)) via air-sea exchange processes, both evasion and deposition during the GEOTRACES GP15 cruise, which was from Seattle to Tahiti from Sept 18 to Nov 24, 2018. We used Tekran 1130/1135 instruments for high-resolution measurements of atmospheric Hg speciation (Hg0, reactive gaseous Hg (RGMg and particulate Hg), which we also compared with a batch method, using multistage filter packs with ion exchange membranes, to assess consistency and comparability between methods for RGMg. We also quantified atmospheric (CH32Hg) using high volume (CH32Hg) using high volume collector, as well as wet deposition, for determination of total Hg and CH3Hg. An automatic high resolution continuous equilibrium system was used for measuring dissolved Hg0 in surface seawater for gas exchange flux quantification. In addition, gaseous (CH32Hg was also determined and measured using selective trapping. Results of these measurements will be discussed in terms of the overall air-sea exchange of inorganic Hg and methylated Hg during the GP15 study, and the results will be discussed and compared with previous studies on Pacific and North Atlantic.

EXPERIMENTAL AND ANALYTICAL APPROACHES TO ELUCIDATE THE ROLE OF PHOTOPHANLON IN BIOTIC AND ABIOTIC MERCURY (Hg) TRANSFORMATION.

GARCÍA-CALLEJA, Javier1 (1)CNRS/PPREM

The determination of the kinetics and prevailing mechanisms of Hg biotransformation pathways mediated by phytoplankton, on one hand, and the examination of which and under which conditions bio-genic ligands are produced by the phytoplankton are new challenges in research on Hg fate in aquatic systems. This work presents analytical approaches to investigate Hg cell fractionation and Hg species transformation in photosynthetic organism cell cultures. Subcellular partitioning and transformation of Hg species in two strains, Chlamydomonas reinhardtii and Synechocystis sp., are studied. In addition, similar approach is evaluated for real freshwater samples collected during summer bloom (eutrophic lake). Phytoplankton species were harvested at exponential and stationary growth phases and exposed to 1nM of 199Hg and 100 pM of 201MeHg for 24h. The cellular accumulation of Hg or MeHg was determined following isolation from the exposure medium by gentle centrifugation. Furthermore, the cell were further separated in order to recover the cytosol (supernatant) and membrane (cell debris) fractions. The incubation with isotopically labelled Hg species (199Hg and 201MeHg) not only allows the determination of methylation and demethylation rates simultaneously, but also the comparison of the localization of the originally added and resulting species of such metabolic processes. To this end Isotope dilution and Gas chromatography coupled to ICPMS was used. In addition, Size Exclusion Chromatography coupled to ICPMS was carried out in order to separate the Hg binding biomolecules on the cytoplasmic and extracellular fractions. Methylation (0-4 %) and Demethylation (1-10 %) interconversion during the analytical method and sample preparation was evidenced in bulk samples. Spike recoveries and mass balance were evaluated for both bulk and whole cell. Depending on the growth phase (exponential or stationary), the mercury species involved and the algae strain, noticeable difference were found. Main results on cell distribution show that both species present a higher uptake on the whole cell in exponential phase (97-70 %) that in stationary phase (36-30 %). These species are mainly localized in the membrane fraction and their percentage in the cytosol varied between 7-42 % in exponential phase and 29-53% in stationary phase. Overall, the experimental and analytical approaches developed in this work demonstrate the possibility to investigate Hg species cell fractionation and biotic transformation at environmentally relevant concentrations. The next step of this project involves the characterization of Hg binding biomolecules in cell culture and lake samples with respect to mercury speciation.
ANTHROPOGENIC AND METEOROLOGICAL DRIVERS OF OBSERVED DECREASE IN ATMOSPHERIC MERCURY IN CHINA DURING 2013-2017

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Due to the long-distance transportation characteristics of mercury in the air, atmospheric mercury pollution in China has caused global attention. Recent observation indicates that air mercury in China has been decreasing rapidly after 2013 when the Minamata Convention on Mercury was formally signed. This study is the first effort to explain the decrease trend of observed atmospheric pollution in China by using state-of-art China Mercury Emission Inventory Model and chemistry and transport model (GEOS-CHEM model), which will shed light on our future action to implement the Convention. Our results indicated that the observed decrease of atmospheric mercury in China was dominated by the reduction of anthropogenic emissions. China’s mercury emissions to air in 2017 decreased by 136 tons compared with that in 2013, which reduced the total gaseous mercury (TGM) concentration and mercury deposition flux (FLX) by 12% and 23%, respectively. The control policies on traditional air pollutants (mainly SO2, NOx and PM) dominated the mitigation of mercury emission during this period. The measure-by-measure evaluation indicates that the implementation of ultra-low emission limit values in coal-fired power plants was the most effective measures, which contributed about 50% of the reduction of both air mercury and deposition flux. However, large variations existed among different regions. In Beijing-Tianjin-Hebei region, TGM and FLX decreased by 20% and 39%, which was the joint effects from the actions of ultra-low emission control in coal-fired power plants, flue gas denitrification in cement clinker production and energy substitution in residential coal combustion. In Hunan, TGM concentration and FLX decreased by 14% and 27%, wherein about 80% of the decline was attributed to the flue gas desulfurization in Zn/Pb smelting plants. In Sichuan-Chongqing region, ultra-low emission control in coal-fired power plants as well as deep dust collection and flue gas desulfurization were the dominant measures. Our study explains the decrease trend of air mercury in China, and the measure-by-measure benefit evaluation provides insights for both China and other developing countries in developing implementation plan of the Minamata Convention on Mercury.

MULTI-YEAR MONITORING OF ATMOSPHERIC TOTAL GASEOUS MERCURY AT A REMOTE HIGH-ALTITUDE SITE (NAM CO. 4730 M A.S.L.) IN THE INLAND TIBETAN PLATEAU REGION

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Total gaseous mercury (TGM) concentrations were continuously measured at the Nam Co Station, a remote high-altitude site (4730 m a.s.l.), in the inland Tibetan Plateau, China from January 2012 to October 2014 using a Tekran 2537B instrument. The mean concentration of TGM during the entire monitoring period was 1.33 ± 0.24 ng m⁻³ (mean ± standard deviation (SD)), ranking the lowest value among all continuous TGM measurements reported all over China, and was lower than most of sites in the Northern Hemisphere. This indicated the pristine atmospheric environment in the inland Tibetan Plateau. Long-term TGM at the Nam Co Station exhibited a slight decrease especially for summer seasons. The seasonal variation of TGM was characterized by higher concentrations during warm seasons and lower concentrations during cold seasons, decreasing in the following order: summer (1.50±0.20 ng m⁻³) > spring (1.28±0.20 ng m⁻³) > autumn (1.22±0.17 ng m⁻³) > winter (1.14±0.18 ng m⁻³). Diurnal variations of TGM exhibited uniform patterns in different seasons: the daily maximum was reached in the morning (around 2-4 hours after sunrise), followed by a decrease until sunset and a subsequent build-up at night, especially in the summer and the spring. Regional surface re-emission and vertical mixing were two major contributors to the temporal variations of TGM while long-range transported atmospheric mercury promoted elevated TGM during warm seasons. Results of multiple linear regression (MLR) revealed that humidity and temperature were the principal covariates of TGM. Potential source contribution function (PSCF) and FLEXible PARticle dispersion model (WRF-FLEXPART) results indicated that the likely high potential source regions of TGM to the Nam Co are central and eastern Indo-Gangetic Plain (IGP) during the measurement period with high biomass burning and anthropogenic emissions. The seasonality of TGM at Nam Co was in phase with the Indian Monsoon Index, implying Indian Summer Monsoon as an important driver for transport boundary transport of air pollution into the Inland Tibetan Plateau. Our results provided atmospheric mercury baseline in the remote inland Tibetan Plateau and serve as new constraint for assessment of Asian mercury emission and pollution.

TRACKING ATMOSPHERIC SOURCES OF MERCURY THROUGH PASSIVE AIR SAMPLING AND ISOTOPIC FINGERPRINTING

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The application of stable isotopes to trace different atmospheric Hg emission sources relies on the ability to collect amounts of Hg sufficient for artifact-free isotopic analysis. Common methods for atmospheric Hg collection use active pumping through gold-coated bead/sand or activated carbon traps. However, such sampling can be compromised by potential trap passivation or contamination during the required long pumping times. These energy requirements also limit the spatial resolution of data generated by active sampling methods. Here we assess the ability of a newly developed gaseous elemental Hg (GEM) passive air sampler (PAS) to track Hg isotopes and include results from a reconnaissance study on the spatial variability in the isotopic signature GEM across a large region (Ontario, Canada). One month deployments of these samplers are sufficient to collect enough Hg (>5 ng) for isotope analysis. While results show no mass independent fractionation (MIF) occurs during GEM diffusion through the PAS’s diffusive barrier, a consistent mass dependent fractionation (MDF) offset of -1 ‰ in delta202Hg was observed and is likely related to adsorption of Hg to the carbon. As temperature is known to influence the PAS sampling rate, we explored the effect of temperature on isotopic fractionation by sampling at -10, 5, 20 and 30°C. The offset in the MDF remained consistently at ~1 ‰ at temperatures between 5 to 30°C, but was larger at ~10°C. An MDF offset of ~1 ‰ was also observed in field experiments, suggesting that above 5°C the PAS should yield reliable MIF and MDF values, if the latter is corrected for the offset. The larger MDF at sub-zero temperatures requires further investigation. In order to test the PAS’s suitability for isotopic characterization of atmospheric GEM, it was deployed at 57 locations across Ontario and the United States. GEM varied spatially, with higher concentrations near point sources and in southern Ontario closer to industry and downwind of US sources. The isotopic compositions also varied, with southern Ontario samples being more similar to samples collected in the US, but diverging from those in the more remote Northern reaches of the province. Results will further be discussed in the context of regional air mass transport.

ORAL ABSTRACTS • ICMGP 2019 • 14th International Conference on Mercury as a Global Pollutant • September 8-13 2019, Krakow, Poland • 83
ATMOSPHERIC MERCURY (Hg(0)) CONCENTRATIONS AND Hg(0) FLUXES DURING THE JOINT RUSSIAN-CHINESE CRUISE ARCTIC SILK WAY 2018

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In September-October 2018, during the joint Russian-Chinese cruise Arctic Silk Way 2018, measurements of gaseous elemental mercury (Hg(0)) in the marine boundary layer (MBL) and Hg(0) fluxes in the Far Eastern seas of Russia and in the Eastern Arctic Seas were carried out using two RA-915M mercury analysers (Lumex LLC, Russia). Hg(0) concentrations in the air (about 2 m above the sea surface) were measured continuously throughout the cruise with a time resolution of 30 minutes. Hg(0) fluxes were measured using a flux chamber. Continuous measurements of Hg(0) fluxes from water taken from a depth of 5 m were carried out in all water areas except the Sea of Japan. Additionally, Hg(0) fluxes were measured during vessel stops in the Eastern Arctic Seas with the flow chamber set directly on the sea surface. Hg(0) concentrations during the cruise varied in the range from 1.02 ng/m3 to 2.50 ng/m3, the mean and median values were 1.45 and 1.44 ng/m3, respectively (N = 2518). The concentration of Hg(0) in the MBL strongly depended on from which regions the air masses came. Elevated concentrations of Hg(0) in the air were registered in the Sea of Japan and were associated with the arrival of air masses from northeastern China, in particular from the Yellow Sea region. The growth of Hg(0) concentrations in the air was observed in the Latpve Sea and coincided with the arrival of air masses from the central part of the Arctic Ocean.

Hg(0) fluxes at the sampling stations in the Eastern Arctic Seas varied in the range from 0.28 to 1.35 ng/m2/h, the mean and median values were 0.70 and 0.69 ng/m2/h, respectively (N = 29). Hg(0) fluxes measured during the vessel movement varied in the range from -0.14 to 0.74, the average and median values were 0.08 and 0.06 ng/m2/h (N = 1330). No significant relationship was found between Hg(0) fluxes and Hg(0) concentrations in the air. A positive relationship between Hg(0) flow and water temperature was observed. Accordingly, the largest Hg(0) fluxes were recorded in September in the Far Eastern seas of Russia, in the Pacific Ocean, the Chukchi Sea, and the East Siberian Sea. The smallest Hg(0) fluxes were observed in the Laptev Sea and in the Arctic Ocean.

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Oxidation of gaseous elemental mercury initiated by OH radical: mechanism and rate constants for use in atmospheric modeling

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Here we present an explicit chemical mechanism and rate constants for the OH-initiated oxidation of Hg(0). This reaction greatly limits the rate of Hg(0) oxidation by OH radical, but most models neglect it. Rather, models of the oxidation of Hg(0) by OH in the gas phase almost all treat the addition of OH to Hg as irreversible:

\[ \text{OH} + \text{Hg} = \text{HOHg} \] (1)

\[ \text{HOHg} = \text{Hg(II)} \] (2)

although the process(es) involved in reaction (2) are not known. This is despite the well-known weakness of the HO-Hg bond, which should lead to rapid dissociation of the HOHg intermediate:

\[ \text{HOHg} + \text{OH} \rightarrow \text{Hg} \] (1)

This rapid dissociation strongly limits the efficiency of OH in transforming Hg(0) to Hg(II). We used high levels of computational chemistry to determine the equilibrium constant for reaction (1), we determined the rate constant for HOHg• dissociation as a function of pressure and temperature. The reactions competing with HOHg• dissociation are addition to atmospherically abundant radicals, such as NO2, HOO, and halogen oxides:

\[ \text{HOHg} + \cdot \text{Y} = \text{HOHgY} \] (3)

Using computational chemistry, we find that the HOHg-Y bond energies are essentially identical to BrHg-Y bond energies. So it is reasonable to assume that rate constants for HOHg• + •Y = HOHgY are very close to those for BrHg• + •Y = BrHgY.

These findings enable us to write a mechanism, complete with rate constants, for the OH-initiated oxidation of Hg(0) to Hg(II). These results are being incorporated into the GEOSChem global model. Here we compute the efficiency of OH-initiated oxidation under two specific conditions to show the impact of HOHg• dissociation. For example, at ground level in somewhat polluted areas ([NO2] = 1 ppbv), OH is highly inefficient in oxidizing Hg(0); only ~10% of HOHg• goes on to make Hg(II) compounds. At the lower temperatures and pressures of the tropopause, HOHg• is much slower to fall apart, so typical radical concentrations are sufficient to cause ~75% HOHg• to produce Hg(II) compounds.

2.4 Health effects and long term studies

ASSOCIATION BETWEEN PRENATAL LOW-LEVEL MERCURY EXPOSURE AND NEURODEVELOPMENT IN AN ITALIAN BIRTH COHORT: A LONGLITTUDINAL ANALYSIS AT 18 AND 40 MONTHS OF CHILD’S AGE.

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Background: In 2007, within PHIME, a EU Commission funded project on the Public health impact of long-term, low-level mixed element exposure, the University of Udine and the Institute for Maternal and Child Health IRCCS Burlo Garofolo of Trieste (Italy) established a prospective mother-child cohort to assess the association between mercury exposure from fish consumption and children neurodevelopment. Here, we show the results of this Italian cohort at 18 and 40 months of age.

Methods: Participant subjects were the 442 children who underwent neurodevelopmental tests, using the Bayley Scales of Infant and Toddler Development (III Edition), both at 18 and 40 months of age, total mercury (THg) levels were measured in: maternal blood and hair during pregnancy, cord blood and breast milk (ng/g). Sociodemographic and socioeconomic information, and nutritional habits were collected through questionnaires at different follow-up points. We describe the cognitive composite scores at 18 (COGN18) and 40 (COGN40) months of age. The relationship between THg levels and COGN18 and COGN40 was modelled through adjusted linear quantile mixed model (LQMM). To evaluate time and covariate effects on the variation of the response for different quantiles, we considered the 10th (p10), 25th (p25), 50th (p50), 75th (p75) and 90th (p90) percentiles of COGN18 and COGN40. The time effect is the difference of scores between COGN18 and COGN40 for different quantiles. For each biological
PREFATAL EXPOSURE TO METHYLMERCURY FROM FISH CONSUMPTION AND CHILD DEVELOPMENT AT 7 YEARS OF AGE IN THE SEYCHELLES CHILD DEVELOPMENT STUDY NUTRITION COHORT 2

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Fish is globally a major protein source and a primary source of nutrients such as long chain polyunsaturated fatty acids (PUFA) which are essential for fetal neurodevelopment. All fish also contain small amounts of naturally acquired methylmercury (MeHg), a known neurotoxicant at high levels of exposure. There is substantial uncertainty regarding the risk, if any, from eating fish with low levels of MeHg during pregnancy. The Seychelles Child Development Study (SCDS) has been studying this issue for nearly 30 years. To date, our studies have revealed that the association between prenatal MeHg exposure from maternal fish consumption and child neurodevelopmental outcomes is far more complex than previously anticipated. To examine these complex relationships, from 2008-2011 we enrolled a cohort of 1,536 mother-child pairs and characterized them for prenatal MeHg exposure, maternal nutritional status, and neurodevelopmental outcomes. When the children were 20 months of age, we found that nutrients in fish, in particular n-3 PUFA, are beneficial for child development and could influence MeHg toxicity. These results suggest that the maternal inflammatory milieu may be important for child development. We subsequently evaluated this cohort at 7 years of age to determine if prenatal nutritional factors affecting inflammation influence associations between prenatal MeHg exposure and neurodevelopmental outcomes. In December 2018, we completed re-examination of 1467 cohort children (95%) using a battery of standardized neurodevelopmental tests focused on communication skills and language development. In our studies these domains have most consistently shown associations with prenatal MeHg exposure and maternal PUFA. We also measured inflammatory biomarkers at 28 weeks gestation as indicators of the role of the maternal inflammatory milieu in modifying MeHg toxicity. Based on this extensive data set, we will present some of the results examining associations between prenatal MeHg, maternal PUFA status, maternal immune markers, and children’s neurodevelopmental outcomes.

THE MEASUREMENT OF HUMAN DEVELOPMENT IN STUDIES OF PRENATAL MERCURY EXPOSURE: EXPERIENCES FROM THE SEYCHELLES CHILD DEVELOPMENT STUDY

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Standardized assessment of human development is an essential element in epidemiological studies of the relationship between toxicant exposures and neurodevelopment. This is particularly important in studies of low-level toxicant exposures, which may be particularly susceptible to the consequences of measurement errors. Common indices of human development and neurodevelopmental integrity include standardized measures of cognition (e.g., IQ), neuropsychological functioning (e.g., attention), adaptive behavior, scholastic achievement, and the presence of specific disorders (e.g., autism spectrum disorder, ADHD). Use of these instruments requires careful consideration of internal and external validity, including those related to instrumentation (e.g., comparisons of data across tests ostensibly measuring the same or similar constructs) and cultural and language differences. Using the 32-year history of the Seychelles Child Development Study (SCDS) as an organizing reference, we will present (a) a review of potential barriers to valid developmental assessment; (b) the principles that we followed in our assessment of human development; and (c) recommendations for researchers in order to accurately measure neurodevelopment in epidemiological studies of toxicant exposures.
ASSOCIATIONS OF BLOOD MERCURY AND FATTY ACID CONCENTRATIONS WITH BLOOD MITOCHONDRIAL DNA COPY NUMBER IN THE SEYCHELLES CHILD DEVELOPMENT NUTRITION STUDY

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Background: Fish contains methylmercury (MeHg) which can cause oxidative stress and neurodevelopmental toxicity at sufficiently high doses. Fish also contains polyunsaturated fatty acids (PUFA) which have both antioxidant (n-3) and oxidant (n-6) properties. Mitochondrial DNA (mtDNA) is sensitive to oxidative stress but has not been previously studied in relation to MeHg exposure or PUFA status.

Objective: To investigate the associations between MeHg exposure and PUFA status during pregnancy with relative mitochondrial DNA (mtDNA) copy numbers.

Methods: In total, 1488 mother-child pairs from the Seychelles Child Development Study Nutrition Cohort 2 were included in this study. Total Hg was measured in maternal blood collected at 28 weeks gestation, maternal hair at delivery, and in fetal cord blood. PUFA (n-3 and n-6) were measured only in maternal blood. RmtDNAcn was measured by qPCR in both maternal and cord blood.

Results: Increasing maternal blood Hg (β = 0.001, 95% CI: 0.000, 0.002) and n-3 PUFA concentrations (β = 0.183, 95% CI: 0.048, 0.317) were associated with higher maternal RmtDNAcn. Increasing maternal n-6 PUFA (β = -0.103, 95% CI: -0.145, -0.062) and n-6/n-3 ratio (β = -0.011, 95% CI: -0.017, -0.004) were associated with lower maternal RmtDNAcn. Increasing fetal cord blood Hg was associated with lower fetal RmtDNAcn (β = -0.002, 95% CI: -0.004, -0.000). Neither maternal blood Hg nor PUFA status was associated with fetal RmtDNAcn.

Conclusions: Our findings suggest that MeHg and PUFA may influence mitochondrial homeostasis although the magnitude of these associations are small. Future studies should confirm the findings and explore the underlying mechanisms.
crowe-assisted extraction and aqueous phase derivatization. Mercury isotopic composition analysis was performed using cold vapor generation (CVG) with MC-ICP-MS (Nu Instruments). We analyzed seals' tissues and herring muscle. Hg speciation changed significantly among tissues. Hair and muscle were predominantly enriched in MMHg (84 to 98% and 74 to 95%, respectively) relative to liver and kidney (7 to 38% and 4 to 27% respectively). δ202Hg values were positively related with levels of MMHg (p > 0.0001, R² = 0.531). Δ199Hg and Δ201 and Δ199Hg/Δ201Hg slope values were not influenced by Hg species composition in tissues. A significant 202Hg trophic enrichment resulted between seal hair and kidney and herring (p = 0.011 and p < 0.001), indicating important MDF between the ingested prey and these tissues. Significant MIF (Δ199Hg and Δ201) was observed only between seals' kidney and herring (p = 0.0003). Our results show that: (1) Hg isotopic composition reflects Hg molecular speciation; (2) as a result of isotopic incorporation during tissue turnover, hair and kidney present a strong trophic MDF; and (3) with the exception of kidney, MIF signal is conserved in all tissues during assimilation of prey items. We propose muscle as the optimal monitoring tissue for tracing of Hg sources since both the MDF and MIF signals are conserved from prey to predator.

**R.O.2.8B-2**

**MERCURY CONTAMINATION OF ARCTIC SEABIRDS: SPATIO-TEMPORAL TRENDS AND IMPACTS**

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Mercury (Hg) is a global pollutant, yet the Arctic is among the most exposed regions. Hg emitted by mid-latitude northern countries is indeed transported over large distances to polar regions by oceanic, atmospheric and riverine currents. As a consequence, Hg is found in high concentrations in Arctic marine food webs and, being highly toxic, raises important environmental concerns. These concerns are especially high as Hg levels should continue to increase in the Arctic marine environment within the next decades, despite a reduction in emissions from developed countries. In that context, a major objective is to further understand the spatio-temporal dynamics of Hg in Arctic marine ecosystems, and as well as its impacts on the Arctic wildlife, especially on top-predators which are among the most vulnerable organisms to environmental pollution. Since 2005, we conduct research in East Greenland on a population of little auks – the most abundant seabird worldwide – in order to investigate impacts of multiple environmental stressors, including Hg, on this vulnerable species. Obtained results first identify long-term changes in bird contamination in relation to their ecology and highlight seasonal and spatial origins of this contamination. For instance, they show that birds are mainly and increasingly exposed to Hg when migrating outside of the Arctic, off Newfoundland during winter. Second, they demonstrate its impacts on little auks, both at short and long-time scales. Long-term changes in bird contamination are indeed related to lowered body condition and a decreased reproductive success. At a shorter scale, females exposed to the highest Hg concentrations during winter tend to lay smaller eggs and have smaller chicks with decreased fledging success. In order to extend these results obtained on a single species and a specific breeding site to the entire Arctic avian community, an international and pan-Arctic network (ARCTOX) was initiated in 2015. Allowing the collection of samples from 20 species at almost 60 sites around the Arctic, ARCTOX provides new knowledge on the vulnerability of Arctic seabirds to Hg and on a large scale distribution of this pollutant, thus highlighting sensitive areas that require particular attention and protection.

**R.O.2.8B-3**

**SPATIAL PATTERNS OF DOSE-RESPONSE RELATIONSHIPS BETWEEN MERCURY AND CORTISOL BIO-MARKERS IN THE FUR OF RIVER OTTER (LONTRA CANADENSIS)**

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Non-invasive biomarkers have become popular in wildlife toxicology of which, fur has been validated to quantify mercury (Hg) exposures and biological responses including cortisol. Hg is known to act as an endocrine disruptor through altering brain neurochemistry. However, the relationship between Hg and cortisol in wildlife is elusive as studies report both negative and positive dose-response relationships. In this study, we use fur from river otter (Lontra canadensis) to quantify total Hg (THg) and cortisol to assess the spatial heterogeneity of this dose-response relationship. Fur samples were obtained from a wildlife biomonitoring program (n=73) and from the North American Fur Auction (n=37) between 2014 and 2017. Samples were geoaggregated to traklines in Northwest Territories, Alberta, Ontario, Quebec, and Nova Scotia, Canada. Fur THg was measured using a mercury analyzer and fur cortisol was measured using an enzyme-linked immunosorbent assay (ELISA). The relationship between fur THg and cortisol was assessed using an ordinary least squares (OLS) regression and a geographically weighted regression (GWR). The mean fur THg was 11.50 ±12.40 μg/g and the mean fur cortisol was 5.63 ±8.24 pg/mg. Results from the OLS regression indicate that there is no relationship between fur cortisol and THg. However, spatially fur THg and cortisol were heterogeneously distributed across our study areas. When the GWR decomposes the global regression into localized regressions, there is a significant positive relationship between fur THg and cortisol in Alberta and a significant negative relationship between fur THg and cortisol in Northern Ontario. The negative dose-response relationship was observed in otters were fur THg exceeding the fur Hg screening guideline of 15 μg/g. This negative relationship may be due to an inhibited stress response associated with Hg exposure. Conversely, we observed the positive dose-response relationship in otters where fur THg was <15 μg/g. In these otters, the stress response appears to function normally, and Hg may also serve as a proxy for other anthropogenic stressors. This research highlights the need to consider the spatial distribution of sampling locations in studies assessing dose-response relationships in free-ranging wildlife.

**R.O.2.8B-4**

**TRANSFER OF MERCURY WITHIN A SEDIMENT-NET-TLE-INSECT FOOD WEB AT A CHLOR-ALKALI LANDFILL**

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Mercury (Hg) commonly enters ecosystems through anthropogenic sources such as atmospheric emissions or wastewater from industries. Sediment landfills from chlor-alkali industries require Hg stabilization to prevent air pollution by evaporated Hg. We recently demonstrated the relevance of phytomanagement process based on poplar plantations to revegetate and confine the Hg released from the soil in an experimental plantation located at a sediment landfill. Five years after the plantation, biotic and abiotic conditions have promoted the appearance of a spontaneous herbaceous cover highly dominated by the stinging nettle (Urtica dioica L.). In natural conditions, this plant species hosts an important diversity of insects playing a key role in trophic interactions within the ecosystem. As demonstrated for aquatic ecosystems, Hg is readily biomagnified through food webs, from plants to
insects, birds and mammals. The present study aimed at evaluating the trophic interactions at the nettle scale in a phytomanagement field trial and their implications for the Hg flux through a sediment-nettle-insect food web system. Insects were collected every month using a sweep net, from April to September 2017 and 2018. Once taxonomically and ecologically characterized, the total Hg (THg) concentrations of the 18 most abundant taxa were analysed using an AMA-254 analyser. Several trophic links were identified with a ratio of herbivorous/predatory of 23%. The mean concentrations of THg for insects collected from the experimental plantation were significantly higher than those from the control site. Within the nettle-related food web, the THg concentration follows the order of nettles (21.2 ± 1.0 µg/kg) < herbivorous (27.5 ± 4.3) < predator specialists (43.0 ± 14.1) < predator generalists (617.3 ± 47.2) showing a significant bioaccumulation. Moreover, we observed that insects, which spend a part of their life cycle directly in Hg sources, have a higher THg concentration average (918.4 ± 80.5 µg/kg) than generalist predators of the nettle food web. Hence, our study showed a complex network of trophic interactions from the studied nettle-insects food web. Overall, taxa that contribute the most to the Hg transfer to the highest trophic links are generalist predators and those in direct contact with Hg sources. Moreover, in revegetated sediment landfills, plants did not seem to be the primary source of Hg exposure for wildlife.

R.O.2.BB-6

MERCURY EFFECTS ON WILD BIRD REPRODUCTION ARE DEPENDENT ON AVAILABILITY OF FOOD – EVIDENCE FROM MULTI-ANNUAL STUDIES OF GREAT EGRETS IN THE EVERGLADES

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While several sub-lethal effects methylmercury on wildlife are known from controlled dosing studies, our understanding of the net effects of MeHg in the context of typical environmental stressors is poor. Here, we examine the effects of MeHg under fluctuating food availability. We analyzed long-term data (>10 years) on hatching success of great egrets in the Everglades, a vast wetland mosaic where egrets are exposed to geographically and temporally variable Hg concentrations. We examined hatching success in relation to geographical and inter-annual variation in exposure to Hg, in prey density (fish density: 140 sites sampled/yr, and in relation to food vulnerability (water recession range [cm], a measure of how fish get concentrated and exposed to predation, measured daily in 128 stations). We used hatching success data of 1,210 nests monitored in 38 colony-year combinations, and feathers sampled from 336 nestlings to estimate Hg exposure. We modeled hatching success in relation to Hg and its interaction with environmental covariates using proportional GLMMs (logit link and binomial error distribution) with colony nested in year as random factor.

Hatching probability for the same feather [Hg] strongly varied with food availability. Hatching success was influenced by the individual effects of [Hg], clutch size, recession range, and by complex interaction among these variables and fish density. When food was highly available (high fish density coupled with big water recession), hatching success was high, regardless of [Hg]. Thus, when food was available in large quantities and egrets were in better nutritional status, they could cope with the deleterious effects of Hg. When fish availability was low, we found a strong negative effect of Hg exposure on hatching success. A small surface-water recession produced a more complex pattern: increasing feather [Hg] increased hatching probability up to a threshold, putatively because low feather [Hg] can be indicative of low food intake rates and therefore poorer nutritional condition. However, after that threshold, deleterious effects increased with increasing Hg exposure. The most influential covariate of hatching success was recession range (explained 13.6% of variation), followed by Hg (10.9%), and fish density (9.5%). Our results indicate that the effects of Hg may often be environmentally mediated, in our case by availability of food. We suggest that understanding the effects of natural stressors on contaminant effects in field situations is a rich area for new research on Hg risk to wildlife populations, and may have relevance for human health studies too.

R.O.2.BB-5

FORMATION OF HGSE NANO PARTICLES IN THE EYE AND EAR OF THE LONG-FINNED PILOT WHALES FROM FAROE ISLANDS

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There is an emerging pattern of mercury (Hg) accumulation in the vertebrates sensory organs, which could contribute to the detrimental effects of Hg exposure on wildlife behaviour. Recent studies showed Hg deposition in the fish sensory systems such as eye, olfactory system, inner ear and lateral line. However, the evidence for similar processes in the mammalian organisms is scarce. The long-finned pilot whales (Globicephala melas) are marine mammals with high mercury load, which are also point source of contaminants exposure (including Hg) to the Faroese and Japanese human populations through consumption of whale meat and blubber. These whales are also notorious for their feeding practices on beaches. Several hypotheses have been proposed to explain mass strandings, however Hg-induced sensory impairment has not been explored.

To test this hypothesis, we probed Hg and Se accumulation patterns as well as Hg speciation in situ in the tissues of long-finned pilot whales, which were sampled in the Faroe Islands in connection with the traditional drive fishery. We surveyed the eyes (retina and optic nerves) from three animals (juvenile and adult) and the middle ear from one adult whale. The Hg and Se distribution images of the thin sections of the paraffin-embedded tissues were obtained using synchrotron X-ray Fluorescence Imaging (XFI). The Hg speciation in situ was probed with synchrotron X-ray Absorption Spectroscopy (XAS).

In the optic and middle ear nerves as well as the retina we detected small deposits composed of Hg and Se with Hg/Se molar ratio close to 1 or equal to 1. The spatial density of these granules was unexpectedly high, especially in the middle ear nerves, and the adult eye tissues had overall higher number of these particles than their juvenile counterparts. The XAS analysis of the single deposits showed that their structure was very similar to the laboratory synthesized HgSe nanoparticles. Consistently, Transmission Electron Microscopy (TEM) showed many of these particles significantly smaller than 1 micrometer. These small HgSe granules were likely formed from toxic Hg deposited in the sensory tissues. However, the high spatial density and small size of these deposits indicate potential for increased toxicity as compared with bulk HgSe, which is considered biologically inert. Therefore, at present it cannot be excluded that these nanoparticles could negatively affect transmission of sensory information from the eye and middle ear to the brain in these whales.

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3.3 Proven Hg Emissions Controls and Effectiveness

R.O.3.3-1

IMPROVED CATALYTIC SOLUTIONS FOR LOWERING MERCURY EMISSIONS FROM COMBUSTION SOURCES

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Increasing emissions regulations on large combustion plants along with the need for operational flexibility (frequent start-ups & shut-downs) has led many utility companies struggling to meet their emissions requirements. In Europe, the release of the LCP-BAT BREF document has put new emission limits on Hg emissions from combustion sources to bring European mercury emissions regulations in line with already established USA Mercury and Air Toxics Standards (MATS). As a result, all existing and new fossil fuel power plants and waste co-incineration plants in Europe must start installing/upgrading their mercury removal systems in order to meet the current targets. Achieving high mercury removal efficiencies in combustion plants greatly depends on the amount of elemental mercury (Hg0) that can effectively be converted to the oxidized form (Hg2+). Catalytic technologies, such as vanadium oxide based catalysts for the selective catalytic reduction (SCR) technology of NOx, have successfully been identified as effective systems to convert Hg0 to Hg2+ in the presence of halides. Unfortunately, the performance of these catalysts strongly depends on several parameters specific to each plant such as, the fuel’s composition, combustion conditions, and the position of the catalyst in the installation. Understanding how all these parameters affect the performance of the vanadium catalysts is crucial to help large and medium combustion plants to meet the new Hg emissions targets. In this work we will discuss the importance of understanding how the synergistic effects between gas composition and operating variables, impact the performance of vanadium catalysts and how by identifying optimal conditions for Hg oxidation, mercury emissions can be reduced. Additionally, an overview of the chemistry taking place within the catalysts will be presented along with improved catalyst formulations that have been specifically customised for the different post-combustion environments of American and European power plants.

R.O.3.3-2

THERMO-DESORPTION MS APPROACH TO MERCURY STABILITY STUDY IN SAMPLES FROM CEMENT PRODUCTION

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Controlled heating methods are useful in identification of different mercury compounds present in solid substrates. The usual method for the study of stability of mercury compounds in solid samples is temperature programmed desorption coupled to the atomic absorption detectors. Such investigation were mostly done on gypsum, coals and other sub-products of coal utilization, soils and sediments. The drawback of this approach lies in the insufficient sensitivity and high limit of detection for samples that have lower concentrations of Hg. In the cement production process, Hg is introduced via fuels and raw materials. Hg concentration in the process is further guided by the counter-current flow of materials and exhaust gases, and different temperature gradients of the system. The investigation of temperature stability of Hg compounds in cement production are lacking. In this research we employed controlled temperature desorption method coupled to quadrupole mass spectrometer (QMS) for investigation of thermal stability of Hg compounds in cement matrices. The obtained result show different thermal release profile of Hg depending where in the process samples are obtained. In a number of samples, several fractions that have absorption spectra in different temperature ranges were observed.

R.O.3.3-3

THE MERCURY EMISSIONS FROM COMBUSTION OF COAL AND LIGNITE IN LARGE COMBUSTION PLANTS IN THE CZECH REPUBLIC

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This paper presents the results of research projects focused on the mercury emission after fossil fuel combustion from large and medium capacity energy sources in the Czech Republic. The research currently respond to future EU legislation on BAT for LCP, which sets lower emission limits for SO2, NOx, Dust, CO and sets new emission limits for concentrations of HF and HCl and also emission limits for concentration of Hg in flue gases and will be valid for existing plants after 2021. The part of research was based on the analyses of fuels used in the Czech Republic. In terms of the analyses, lignite and coal samples were analysed for concentration of Hg and Cl. Then, numerous measurements were conducted at power plants in the Czech Republic with the aim to define value of concentration of Hg and various Hg species in flue gases and to analyse combustion by-products – ash and gypsum including suspension. For analyses of the concentrations of Hg and Hg species in flue gases, we used continual measurement and "Ontario Hydro method". The main aim of our research was construction and research on a pilot unit intended for oxidation of Hg0 to Hg2+ using a layer of catalyst at high temperature of flue gases. The research will continue with new project which include several research areas it means low temperature mercury oxidation, mercury sorption on the solid sorbent and mercury reemission problem in absorber in wet method desulphurization.

R.O.3.3-4

STUDY ON THE MERCURY REMOVAL CAPABILITY OF CHEMICAL-MECHANICAL BROMINE MODIFIED COAL FLY ASH

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Coal fly ash, an industrial by-product, is a good substitute of activated carbon due to its low cost and sufficient for convenient injection at power plant. In order to find a cost-effective modification method to improve the mercury removal efficiency of fly ash, chemical-mechanical modification was carried out using an omnidirectional planetary ball mill. The mercury removal efficiency of raw fly ash(FA), chemical-mechanical modified fly ash(FA-MC), chemical-mechanical bromine modified fly ash(FA-MC-Br) and impregnation bromine modified fly ash(FA-I-Br) was evaluated on a fixed-bed reactor. The physicochemical properties of four samples were characterized and discussed on the basis of BET, SEM, XRD, XPS and TPDD analysis. The results show that under the atmosphere of N2+O2(4%), the mercury removal efficiency of four samples follows the order of FA-MC-Br > FA-I-Br > FA-MC.
> FA, which value were 68%, 27%, 21% and 10%, respectively. The main component of fly ash is aluminosilicate. Its pore structure is not developed and the content of unburned carbon is only 5.3%, that's why the mercury removal efficiency of FA is too poor to replace the activated carbon. The mercury removal efficiency of FA-MC is slightly improved, which is due to the Calcium, weakly adsorbed oxygen and organic carbon content of fly ash increased after ball mill. Compared with FA-I-Br, the bromine loading capacity of FA-MC-Br is much better, this is because under the effect of chemical- mechanical, calcium inside the fly will be exposed and reacted with NH4Br to form CaBr2 which play an important part on mercury oxidation. Based on the results of TPDD, the mercury adsorption species of FA and FA-MC is HgCl2, but for FA-MC-Br and FA-I-Br is HgBr2/HgO and HgBr2. Mercury oxidation, follows the Eley-Rideal heterogeneous reaction mechanism, is the leading role of FA-MC-Br mercury removal. As results of this study, it’s demonstrate that FA-MC-Br is a cost-effective alternative of activated carbon for further industrial applications.

R.O.3.3-5

NANOSIZED COPPER SELENIDE FUNCTIONALIZED ZEOLITIC IMIDAZOLATE FRAMEWORK-8 (CUSE/ZIF-8) FOR EFFICIENT IMMOBILIZATION OF GAS-PHASE ELEMENTAL MERCURY

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A key challenge in developing an effective measure for controlling elemental mercury (Hg0) emission from various industrial processes is the design of sorbents bearing abundant adsorption site with high affinity towards Hg0, to achieve long-term capture and rapid uptake simultaneously. Herein, the first example of selenide based sorbent was applied in vapor phase Hg0 capture from industrial flue gas. The copper selenide (CuSe) nanocrystals supported by zeolitic imidazolate framework-8 (ZIF-8) was synthesized by a newly designed two-step surfactant-assisted method to demonstrate an ideal Hg0 trap. The as-prepared CuSe/ZIF-8 with CuSe to ZIF-8 mass ratio of 80% (0.8NC-ZIF) established unparalleled performance towards Hg0 adsorption with equilibrium capacity and average rate reaching 309.8 mg g-1 and 105.3 μg g-1 min-1, respectively, surpassing all reported metal sulfides and traditional activated carbon based sorbents. The impressive performance of 0.8NC-ZIF for Hg0 immobilization was primarily attributed to the adequate exposure of the Se-terminated sites with high affinity towards Hg0 resulted from the support of ZIF-8 and the layered structure of CuSe. The adsorbed mercury selenide exhibited even higher stability than the most stable natural mercury ore, i.e., mercury sulfide. This minimized the possibility of mercury re-emission when the Hg-laden CuSe/ZIF-8 sorbent was dumped. This work gives an in-depth illustration of how fabricating the active component and supporter to attain an ideal Hg0 sorbent. The results also provide a new mindset guiding for further development of selenide contained sorbent for efficiently decontaminating Hg0 pollution and mitigating mercury exposure in the future.

R.O.3.3-6

EFFECTS OF FLUE GAS COMPONENTS ON REMOVAL OF ELEMENTAL MERCURY OVER CUBR2-MODIFIED MINERAL SORBENTS

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Abstract: Two novel mineral sorbents (CuBr2-Atp and CuBr2-Dia) for elemental mercury (Hg0) removal from coal-fired flue gas were prepared by modifying attapulgite (Atp) and diatomite (Dia) with copper bromide (CuBr2), respectively, and their performances were studied in a fixed-bed reactor system under simulated flue gas. In addition, their reaction mechanisms were investigated by combining various characterizations methods. After modification, the specific surface area of Atp was reduced by half while that of Dia was increased 13-fold, which should be attributed to their unique physical structures. Experiment results showed that both CuBr2-Atp and CuBr2-Dia exhibited excellent Hg0 removal efficiencies (> 90%). HCl and O2 were beneficial to increasing their Hg0 removal efficiencies at 140 °C. SO2 exhibited inhibitory effect for the two mineral sorbents, however, the degrees were different. The average Hg0 removal efficiencies of CuBr2-Atp and CuBr2-Dia were reduced by 5% and 33%, respectively, under 1200 ppm SO2. Interestingly, NO had a slight negative effect on the performance of CuBr2-Atp, but an obvious promoting effect on that of CuBr2-Dia. 300 ppm NO could overcome the negative effect of SO2 on CuBr2-Dia by increasing its Hg0 removal efficiency to 87% alone and to 93% together with 4% O2. The order in which SO2 and NO were added in also affected the performances of CuBr2-Dia, suggesting that the active sites for Hg0 adsorption and oxidation changed and these changes in the surface chemistry caused by NO alone and those caused by NO+SO2 were different. In the process of Hg0 removal by the two mineral sorbents, both Cu2+ and Br radicals were the active sites for Hg0 oxidation and adsorption. In addition, the mercury-containing compounds fixed on the surface of the mineral sorbents exhibited good thermal stability.
ORAL ABSTRACTS

Friday 13th September 2019
1.12 Metrological traceability for mercury analysis and speciation

F.O.1.12-1

TRACEABILITY OF OXIDIZED MERCURY MEASUREMENTS IN AIR - THE MERCOX PROJECT

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The EURAMET has approved a project in the framework of the European Metrology Programme for Innovation and Research related to comparability of oxidized Hg measurements – MercOx. The overall objective is a traceable on-line and sorbent-based measurement for the monitoring and control of mercury in its different oxidized forms in emission sources and in the atmosphere in order to achieve significant improvements in measurement uncertainty. The specific objectives are: (1) To develop, establish and implement a traceable calibration methodology for the most important oxidized mercury species, especially for HgCl₂. Possible methods are evaporation of known mercury chloride solutions, sublimation of solid mercury chloride or oxidation of elemental mercury. (2) To study, develop and compare different methods of measuring oxidized mercury. (3) To compare, develop and establish conversion and sample transportation methods employing traceable reference standards developed for Hg(0) and oxidized mercury. Regarding species inter-conversion, different measurement methods and their long-term efficiency and reliability in different matrices have to be taken into account. This can include, for example, the validation of currently available conversion methods with new (more accurate) calibration standards, addressing more theoretical approaches for predicting mercury chemistry or employing more advanced techniques based on compound specific mass spectrometric measurements. (4) To apply the developed methodologies in order to test and validate new and existing methods for on-line mercury measurement under field conditions by employing developed gas standards or generators. This will include typical direct measurement of mercury via different conversion and optical detection methods, but also sorbent traps commonly used for mercury measurement. The methods developed will be also applied to the measurements of stack gas emission and atmospheric mercury speciation. Mercury stable isotope ratio measurements of Hg(0) and Hg(II) will be applied in the field. (5) To facilitate the take up of the technology and measurement infrastructure developed in the project across the measurement supply chain (accredited laboratories), standards developing organisations (such as CEN/TC264/WG8 and those linked to the IED Directive 2010/75/EU, the Air Quality Directive 2004/107/EC and the Waste Incineration Directive 2000/76/EC) and end users (environmental monitoring, research community, regional and global programmes). The aim of the presentation is to provide an overview and invite participants to collaborate as stakeholders.

F.O.1.12-2

COMPARABLE MEASUREMENTS FOR ELEMENTAL AND OXIDIZED MERCURY CONCENTRATIONS

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A primary mercury vapour generator was developed at VSL to establish a traceable measurement standard for mercury concentrations in gas emission sources and in atmosphere. The majority of mercury concentration measurements are currently traceable to the vapour pressure of mercury. The primary mercury vapour generator contributes to comparable measurement results of mercury concentration in air and is especially important for certification of services related to ambient air monitoring (1 ng Hg/m³ – 2 ng Hg/m³), indoor and work place related mercury concentration levels according to health standards (from 50 ng Hg/m³ upwards) as well as to stationary source emissions (from 1 µg Hg/m³ upwards).

During ICMGP2017 the development and working principle of the primary mercury vapour generator, based on diffusion according to ISO 6154-8, was presented. In this paper, we present the results of comparisons with current calibration facilities maintained by National Metrology Institutes (NMI)s, Designated Institutes (DI)s and companies. For the comparisons different types of sorbents were loaded with mercury to obtain transfer standards with levels between 2 ng and 1000 ng. Apart from its elemental form, mercury also occurs in oxidized forms in the environment. These forms are reactive and can be transformed into species such as methylmercury, the most toxic mercury species because of its bioaccumulation in aquatic systems. Within the European “Metrology for oxidised mercury” project the primary mercury standard is used to establish a traceable calibration methodology for the most important oxidised mercury-containing species, especially for HgCl₂. The first results are presented.

F.O.1.12-3

DYNAMIC GENERATION OF OXIDIZED MERCURY REFERENCE GAS AND VALIDATION OF MERCURY MEASUREMENTS AT FIELD CONDITIONS

RAJAMÄKI, Timo

Reliability of the online monitoring result of gas concentration is dependent on availability of accurate calibration standards. For reactive gases like oxidized mercury this is a challenge since these sticky water-soluble gases easily adsorb to surfaces. This complicates or even prevents the use of traditional static tools like gas cylinders or permeation devices. We apply the liquid evaporation method to dynamically generate oxidized mercury with accurately known concentration. A portable system based on this principle is capable to provide a gas flow with well-known mercury concentration.

In this system, a solution with selected concentration is dosed using e.g. stepper motor controlled automatic syringe pump and mixed with the carrier gas flow. Mixing is the key part of this process in order to prevent liquid droplets to stick to evaporation chamber surfaces before evaporation takes place. A heated spray chamber is applied in connection with a gas-assisted nebulizer for liquid spraying. Great care is needed when selecting inert materials for the spraying chamber and subsequent parts of the gas transportation system. Also, especially temperatures and gas flow rates play an important role when optimizing the response time of the system and minimizing losses caused by possible surface reactions. We estimate performance, uncertainty and applicability of this method for oxidized mercury. Operational parameters of the system are optimized in order to reach the best possible results for output stability and to minimize memory effects. Key parameters to study are calibration response time, stability, possible non-linear behavior, sensitivity to interferences caused by other reactive gas compounds, and residual atomic mercury due to surface reactions.
During the EMPIR project MercOx a comprehensive field studies are conducted as well in order to test and validate the new and existing methods for on-line and sorbent trap mercury measurement. The studied applications cover both process stack emissions and atmospheric measurement and hence mercury concentrations in several different matrices over a wide dynamic range, i.e. from sub-ng/m³ in ambient air to µg/m³ in process emissions. For stack emissions, coal fired power plants and cement kilns are the most representative sources and for measurement and hence mercury concentrations in several different procedures is crucial to obtain reliable measurements of GOM in air. Therefore, the evaluation and optimization of sampling procedures require preconcentration. Most commonly used preconcentration methods such as KCI impregnated denuders, KCI sorbent traps and KCl impingers pose various problems such as occurrence of artefacts, oxidation/reduction transformations, water vapour passivation and incomplete GOM retention — all combined resulting in biased measurements. Therefore, the evaluation and optimization of sampling procedures is crucial to obtain reliable measurements of GOM in air. The radiochemical tracer 197Hg (t1/2 = 2.673 d) presents an alternative to isotope dilution method (radiochemical tracer achieving considerably lower detection limits) in studying the calibration and potential transformations of different atmospheric Hg species that could occur during the conventional atmospheric mercury sampling. Mercury labelled with 197Hg was obtained by irradiation of 196Hg with thermal neutrons in the TRIGA Mark II research nuclear reactor at the Jožef Stefan Institute. Considering that 196Hg has a natural abundance of 0.15%, mercury enriched in the 196Hg isotope (51.58% 196Hg) was used to achieve higher specific activity of the 197Hg tracer, allowing the spike and measurements in the picogram range. The radiotracer activity was evaluated by means of HPGe well and coaxial detectors. GEM and GOM labelled with 197Hg were studied to get insight into above noted preconcentration methods at ambient spike levels, in particular specificity of trapping system and transformation processes between the species during preconcentration steps. Also, the GOM generators for calibration were assessed for low level ambient GOM and GEM measurements.

**F.O.1.12-5**

**COMPARISON OF METHODS FOR ACCURATE HG ISOTOPIC COMPOSITION IN ATMOSPHERIC BIOMONITORS (PINE NEEDLES, LICHENS, MOSSES): APPLICATION FOR HG ATMOSPHERIC MONITORING**

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Atmospheric biomonitor are characteristic of different integration times displaying useful information on the atmospheric contamination over various areas. Hg isotopic composition of three different bioaccumulators such as pine needles, mosses and lichens, was evaluated in terms of analytical methods validation/intercomparability and of specific isotopic information on atmospheric Hg inputs. In addition, Hg isotopic compositions were also investigated on selected sites (France, Germany) to assess their applicability for spatial and temporal studies. Different extraction methods were evaluated for biomonitor material solubilisation and are compared for both Hg isotopic composition accuracy and precision. Isotopic fingerprint of Hg allows to discriminate the fraction accumulate in each bioaccumulator according to their odd and even mass independent fractionation (MIF). For example, mosses seem to accumulate more Hg from precipitation with a MIF close to zero contrary to lichens mainly deriving Hg accumulation from the gaseous phase. This study demonstrated that pine needles, lichens and mosses or any bioaccumulators having different accumulation integration time combined with isotopic composition of Hg can provide complementary information about Hg atmospheric deposition mode and source apportionment in the environment.

**F.O.1.12-6**

**LABORATORY AND FIELD EVALUATION OF THE PERFORMANCE OF KCI-COATED DENUDERS IN MEASURING GASEOUS OXIDIZED MERCURY SPECIES**

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It has been known for many years that KCl-coated denuders, commonly used in manual and automated techniques for the measurement of Gaseous Oxidized Mercury (GOM) species, can suffer from serious bias and artifacts in the presence of atmospheric ozone (O3) and water vapor (H2O). The NOAA/Air Resources Laboratory has developed a permeation-based calibration system for GOM species, which allows for the efficient delivery of HgCl2 and/or HgBr2 without significant contamination by gaseous elemental mercury (GEM). This calibration system has been used with a Tekran mercury speciation system to systematically investigate the performance of KCI-coated denuders in both laboratory and field settings, in synthetic and ambient air matrices. This paper will present the results of this evaluation, with a discussion of matrix effects and potential improvements to the KCl-coated denuder technique for GOM measurements.
1.11B Methylation and demethylation of mercury – session to honor work of the late Dr. Mark Hines

F.O.1.11B-1

METHYLATION AND DEMETHYLATION ACTIVITY IN THE MERCURY CYCLING IN COASTAL WATERS (GULF OF TRIESTE, NORTHERN ADRIATIC)

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The Gulf of Trieste and adjacent Grado and Marano Lagoon (northern Adriatic Sea) are considered as an important “natural bioreactor” that can increase sedimentary methylmercury (MeHg) production by mobilizing the extensive mercury (Hg) pool as a result of historical (500 years) Hg mining and smelting activities in Idrija (NW Slovenia), the world’s second largest Hg mine. Even though the mine was definitely closed in 1995 the SoCa/Isonzo River system still delivers about 1.5 t of Hg to the gulf annually and the MeHg is elevated in this marine environment. Research conducted by late M.E. Hines showed that Hg is readily methylated and demethylated in marine, lagoonary and freshwater sediments but the relative activities varied greatly with locality. Methylation activity increased from freshwater to the marine sites, conversely the highest demethylation was found in estuarine and lagoon sites. The methylation/demethylation ratios were consequently low in coastal sites but increased in the gulf. Subsequent investigations in the southern, less contaminated (“pristine”) sediments of the gulf revealed that MeHg is also continuously produced especially in autumn in parallel with higher bottom water temperature and lower oxygen content. Sulphate reduction was found to control both processes. Hg methylation in sediments of coastal lagoon was controlled by rapid demethylation and the Hg bioavailability was affected by Hg adsorption and precipitation, In offshore marine sites, the sulphide produced by sulphate reduction lowers Hg methylation. Methylation of dissolved Hg, nearly 100% colloidally bonded, in the seawater column of the gulf was not detected (showing a pronounced Hg reduction potential) suggesting that sediments are the principal methylation site and the source of MeHg to the water column. It is likely that demethylation and reduction prevent the excessive accumulation of MeHg in the food webs of the Gulf of Trieste.

F.O.1.11B-2

BIOGEOGRAPHY AND EXPRESSION PATTERNS OF THE GENES INVOLVED IN METHYL/mercury DEGRADATION AND MERCURY REDUCTION IN THE GLOBAL DEEP OCEAN.

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Microbes are important drivers of biogeochemical processes determining the fate of mercury (Hg) in the aquatic systems. In particular, they have a relevant role on formation and degradation of methylmercury (MeHg) but also on the reduction of inorganic divalent Hg (HgII) to elemental Hg0. The recent discovery of the gene cluster involved in MeHg formation (hgCA/hgCB) has improved the knowledge on identity and metabolic features of the microbial community performing this process. Yet, little is known about the diversity and expression of the organisms involved in MeHg demethylation and HgII reduction, which are carried out by the merB and merA genes, respectively. Here, we explore the temperate global deep ocean metagenomes and metatranscriptomes of the Malapasiona 2010 circumnavigation from two different plankton size fractions (0.2-0.8 μm and 0.8-20 μm), commonly referred to the life-style of free-living and particle–attached microorganisms, respectively. By using multiple-specific hidden markov models (HMM), here we show the biogeography and expression patterns of merA and merB genes. Analysing the metagenomes, we observed that the abundance patterns of merA and merB responded to the life-style of the organisms, with higher abundance in the particle-attached size fraction, as well as to the oceanographic basin. Interestingly, the metatranscriptomes revealed that expression patterns of merA and merB genes differed with their corresponding abundances. For example, merA and merB expression patterns in the Canary Islands basin were significantly lower in particle-attached compared to the free-living fraction. Alteromonas and Pseudoalteromonas (Gammaproteobacteria) were important contributors to both the abundance and expression of merA and merB at a global scale. This study represents the first global deep ocean analysis of the merAB genes and transcripts and reveals the main players involved in the divalent-Hg reduction and MeHg degradation in the marine Hg biogeochemical cycle.

F.O.1.11B-3

PERIPHERY ASSOCIATED WITH MACROPHOTIES: ECOLOGICAL NICHE FOR MICROBIAL COMMUNITIES INVOLVED IN MERCURY TRANSFORMATIONS.

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(6)IPREM

Since 2012, a ban of consumption of predatory fishes was established in some natural freshwater lakes in southwestern France, even though no source of mercury (Hg) is known in this region. Understanding biogeochemical processes leading to Hg bioaccumulation and biomagnification in aquatic ecosystems is essential to assess the risk of this health hazard to humans and wildlife. Since periphyton associated with macrophytes accumulates metals through adsorption on inorganic and organic particulate matter, the vast diversity of microorganisms in such matrices can be a contamination source for food webs. However, macrophyte-microorganism associations are poorly documented in this region and more generally in temperate ecosystems. In this context, Hg dynamics in different compartments at the base of the food webs, particularly macrophytes, was investigated in order to identify the entry points of Hg in trophic chains. The highest (Car- cans-Hourtin, CH) and the lowest (Parentis-Biscarrosse) contaminated lakes in the study region were chosen. Both are eutrophic and represent high economic and leisure interests. There are subject to invasive macrophytes like Lagarosiphon major and Egeria densa, which cause damages to aquatic ecosystems and could interact with Hg biogeochemistry. At each lake, (1) Hg methylation and demethylation potentials in different compartments (water, different types of sediment, endemic and invasive macrophytes and their periphyton, cyanobacteria) were evaluated, (2) the microbial diversity associated to each compartment was assessed by a metabarcoding approach (MiSeq), (3) MeHg net production for each compartment was assessed at the ecosystem level. Incubations realized with stable isotopes of Hg (199Hg(II), Me201Hg) demonstrated for the two sites high Hg methylation and demethylation yields in plant roots and periphyton, whereas results for sediment and water were low to negligible. Cyanobacteria demethylated Hg
strictly (no methylation potential detected). The occurrence of functional groups involved in Hg methylation has been demonstrated in all compartments by 16S rDNA sequencing (Desulfobulbaceae, Desulfofobulbaceae, Syntrophobacteraeae, Desulfovibonaceae, Geobacteraceae). The relative abundance of these functional groups was higher in plants and periphyton than in sediment. These results suggested that the rhizosphere of aquatic plants (endemic or invasive) is a suitable micro-environment for the sulfate reducing prokaryotes contributing to Hg methylation. Sulphate concentrations in water, favoring the sulfate reducer activity and by extension here Hg methylation, seemed to be the main factor involved in the difference of Hg bioaccumulation. This hypothesis is thus retained to explain site-specific geochemical processes involved in Hg bioavailability and the difference in Hg biomagnification between lakes.

F.O.1.11B-4

MERCURY METHYLATION AND REDUCTION IN MARINE SYSTEMS USING THE HIGH SPECIFIC ACTIVITY RADIOTRACER 197Hg

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Mercury (Hg) methylation and reduction are key processes in Hg cycling in aquatic systems. The transformation of Hg+2, the most abundant Hg species in waters and sediments, to the neurotoxic species methylmercury (MeHg) in these aquatic compartments determines the Hg impact in biota at different levels of the trophic webs, and also in external consumers. On the other side, Hg+2 reduction to Hg0 in waters is a deproportionation process of the ecosystem by further Hg0 vapour evasion. A well known technique to evaluate Hg+2 reduction and methylation rates in laboratory experiments is the addition of a known amount of labelled Hg+2 to incubation setups, measuring the ratio of labelled Hg in the species produced respective to the spike. But two methodological aspects revealed crucial to obtain reliable results: high sensibility of the tracer to allow spikes at natural levels, and separation techniques that allow measuring very low concentrations of the Hg species produced with negligible contamination of the labelled Hg+2 spiked. The high specific activity 197Hg (T1/2=64.14 h) radiotracer showed excellent performance in the evaluation of Hg+2 methylation and reduction processes in marine environments. It was produced by irradiation of Hg targets enriched to 52 % in 196Hg (natural abundance: 0.15%) in a nuclear research reactor and evaluated in the Hg products by the X and gamma ray emissions with High Purity Germanium well analytiques et de Physicochimie pour l’Environnement et les Materiaux–CEMAGREF, 31057 Toulouse, France.

F.O.1.11B-6

MERCURY METHYLATION IS PROMOTED BY NUTRIENT INPUTS TO AN ALASKAN FEN-TYPE WETLAND WHERE PEAT INCUBATIONS SUGGEST A ROLE FOR SYNTROPHY IN METHYLATION

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Mercury (Hg) methylation is specified by the hgAC gene cluster which is present in many groups of anaerobic microbes. The contribution of specific microbial groups to methylmercury (MeHg) production and how methylation is affected by environmental constraints in the Arctic and subarctic remain to be understood. Climate change in these high latitude ecosystems may greatly impact MeHg production. To investigate this, we identified a nutrient gradient in a fen-type wetland near Fairbanks, AK, USA, that simulates warming-associated increased nutrient inputs. We collected samples for biogeochemical characterizations, microbial community and hgCA gene abundance analyses, and for the determination of methylation potentials (Kmeth) along this nutrient gradient. The results showed that the potential mercury methylation rates decreased with the age of the peatlands, being up to 53 times higher in the youngest peatland compared to the oldest. Mercury methylation in young mires was mainly driven by sulfate reduction, while methanogenic and syntrophic metabolism became more important in older systems. Also demethylation rates were highest in young wetlands, with a gradual shift from biotic to abiotic degradation along the chronosequence. Our findings reveal how metabolic shifts drive mercury methylation and its ratio to demethylation as peatlands age and advance our understanding of mercury dynamics in nature.

F.O.1.11B-5

SHIFTS IN MERCURY METHYLATION AND DEMETHYLATION PROCESSES ACROSS THE CHRONOSEQUENCE OF PEATLANDS

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Peatlands are globally important ecosystems where inorganic mercury is converted to bioaccumulating and highly toxic methylmercury, which causes severe impacts on wildlife and humans. Although biological mercury methylation has been known for decades, we still have an incomplete understanding of organisms and processes driving methylation in different environments. We hypothesize that the changes in the trophic status of peatlands across the chronosequence of peatlands will be expressed in the composition of their microbial communities and thus in their potential to form MeHg. Here we used experimental laboratory incubations of peat samples from a mire chronosequence (0-3000 years) with fundamentally different biogeochemical conditions to identify master controls of mercury methylation and demethylation. The results showed that the potential mercury methylation rates decreased with the age of the peatlands, being up to 53 times higher in the youngest peatland compared to the oldest. Mercury methylation in young mires was mainly driven by sulfate reduction, while methanogenic and syntrophic metabolism became more important in older systems. Also demethylation rates were highest in young wetlands, with a gradual shift from biotic to abiotic degradation along the chronosequence. Our findings reveal how metabolic shifts drive mercury methylation and its ratio to demethylation as peatlands age and advance our understanding of mercury dynamics in nature.
sites. Decreasing kmeth with distance from the nutrient input correlated with declined abundance of sulfate reducing bacteria (SRB), iron reducing bacteria, and syntrophs, suggesting a role in MeHg production. Addition of sulfate to peat incubations from an upgradient site stimulated methylation while the sulfate reduction inhibitor molybdate had no effect on kmeth. These results suggest sulfate limitation on methylation; such treatments did not affect kmeth in nutrient poor downgradient sites. While the addition of the methanogenic inhibitor BESA did not affect methylation, its addition together with molybdate significantly decreased kmeth. Together the results suggest that SRB metabolizing in syntrophy with methanogens contributed to MeHg formation nutrient-rich sites. Previously shown in laboratory incubations, this is the first demonstration of the role of syntrophy in Hg methylation in the environment where MeHg accumulates. Our results may serve as a model for predicting future MeHg accumulation as permafrost loss drives nutrient input and liberates Hg in Arctic and subarctic wetlands.

1.7D Sources and cycling of mercury in freshwater ecosystems and oceans

DISTRIBUTION OF HG IN LAKE SYSTEMS – CONIFEROUS VERSUS DECIDUOUS FOREST AND THE IMPORTANT ROLE OF HG SCAVENGING BY ALGAE

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Catchment characteristics such as organic matter (OM) quality, vegetation, erosion and leaching of mercury (Hg) from soils, as well as in-lake productivity are essential factors of influencing the natural variation of Hg accumulation in lakes. The importance of the role of Hg scavenging by algae and the general Hg mass balance in these systems are still poorly understood. In this multi-lake study, we aimed to assess the transport pathways of Hg from leaves to lake sediments to evaluate the role of Hg scavenging by algae. We investigated the effects of catchment vegetation (coniferous versus deciduous forest) on Hg fluxes from catchments to the lakes and analysed dissolved and suspended matter (SM) at six lake sites in Germany (Black Forest and Harz Mountains). Mean Hg concentrations in litterfall (0.14 ± 0.04 µg g⁻¹) and the soil organic horizon (0.25 ± 0.11 µg g⁻¹) varied moderately among the sites. High concentrations of dissolved organic carbon (13.7 mg L⁻¹) and dissolved Hg (7.9 ng L⁻¹) in the lakes and their in-flows were higher at the coniferous dominated sites compared to the deciduous sites (7.1 mg L⁻¹ and 3.3 ng L⁻¹, respectively). Higher Hg concentrations were also observed in the SM, derived from sediment traps (n = 13), at the coniferous sites (0.57 to 0.70 µg g⁻¹) compared to the deciduous sites (0.12 to 0.17 µg g⁻¹). In contrast, Hg accumulation rates show values up to eleven times lower in coniferous forest lakes compared to deciduous forest lakes (41 to 85 µg m⁻² y⁻¹) compared to deciduous forest lakes (113 to 442 µg m⁻² y⁻¹). The high Hg accumulation rates in the mesotrophic sites of the deciduous sites could not be explained by differences in atmospheric Hg deposition or catchment size. Trapped SM at the deciduous sites shows low mean carbon/nitrogen ratios (8.5 ± 0.7) and higher proportions of algae-derived polysaccharides and proteins, indicating that algae-derived OM dominates the SM in these lakes. Although the high sedimentation rate in the algae-dominated deciduous forest lakes may provoke dilution, the high observed Hg accumulation rates suggest surface water Hg scavenging by algae. This could be driving reduced Hg re-emission to the atmosphere by changes in the dissolution equilibrium, which in turn would reduce photochemical destruction of DOM-Hg complexes. Our results show that Hg scavenging by algae is a key factor for Hg sedimentation in productive lakes and may even surpass the effects of catchment vegetation for Hg fluxes to lakes.

F.O.1.7D-2

MERCURY CYCLING IN THE SALTMARSH OF THE PARKER RIVER WILDLIFE ESTUARY IN MASSACHUSETTS, US

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Among aquatic ecosystems, salt marshes are among the most productive and play an important role at the interface between land and sea ecosystems. They provide critical ecosystems services, and are important as sources and sinks for nutrients and contaminants. In this study, we aim to address the dynamics of mercury (Hg), an important global contaminant in the Great Marsh in the Parker River Wildlife Estuary in Massachusetts. This area, together with larger parts of New England, is known to be a hot spot of Hg contamination, with high Hg levels observed in the blood of birds and other wildlife. However, the reasons for these high Hg exposures are not fully understood. We collected samples of plants, soils and water to study the dynamics of Hg in the salt marsh ecosystems and its potential role as source to the estuary. One of our hypothesis is that salt marsh plants, which show a high primary productivity, absorb substantial Hg from the atmosphere and hence serve as an important source of Hg inputs to this estuary. We collected samples from the dominant plant species, to assess plant Hg concentrations and contributions to the estuary by litterfall and plant senescence. We find salt marsh Hg concentrations in the range of 3 to 16 µg kg⁻¹, lower than vegetation in adjacent forests and showing substantial differences among different plant types. In spite of lower plant Hg levels, salt marsh soils collected to a depth of 2 meters show very high Hg concentrations up to 850 µg kg⁻¹, which is several fold higher compared to levels observed in adjacent forest soils. Gradient sampling of tidal water in the saltmarsh show that tidal water is enriched in Hg compared to freshwater concentrations at the incoming stream and compared to low ocean water concentrations. Water sample data suggest a source of Hg from salt marsh soils to tidal waters, and relationships to salinity and auxiliary parameters such as organic carbon (DOC). Our work is a step towards addressing sources and sinks of Hg in the Parker River salt marsh ecosystems and towards understanding possible reasons for high biological Hg exposure in this area.

F.O.1.7D-3

THE INFLUENCE OF MICROPLASTICS ON MERCURY BIOGEOCHEMISTRY IN URBAN WATERWAYS

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Microplastics are an emerging contaminant that threatens the health of aquatic ecosystems. These small (<5 mm) fragments of deteriorated plastic absorb and concentrate contaminants before they are ingested by zooplankton, fish, marine mammals, and sea birds. Microplastics also host microbial biofilms which warrants the question – how do microplastics influence the biogeochemistry of adsorbed mercury? We quantified total mercury and methylmercury adsorbed to microplastics collected from two urban waterways in the United States, San Francisco Bay California, and Lake Erie near Cleveland, Ohio. Microplastics from San Francisco Bay had methylmercury concentrations similar to suspended particles collected from the same water. In Lake Erie, microplastic methylmercury concentrations were an order of magnitude less than suspended particles, and greatest near the mouth of the Cuyahoga River. Microfibers were found in the guts of whole fish obtained from commercial fisheries at both study sites, however, there was no correlation between microfiber abundance and mercury concentration in muscle tissue. Genetic material was extracted from microplastics to characterize microbial communities and search for mercury cycling genes (mer genes and hgAB). Finally, under controlled laboratory conditions, chemical transformation rates of mercury were determined for coastal seawater containing different size and concentration of microplastics.
UPTRA KINETICS OF METHYLMERCURY IN A FRESHWATER ALGA EXPOSED TO METHYLMERCURY COMPLEXES WITH ENVIRONMENTALLY RELEVANT THIOLS

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Cellular uptake of dissolved methylmercury (MeHg) by phytoplankton is the most important point of entry for MeHg into aquatic food webs. However, the process is not fully understood. In this study we investigate the influence of chemical speciation on MeHg uptake rate by the freshwater green microalga Selenastrum capricornutum. We used six MeHg-thiol complexes which have moderate but important structural differences and which are commonly found in the environment. Methylmercury cellular uptake rate constants were determined for all MeHg-thiol treatments and compared with the uptake rate constant for a control assay to which the thermodynamically less stable MeHg-Cl complex was added. Methylmercury concentrations were measured during 8 h exposure experiments in algal whole cells and intracellular fractions. Elevated amounts of MeHg associated with cells and higher MeHg uptake rate constants were found in the control compared to the thiol treatments. Furthermore, the results indicated that the uptake rate constants were lower in the MeHg-thiol treatments with larger complexed and more “branched” chemical structures compared to complexes with simpler structures. Our results are in line with uptake mechanisms involving formation of metal-ligand complexes at the cell surface prior to internalization. Combined with thiol content and speciation information in natural waters, the results from our study will contribute to improved predictions of MeHg uptake into the base of the aquatic food web and its further bioaccumulation in higher trophic levels.

GENETIC POTENTIAL REGARDING THE MERCURY CYCLING IN CONTAMINATED MARINE SEDIMENT IDENTIFIED BY METAGENOMIC ANALYSIS

CHUTIVISUT, Pokchat; RUNGKITWATANAKUL, Phatchaiya; MHUANTONG, Wutticha; CHAWALOESPONSITA, Nattawin; HONGPRAITH, Narapong; LOHWACHARIN, Jenyuk; GETWECI, Chiratthanak; DHANASIN, Phanakit; PHANICHTRAIPHOP, Phereasak; PUNYAPALAKUL, Pattiporn

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Contamination of mercury (Hg) is one of the major environmental concerns due to its harmful impacts on living organisms and the resulting bioaccumulation and biomagnification in the food chain. During mercury contamination, fate and transport of mercury can be governed by several factors, including the activity of indigenous microorganisms of the contaminated site. Various bacteria and certain archaea have been known to possess mercury detoxifying mechanisms by converting the harmful mercuric ion (Hg2+) to a more stable elemental mercury (Hg0) through a pathway encoding by mer operon. On the other hand, some microorganisms can form toxic organomercuric compounds, e.g. methylmercury, in a process called ionic mercury methylation. The information regarding the genetic potential of microorganisms in contaminated ecosystems is therefore crucial for the prediction of mercury fate and transport in that ecosystem, which include the process of mercury detoxification, mercury oxidation, methylation, and demethylation. This study investigated microbial mercury cycle in a contaminated marine sediment by exploring the genetic pool through metagenomic and 16S rRNA gene analyses. The obtained metagenome revealed the detection of a full set of major genes for mercury detoxification, which encodes mercuric reductase (merA), regulatory protein (merR), and mercury transport proteins (merT and merP). Furthermore, other supporting genes of the mer operon, encoding for proteins that assist mercury transport into cell (merC, merF, merE) as well as an additional regulatory protein (merD) were also identified in the metagenomic data. Gene responsible for demethylation, merB, was also detected, though with a lower relative abundance than merA. The major phyotypes of the mer-containing bacteria were mainly associated with Alteromonadales and Oceanospirillales, which included the ones related to Marinobacter, Alcanivorax, Halomonas, Idiomarina, and Pseudoalteromonas. These bacterial taxa were also affiliated with the dominant populations identified by 16S rRNA gene analysis. For mercury methylation, the genes encode for the pathway, hgCA and hgCB, were also screened, but could not be identified in the assembled metagenome. Genes for mercury oxidation, which convert elemental mercury to the ionic form, were detected in the dataset, which indicate the potential cycling of mercury between ionic and elemental forms. The metagenomic result of this study thus demonstrates the functional potential of in situ microorganisms in driving mercury cycle in this marine sediment, where it reveals the pathways of mercury detoxification, mercury oxidation, and demethylation of methylmercury.

ORAL ABSTRACTS ▪ ICMGP 2019 ▪ 14th International Conference on Mercury as a Global Pollutant ▪ September 8-13 2019, Krakow, Poland ▪ 97
2.3 Human Biomonitoring

F.O.2.3-1

BASELINE MERCURY DATA OF ARTISANAL AND SMALL-SCALE GOLD MINERS IN ZIMBABWE

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Background:
Artisanal and small-scale gold mining is becoming increasingly popular in Zimbabwe due to the worsening economic crisis which has resulted in rampant company closures, high unemployment rates of up to 95% and loss of livelihoods. Small scale formal and informal gold mining has presented the population with some economic respite. The use of mercury to extract gold from ore remains the technology of choice in this subsector.

Objective
To report the levels of mercury in miners as measured in blood, urine and hair samples from Zimbabwe and compare these human-biomonitoring parameters with the ones from previous studies.

Methods:
Over 200 Artisanal Small Scale Gold Miners (ASGM) were examined in March 2019 in Kadoma and Shurugwi in Zimbabwe. Blood, urine and hair samples were taken. The samples were analyzed using a DMA-80 AAS analyzer.

Results:
Compared to threshold levels the urine levels were the highest (max. 683 μg/l), followed by blood, and hair. Some miners still have levels of mercury well above international threshold limits. There is a trend over time that the exposure decreased.

Conclusion:
The baseline data of ASG-miners in Zimbabwe clearly shows, that a strong, solid and immediate governmental program is needed to reduce and replace mercury from mining sites.

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2.3 Human Biomonitoring

F.O.2.3-2

THE MERCURY CONTENT IN THE HAIR OF RESIDENTS OF THE VOLOGDA REGION (NORTHWEST OF THE EURASIAN PART OF RUSSIA)

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The population of the north-west of the European part of Russia is at risk of mercury accumulation in the body. In local water bodies, high values of mercury content in fish muscles were repeatedly recorded, which, in turn, are consumed by the population.

Using the biomonitoring method recommended by the World Health Organization, the mercury content in the hair of residents (n = 1643) in different areas of the Vologda region was determined. The mercury in the hair was determined on a RA-915M mercury analyzer. CRMs DORM – 4.

The average mercury content in the hair (mg/ kg) of the residents of the Vologda region is 0.445 (0.001 - 7.640). Maximum values of mercury content - 0.884 (0.001-7.640) were set in the hair of residents of rural western regions of the studied region, where high lakes prevail, high degree of waterlogging, unlike other areas (parts) of the region.

In rural settlements of the eastern part of the region, where there are no large lakes and wetlands, the average mercury content in the hair of people is 2.5 times lower — 0.367 (0.001 - 3.548) than from the western part of the region.

The minimum average mercury content is noted in the hairs of urban residents — 0.307 (0.001-4.056), where the consumption of wild local fish is insignificant.

Positive correlation dependences were established between the mercury content in the hair of people and their age (R²=0.43, p≤0.001) and the amount of fish in their diets ration (R²=0.45, p≤0.001). The content of mercury in the body increases with the amount of fish in weekly diet. About 10% of the population of the Vologda region have a mercury content in hair of 1 mg/kg and above. At the same time, people living in the west of the region had the maximum percentage excess (26.8%).

The average values of the amount of metal in the hair of residents of the studied region are comparable with the results of Calcutta, India, a coastal region in Naples, Italy. At the same time, the results of mercury content in the hair of residents of central Poland, the Czech Republic - 0.24, Germany, in northern India.

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F.O.2.3-3

THE TARDIVE HEALTH EFFECTS CAUSED BY METHYL-MERCURY POISONING AROUND MINAMATA.

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After exposure to methylmercury, no immediate health changes are apparent. Even in cases of very short exposure, as recorded in Iraq, at least sixteen days were necessary before symptoms appeared. In chronic cases, the latent period is supposed to be much longer. In 2009, we performed health surveys and examined residents in the polluted area around Minamata. We analyzed data collected on 973 people (age = 62.3±11.7), who had lived in the four polluted areas and had eaten the fish there, and a control group, consisting of 142 people (age = 62.0±10.5), most of whom had not lived in the polluted area. Symptoms and neurological signs were statistically more prevalent in the polluted areas.

In cases of pollution around Minamata, most of the residents had not previously had their mercury levels measured. Instead of such direct mercury pollution values, we used the frequency of fish ingestion as an indirect indication of methylmercury exposure. To estimate dose-response relationships, we calculated the scores of signs and symptoms for the frequencies of fish ingestion. In order to estimate the variation in latency period from exposure to mercury by exposure levels, we calculated the average year of onset and the average interval between the first symptom and the onset of each following symptom for the fish ingestion frequencies.

The average year of the first symptom is 1979.0 ± 14.8 in the Minamata Area, more than 10 years after the Chisso Factory stopped releasing polluted waste-water in 1968. The onset of the first symptom, muscle cramps, four-limb numbness, stumbling tendency, difficulty in fine finger tasks (13.2±12.7), stumbling tendency (14.3±13.5) and limited peripheral vision (17.2±13.3). The frequency of fish ingestion was closely related to the onset of symptoms. Increased fish ingestion gave shorter latency periods.

As the Central Nervous System (CNS) consists of millions of neurons, mild or moderate cases of methyl mercury poisoning damage only a small percentage of them. Therefore, symptoms of poisoning may not appear immediately. Also, due to the reconstructive plasticity of the CNS and allowing for ageing effects, tardive onset of symptoms can occur.
HUMAN BIOMONITORING DATA FROM THE NORTHWEST TERRITORIES (CANADA): FROM THE NORTHERN CONTAMINANTS PROGRAM TO ARCTIC MONITORING ASSESSMENT PROGRAMME.

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The Arctic Monitoring Assessment Programme (AMAP) is an intergovernmental effort to monitor and document trends in the Arctic region with respect to pollution and climate change. While the means is through the assessment of issues, the aim is to propose actions to reduce associated threats and to inform policy and decision-making processes. The synthesis of international results of mercury into AMAP assessments have contributed to the development and implementation of the Minamata Convention. Partnerships fostered among Canadian scientists and northern Indigenous communities have advanced AMAP assessments while attempting to address local needs and concerns. The environmental fate of mercury, regulated by complex biogeochemical cycles, can impact communities where country foods are integrated into the daily diet. In the Northwest Territories, Canada, elevated levels of mercury have been measured in locally caught fish, leading to a potentially significant route of mercury exposure. Since these regions are not included in national biomonitoring initiatives (i.e., limited human data were available), the Northern Contaminants Program supported the creation of a biomonitoring project among subarctic Indigenous communities. Biological sampling of hair, urine and blood was conducted. In addition, participants completed dietary questionnaires to estimate food consumption patterns as well as a survey to evaluate the awareness and perception of contaminants and health recommendations. The determinants of exposure levels were assessed and the human data were cross-linked with co-located environmental data. For the participants who chose to provide blood (n=276), 0.4% exceeded available health-based guidelines for blood mercury. Therefore, although fish in the region occasionally contain elevated levels of mercury, human exposure to mercury has generally remained low. In addition, the AMAP report could improve the dissemination of the hair mercury dataset (n=443), offering a comparison to other projects worldwide. The mercury data are relatively low when compared to those reported for other northern populations included in previous international assessments (e.g., AMAP 2015). However, climate change (e.g. permafrost, long-range transport) may increase environmental concentrations of mercury and these baseline levels will be critical to the assessment of temporal changes.

Local, regional, and national stakeholders were involved in the implementation of the project and dissemination of the results. However, the AMAP will contribute to knowledge dissemination at the international level. The next AMAP report, planned to be released in 2020, will inform on environmental health issue prioritization in the Arctic and the fate of mercury in the Arctic region.

MECONIUM: HG EXPOSURE BIOMARKER DURING PRENATAL PERIOD

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The general population is exposed to organic mercury (mostly as monomethyl Hg, MeHg) mainly through seafood consumption and to environmental Hg vapour released from dental amalgam fillings. The effects of chronic prenatal exposure to low levels of MeHg on child development remain controversial, with inconsistent conclusions; therefore, it is crucial to measure Hg in relevant exposure biomarkers, to minimise the possibility of misinterpretation. For population monitoring purposes Hg in hair and blood are most commonly used biomarkers to assess MeHg exposure. Meconium, as a uncommon biomarker of exposure, can be obtained easily and noninvasively after birth and presents wider window of exposure in the foetus during gestation, presumably from the 12th week of pregnancy onward.

The aim of this study was to measure total Hg (THg) and MeHg concentrations in meconium in a general population exposed to low-to-moderate levels of Hg through seafood consumption and/or amalgam fillings. Mothers from coastal Croatia (n=234) and central Slovenia (n=571) and their new-borns (n=210, N=435, respectively), participants of EU project PHIME, were included in the study. We used existed data set of personal and lifestyle characteristics, THg in maternal hair, THg and MeHg in maternal blood and cord blood. We analysed THg (N=488) in meconium using Direct Mercury Analyser, Milestone, USA) and cold vapour atomic absorption spectrometry (CVAAAS; Model Hg-201. San-so Seiaskusho Co., Ltd., Japan); and MeHg (N=349) by CV atomic fluorescence spectrometry (CVAFS; Tekran 2700, Canada). Inorganic Hg (IHg) levels were calculated by subtracting MeHg from THg. Geometric means of THg in maternal and in cord blood were 2.05 ng/g and 1.90 ng/g, respectively. In average, MeHg presented 70% of THg in maternal blood and 86% in cord blood with considerable range of 4-100% (CV=32%) for maternal and 8-100% (CV=20%) for cord blood. On the other hand, MeHg in meconium presented 0.89% (range: 0.01-18.3%, CV=119%) of THg. Percentage of meconium MeHg was correlated with: maternal hair THg (Rs=0.585; p<0.001); maternal blood MeHg (Rs=0.609; p<0.001); cord blood MeHg (Rs=0.590; p<0.001); seafood intake (Rs=0.324; p<0.001); pre-pregnancy BMI (Rs=-0.137; p=0.01); child gestational age (Rs=-0.147; p=0.016); and sex (Rs=-0.231; p<0.01). We assume that some demethylation processes may take place in foetus or amnion fluid and trigger slow accumulation of IHg in meconium during pregnancy. However, some IHg amounts can also arise from HgO oxidation and Hg(II) accumulation during gestation. The mechanism behind is not fully understood and further research is needed.

COMPARATIVE STUDY OF HUMAN EXPOSURE TO MERCURY IN RIPARIAN COMMUNITIES IN THE BRAZILIAN AMAZON

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Traditional gold mining, in addition to deforestation and damming of rivers, are the major causes for mercury pollution in Amazonian environment. Riverine communities in the Amazon are chronically exposed to mercury mainly through occupational and diet exposure. One special case of interest is the Tapajós River basin, a major tributary of the Amazon River and one of the largest regions dedicated to gold mining. The analysis of riparian communities in the Tapajós area offers a unique model to study human exposure to mercury of anthropogenic origin. Moreover, two dams are planned in Tapajós area that could in-
fluened mercury cycle and human exposure. The increasing number of dams on the rivers of the Amazon rainforest has also a great impact in the environment and human health of the riverside populations of the Amazon. Concretely, our studies revealed that human populations living near the Tucurui Dam, the fifth largest dam in the world, have been considerably affected by mercury exposure even though this area is not impacted by mining activities using mercury. Therefore, this study is focused on the evaluation and comparison of human exposure to mercury in different areas of the Brazilian Amazon, which is an issue of current concern due to the alarming mercury levels recently reported. For this purpose, mercury species and total mercury and selenium concentrations in human hair and some biochemical parameters in blood were determined in more than 900 individuals from both Tapajós River basin and Tucurui Dam areas. Significantly higher concentrations have been found in communities from Tucurui than in Tapajós. The medium level of total mercury in hair in both areas has been below the tolerance limit (10 µg/g) recommended by the international organizations. However, in Tucurui around 40% of individuals have presented concentrations above this limit, indicating a high risk for the population. In addition, statistically significant differences were found between gender with higher levels in men, whereas mercury concentrations do not seem to depend on age. The relationships between total mercury and selenium concentrations in hair have also been studied. The results of this work, which is the largest epidemiological study ever performed in the Amazon, confirmed the need for continuous monitoring of the impact of large-scale projects in this region, which will assist in the development of prevention strategies and government actions to face mercury pollution in the Brazilian Amazon.

2.5 Genetics, gastrointestinal and nutrient factors impaching effects and uptake of Mercury

F.O.2.5-1

GUT MICROBIOME CHARACTERISTICS ASSOCIATED WITH VARIATION IN METHYLMERCURY METABOLISM AND ELIMINATION IN HUMANS FOLLOWING FISH CONSUMPTION

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The slow elimination rate, or long biological half-life, of methylmercury MeHg in humans (kel ~0.014 days⁻¹ or t1/2~ 50 days) directly influences Hg accumulation in the body. Studies have shown wide variation in MeHg elimination with t1/2 ~30 to >120 days. Recent findings show that MeHg elimination rate in an individual can vary significantly over time and, furthermore, is slowed with exposure to antibiotics. Animal studies support a role for gut microbiota in the biotransformation (demethylation) of MeHg to inorganic Hg (iHg), which precedes efficient Hg excretion via feces. The role of the human gut microbiome in MeHg metabolism and elimination is less well understood. In 37 human subjects, previously characterized for their MeHg elimination kinetics after fish consumption, we examined the relationship of MeHg elimination rate with MeHg demethylation activity associated with the gut microbiome. Demethylation in vivo was assessed by speciation of total (tHg) and iHg measured in fecal samples. Across the cohort, the degree of demethylation positively correlated with rates of MeHg elimination. Using 16s rRNA sequence analysis, we find that global characteristics of microbial taxa diversity and abundance do not correlate with MeHg demethylation or elimination rates. However, a number of individual taxa show relative abundance that does correlate with either MeHg demethylation activity and/or elimination rate, including Bifidobacterium bifidum, a common probiotic species in the gut. Our findings point to a central role of the gut microbiome in mediating MeHg demethylation and elimination kinetics in people.

F.O.2.5-2

MONOMETHYL MercURY DEGRADATION BY THE HUMAN GUT MICROBIOTA IS STIMULATED BY PROTEIN AMENDMENTS

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Mercury (Hg) is considered by the World Health Organization as one of the top ten chemicals of major public health concern. Its organic form, monomethylmercury (MMHg), poses the highest risk as it can be biomagnified in aquatic systems resulting in elevated exposure among fish and rice consumers. The gut microbiome was identified as a potential factor for the variations among individuals in Hg uptake. However, little is known about the role of gut microbiota in the gastrointestinal tract on Hg transformations and bioavailability. Current literature has shown that the human gut microbiome can demethylate MMHg, however, no known demethylating genes or microbial guilds have been identified. Our goal is to determine if the alteration of the gut microbiome by diet amendment would alter MMHg demethylation. Using a series of batch experiments, we evaluated the effects of changing composition of the culture media (by altering relative abundances of carbohydrate or protein) on Hg metabolism and the gut microbial community structure of fecal extract collected from two volunteers. We measured Hg methylation and demethylation rates using stable isotope tracers and conducted high throughput 16S rRNA amplicon sequencing to determine the microbial community structure. We observed >90% decrease in initial MMHg concentration in protein-rich treatment mixed with the fecal slurry of individual A; individual B gut microbiota did not exhibit such demethylation trend. No methylation was observed in any treatments. We followed up this experiment by mixing in different ratios of the fecal microbiota of individual A and B. The MMHg demethylation phenotype was conserved, suggesting individual A contains microbes that are responsible for MMHg demethylation that individual B does not possess. Lastly, to identify microbes involved in demethylation, we performed a series of biochemical assay using inhibitors of 2 known demethylation reactions (i.e., sulfate reduction, methanogenesis). None of the inhibitors tested prevented demethylation indicating a new mechanism is involved. Our results indicate that the gut microbiome of individual A contains microbes required for demethylation of MeHg that individual B lacks. A comparative metagenomic analysis between the different nutritional amendment and individuals is underway. Our results are important in the understanding of the mechanisms for MMHg demethylation in the human gut and the variations in MMHg absorption and toxicity.

F.O.2.5-3

MERCURY EXPOSURE SEVERELY DISRUPTS TRANSPORT OF SelenIUM ACROSS THE TISSUES OF ZEBRAFISH LARVAE AND PREVENTS RESTORATION OF SelenIUM AND SelenOPROTEIN FUNCTIONS IN AFFECTED ORGANISMS

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Mercury compounds are among the most toxic non-radioactive substances in the biosphere, and a significant part of their toxicity may be due to inactivation and depletion of selenium and the selenoproteome in living organisms. Selenium and selenoproteins are essential for redox balance in cells and tissues as well as the metabolism of thyroid hormones which regulate a range of biological processes in vertebrates.
including energy metabolism, development and neurological functions. Disruption of selenoproteome function can therefore lead to severe health consequences ranging from fatigue and memory loss to premature death. Mercury has a very high affinity for selenium including the selenocysteine of selenoproteins, leading to fast and irreversible inactivation of these proteins. Using zebrafish larvae as a model vertebrate, we showed that acute exposure to inorganic mercury leads to complete shutdown of selenium transport into and out of cells, making restoration of normal selenoprotein functions impossible. Methylmercury exposure led to partial but significant inhibition of selenium transport. We also found that inorganic mercury inhibited selenoprotein-dependent production of thyroid hormones, and that this effect could not be reversed by selenium treatment following mercury exposure. These findings provide a new perspective on the mechanism of mercury toxicity for biological organisms, and pose an additional question on food safety of high mercury fish.

THE INVERSE ASSOCIATION BETWEEN METHYLMERCURY AND DISEASE ACTIVITY IN SYSTEMIC LUPUS ERYTHEMATOSUS PATIENTS IS EXPLAINED BY N-3 POLYUNSATURATED FATTY ACIDS FROM FISH CONSUMPTION.

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Mercury (Hg) is a proposed environmental factor in the pathogenesis of systemic lupus erythematosus (SLE). Humans are exposed to Hg in the form of methylmercury (MeHg) from fish consumption and in the form of elemental Hg0 from dental amalgams. Fish are also a source of n-3 long chain polyunsaturated fatty acids (LCPUFA) which are suggested to be beneficial in the management of SLE. This study assessed the relationship between markers of Hg exposure (hair Hg, urinary Hg, and dental amalgams) with disease activity and disease associated damage in SLE patients, controlling for the potential modifying factor n-3 LCPUFA status. Hair and urine samples were collected from 48 SLE patients to assess exposure to MeHg and Hg0, respectively. Patients were assessed for disease activity and disease associated damage using four indices; the British Isles Lupus Assessment Group (BILAG) index, the Systemic Lupus Activity Measure (SLAM), the Safety of Estrogens in Lupus Erythematosus National Assessment Systemic Lupus Erythematosus Disease Activity Index (SELENA SLEDAI) and the Systemic Lupus International Collaborating Clinics/American College of Rheumatology (SLICC/ACR) damage index. Standard multiple regression identified a significant inverse relationship between hair Hg and BILAG (β= -0.316, p = 0.042, 95% confidence interval (CI): -0.603, -0.012) and between total serum n-3 LCPUFA and BILAG (-0.290, p = 0.058, 95% CI -0.574, -0.001). There was no association between urinary Hg or dental amalgams and any measure of disease activity or disease associated damage. Findings from this study suggest that the beneficial effects of n-3 LCPUFA outweigh the detrimental effects of MeHg in SLE patients. Furthermore, low level Hg0 exposure from dental amalgams was not associated with disease activity or damage in SLE.

A NEW INSIGHT INTO METHYLMERCURY (MEHg) ACCUMULATION PROCESS IN RICE GRAIN: EVIDENCE FROM PRIMARY AMINO ACIDS

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The accumulation of MeHg in rice grain receives considerable concerns in last decades because the intake of MeHg-laden rice poses a big health risk to the rice consumers. Rice has been shown to accumulate MeHg 2 to 3 magnitudes higher than other crops. Although many efforts have been done to investigate the underlying mechanisms of MeHg accumulation in rice, a knowledge gap of how MeHg was accumulated by the rice grain still remained to be addressed. A well-recogized finding is that MeHg was firstly accumulated by the stalk and leaf of rice plants during the rice growing season, and it was ultimately translocated to rice grains with unknown molecular during the rice filling stage. We hypothesized that primary amino acids, particularly cysteine might play a critical role in MeHg translocation process in rice tissues. To verify this hypothesis, we took 15 rice plant samples together with their paired soils cross a Hg pollution hotspot -Wanshan Hg mine, in China, and analyzed THg, MeHg contents, as well as 17 primary amino acids contents in the roots, stems, leaves, and grains of rice plants. The key results showed that rice grain contained the highest contents of total primary amino acids, followed by leaves, roots and stems. We found a significant positive between cysteine and MeHg (r=0.46, p<0.0001)/THg (r=0.30, p=0.02), suggesting a critical role cysteine may be a potential drive for MeHg and THg accumulation in rice plants. Therefore, it can be inferred that the transport of MeHg in rice is related to cysteine. MeHg may be transported to rice together with cysteine and the accumulation of MeHg in rice depends on the concentration of cysteine in rice.

RISKYVERSUS BENEFICIAL: MERCURY AND POLYUNSATURATED FATTY ACIDS IN FISH IN CHINESE RESERVOIRS AND SWEDISH LAKES ACROSS A RANGE OF TROPHIC STATUS

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Fish mercury (Hg) bioaccumulation contrasts greatly in Sweden and China, with generally lower methylmercury (MeHg) contents in fish from China than Sweden, although aqueous MeHg concentrations are very similar. We ask how the discrepancy in Hg bioaccumulation is coupled with differences in physiologically required long-chain polyunsaturated fatty acids (PUFA) in fish. We sampled freshwater omnivorous fishes from 7 oligotrophic to mesotrophic Swedish lakes and 2 eutrophic Chinese reservoirs to investigate their total Hg, MeHg, and PUFA contents. Omnivorous fish total Hg and MeHg bioaccumulation in Swedish lakes increased with increasing fish length (R2=0.55, p<0.0001), but it was decreasing with increasing fish length (R2=0.53, p=0.01) in omnivorous fishes from Chinese reservoirs. The PUFA contents, especially linoleic
3.4 Novel remediation, Control Technologies and ASGM Practices

F.O.3.4-1

BARRIERS AND SUGGESTED SOLUTIONS TO REPLACE THE USE OF MERCURY IN ARTISANAL GOLD MINING

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Worldwide, the number of artisanal gold miners (AGM) is an increasing with over 20 million people directly involved in more than 80 countries, producing around 400 tonnes of gold/a. The amount of mercury released is also increasing and close to 1500 tonnes/a. This presentation assesses social, economic, political and technical barriers to transform artisanal gold miners into Hg-free responsible-formal small miners and propose solutions. In first place it is important to characterize that solutions for micro-miners (processing <2 tonnes per day of ore) are not quite the same as for small miners processing from 2 to 200 tpd. Secondly, most of the gold deposits found by AGM are now on the hands of large conventional mining companies, as small miners do not have resources to deal with the bureaucratic process of legalizing the gold deposits they have discovered. Thirdly, the investment (CAPEX) for a Hg-free plant ranges from US$/20,000/tpd (for 200 tpd) to US$/13,000/tpd (for 0.2 tpd). Even using different and affordable pieces of equipment, sometimes is economically convenient for miners to use the existing processing centers to amalgamate the whole ore. Artisanal gold miners do not have credits in banks to raise capital for their own processing facility and without funds and training the use of mercury in the toll-milling processing center is the only alternative. The short term suggested solutions to deal with Hg problems are: 1) Before eliminating Hg use... reduce it; 2) Enforce the law against those importing, smuggling, and selling mercury; 3) Identify the main pollutants (processing centers); 4) Stop amalgamation of the whole ore; 5) No amalgams must be burned in populated areas; 6) Better techniques must be demonstrated to miners to convince them that amalgamation has low gold recoveries; 7) No cyanidation of Hg-contaminated tailings allowed; 8) Awareness campaigns to show the impacts of atmospheric Hg.

F.O.3.4-2

SYNERGISTIC OXIDATION OF ELEMENTAL MERCURY AND NO IN THE OXIDATION SECTION OF THE FAST SELECTIVE CATALYTIC REDUCTION PROCESS

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Coal-fired power plants are the main sources of anthropogenic mercury emission. In the coal-fired flue gas, elemental mercury (Hg0) is difficult to be controlled due to its high volatility and low solubility. The selective catalytic reduction (NO-NH3 SCR, denoted as “standard SCR”) DeNOx unit in coal-fired power plants is obtained as co-benefit of Hg0 oxidation. During the oxidation process, the Hg0 will be converted to soluble Hg2+. Nevertheless, in the standard SCR reaction (NO+NH3+1/4O2=N2+3/2H2O), NO adsorption on the commercial SCR catalyst is usually weak at the typical reaction temperature and atmosphere. Accordingly, the promotional effect of NO on Hg0 oxidation is always negligible. In addition, the NH3 will inhibit the Hg0 adsorption and oxidation, because the NO reduction and Hg0 oxidation reactions occur in the same reactor. Therefore, we investigated the Hg0 oxidation behavior in the fast SCR process with higher NOx removal efficiency. In this process, the reaction can be divided into two distinct steps: NO catalytic oxidation (NO + 1/2O2 = NO2) in one reactor and NOx–NH3 SCR (NO + NO2 + 2NH3 = 2N2 +3H2O) in the other separate reactor. In the NO oxidation reactor, there is no NH3 in the flue gas. In the present study, Hg0 oxidation behavior in the NO oxidation step of fast SCR process was investigated. The Mn doped CeO2-ZrO2 was selected as the catalyst, due to its superior oxygen storage capacity. The results showed that NO could be oxidized efficiently over the catalyst within the temperature around ~250 °C. In the Hg0/NO2/N2 reaction system, Hg0 had negligible effects on NO oxidation efficiency, however, NO exhibited remarkable promotional influences on the Hg0 oxidation efficiency. Two domination reaction pathways were proposed to interpret the positive influence. One route for the influence of NO on Hg0 oxidation was a heterogeneous oxidation process. In this way, the NO was adsorbed on the active sites and activated by the surface oxygen to form more active intermediates for Hg0 oxidation and Hg0 was probably oxidized in its gaseous state. The other route for the influence of NO on Hg0 oxidation was a homogeneous reaction. In this route, the gaseous NO2 generated by NO oxidation could oxidize the gaseous Hg0 within the designed reaction conditions. According to the present research, synergistic oxidation of NO and Hg0 in the first step of fast SCR seems a promising way to remove Hg0 and NOx in coal-fired power plant.

F.O.3.4-3

COMPARATIVE STUDY ON REMOVAL EFFICIENCY OF MERCURY BASED ON DIFFERENT DUST REMOVAL TECHNOLOGIES IN THREE ULTRALOW EMISSION COAL-FIRED POWER PLANTS IN CHINA

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China, as the top producer and consumer of coal in the world, mercury pollution emitted from coal-fired power plants (CFPPs) has attracted global attention due to long-range transportation and deposition. Migration and emission characteristics of mercury in three 300 MW level ultralow emission (ULE) CFPPs equipped with different dust removal technologies were studied based on the Ontario Hydro Method (OHM). Air pollution control devices (APCDs) installed in the tested CFPPs are selective catalytic reduction (SCR) + electrostatic precipitators (ESP)/fabric filter (FF)/ESP&FF + wet flue gas desulfurization
(WFGD) + wet electrostatic precipitators (WESP). Field measurements based on OHM were conducted simultaneously at the inlet and outlet of each APCDs. By passing dry dust collectors, the order of average total mercury removal efficiencies is ESP&FF (94.45%) > FF (89.69%) > ESP (88.51%), which depends mainly on the capture efficiency of dust. Through WFGD combined with ESP, FF, and ESP&FF, the synergistic removal efficiency of mercury is 96.90%, 98.67%, and 98.36%, respectively. However, there is no obvious change in the synergistic removal efficiency of total Hg after WESP. Oxidized mercury (Hg2+), elemental mercury (Hg0), and particle-bound mercury (HgP) are investigated through each APCDs. The results showed that Hg2+ was the main form of mercury after dry dust collectors with the range of 63.28%-91.64%. After WFGD, Hg2+ was effectively removed, thus Hg0 dominate the form of mercury with the range of 66.65%-82.91%. The mass concentrations of Hg2+, Hg0, and HgP accounted the total mercury after WESP are at the range of 11.51%-37.94%, 61.60%-87.58%, and 0.46%-3.32%, respectively. Average mercury mass concentration emitted into the atmosphere was much less than the regulatory limit of 30 μg/m3 in Chinese CFPPs. Mercury emission factors calculated in this study were 0.005-0.011 g/t of coal. Actually, contamination of mercury in the process of utilization and disposal of fly ash, gypsum, and desulfurization wastewater should be given more focus.

Keywords: Mercury; Removal Efficiency; ULE CFPPs; Air pollutant control devices (APCDs).

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F.O.3.4-5

MERCURY USE BY ASGM IN AFRICA: AN EVOLVING LANDSCAPE, WHICH REQUIRE BUSINESS SOLUTIONS FOR MERCURY REDUCTION

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Despite rises and falls in the price of gold (Au) over the past decade, gold production by Artisanal and Small-scale Gold Miners (ASGM) in Africa has surged, providing mining populations with opportunities for SME development, poverty alleviation, and bolstering economic resilience in rural areas. ASGM exists in nearly every country on the continent, and evidence of gold production increases are not hard to find, despite the industry’s reluctance to share production and trade quantities. Many ASGM production networks (business-models) continue to rely on mercury for processing gold, and safer mercury use must be prioritized. Key enablers for increased production have included an increase in semi-mechanized mines, as well as increase in processing sites where cyanide (CN) is used for smelting with cyanide (CN) which enable operators to process tailings with little effort, and to exploit lower grade gold deposits. Unfortunately these operations come with grave health and environmental risks including mobilizing mercury (Hg) present in tailings from ASGM operations, that are re-processed with CN.

This paper (and presentation) will present new estimates of gold production and mercury use by ASGM in Africa, by highlighting specific examples and active developments in ASGM from several countries in Africa. The gold production model is based on production estimates from: 19 productive countries for which multiple citations (2015 or younger) have been used to triangulate Au production estimates. Following presentation of this conceptual production model, an analysis of gold production methods will be used to present a new mercury emission estimate from ASGM in Africa. Finally, a discussion of ASGM business models will be provided to highlight how mercury users remain vulnerable and lacking alternatives. This discussion will include a presentation of pilot projects currently underway to support ASGM groups to move away from reliance on mercury amalgamation. Past failures, current challenges and promising developments will be shared, including Pact’s current work to support new business models in ASGM communities, including through the deployment of shaking tables (through partnership with mining equipment manufacture Mount Baker Mining and Metals), which is followed by ‘direct smelting’ of the mineral concentrates from the shaking table – to produce a tradeable gold doré.

F.O.3.4-6

IMPROVING THE CHARACTERIZATION OF MERCURY USE IN ARTISANAL AND SMALL-SCALE GOLD MINING: LESSONS FROM MINAMATA CONVENTION NATIONAL ACTION PLANS

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Mercury amalgamation is a common technique used in artisanal and small-scale gold mining (ASGM) throughout the world. The ASGM sector is the largest global source of anthropogenic mercury releases, contributing to the global pool of mercury as well and to immediate impacts on human health and the environment in mining areas. Recognizing this and the imperatives of the Minamata Convention on Mercury (MCP), a research project to develop a reliable method for the analysis of mercury use in ASGM operations was undertaken. The study prepared a high SO2 resistant catalyst for mercury oxidation and NO reduction. The research and development will be conducive to the mercury oxidation application in actual coal-fired flue gases.
nizing the importance of the sector, the drafters of the Minamata Convention on Mercury added an obligation for all parties with more than insignificant ASGM to develop and implement ASGM National Action Plans, which must include, inter alia, baseline estimates of the quantities of mercury used and the practices employed in ASGM. Over 30 countries are currently developing or have completed ASGM National Action Plans, including 24 implemented by the United Nations Environment Programme (UN Environment). Through the use of tools such as the Baseline Estimates Toolkit and the MapX platform, and through training provided by UN Environment and others, many of these countries have completed improved characterizations of their ASGM sector. The improved understanding of the sector will allow them to better craft strategies to reduce, and where feasible, eliminate, mercury use. And improved estimates of mercury use will contribute to global mercury release inventory efforts and spatial modeling of mercury transport and fate in the environment. However, due to the informal, rural, and distributed nature of ASGM, challenges remain and uncertainties in baseline estimates of mercury use are still relatively high. Improved tools, as well as continued training and capacity-building are necessary to ensure that ASGM countries are able to create reliable baseline estimates as well as future estimates to measure progress in reducing mercury use in ASGM.
M.P.1.1

MERCURY WET DEPOSITION DIFFERENCES BY PRECIPITATION TYPE AT REMOTE ISLAND, MOUNTAIN AND URBAN SITES IN SUBTROPICAL EAST ASIA

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A nation-wide mercury (Hg) wet deposition monitoring network, consisting of 11 sampling sites in the main island of Taiwan and a remote island site in subtropical Northwest Pacific Ocean, was established to collect weekly rainwater samples for total Hg analysis since 2009 and is still ongoing. Few recent studies indicate that Hg wet deposition is influenced by precipitation type, usually higher Hg concentrations and/or depositions associate with thunderstorms. Using 6 years (2010-2015) of wet Hg deposition measurements collected at a remote island site (Pengjiayu) in Northwest Pacific Ocean and 2 sites (Anbu and Taipei) in northern Taiwan, we explored and reported here the effect of precipitation type on Hg wet deposition in subtropical East Asia region. Taipei is an urban site and Anbu is a mountain site inside a national park near the city of Taipei. Six-year volume-weighted mean (VWM) concentrations of rainwater Hg were 7.77, 10.01 and 10.60 ng L\(^{-1}\) at Pengjiayu, Mt. Bamboo and Taipei, respectively. Average annual wet deposition fluxes were 11.89, 41.24, and 26.03 μg m\(^{-2}\) yr\(^{-1}\), respectively. Much higher wet Hg deposition flux at Anbu was because of much higher rainfall amount (4549 mm) compared to Pengjiayu (1662 mm) and Taipei (2369 mm). Wet deposition events were classified into 7 precipitation types, including frontal system in spring (FS), circulation associates with high pressure in spring (HS), Pacific high pressure in summer (PH), typhoon (TP), low pressure in southern China or the Pacific high pressure in winter (PHW), and northeast monsoon flow (NE). Because of notable surface heating under the influence of strong convection. The highest VVM concentrations of rainwater Hg were associated with the PH precipitation type at all the sites, with values of 18.35, 16.34, and 17.39 ng L\(^{-1}\) at Pengjiayu, Anbu and Taipei, respectively. This is possibly due to the scavenging of gaseous oxidized Hg (GOM) from above the mixing layer by convective precipitation in summer.

M.P.1.2

GAS-PHASE MERCURY PHOTOREDUCTION IN THE ATMOSPHERE: A MODEL STUDY

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Atmospheric chemistry plays an important role in cycling of mercury (Hg) in the atmosphere defining the character of its dispersion from emission sources and deposition to terrestrial and aquatic ecosystems. Mutual transformations of long-lived elemental Hg (Hg0) and short-lived oxidized Hg forms (HgII) in gaseous phase, aqueous phase of cloud water as well as at various surfaces affects both total residence time of Hg in the atmosphere and its long-range transport potential. In spite of significant improvements in understanding of Hg oxidation and reduction mechanisms, current knowledge on Hg atmospheric chemistry remains incomplete. The newly found pathways of Hg0 oxidation by atomic Br with participation of various secondary oxidants (e.g. OH, Br, BrO, NO\(_2\), HO\(_2\)) expect relatively short life-time of Hg0 with respect to oxidation that conflicts with observed low variability of Hg0 concentration in the low atmosphere. It implies necessity of existence of HgII reduction channel, which nature has been unknown for a long time. Recently suggested photoreduction mechanism through the gas-phase HgII photolysis allowed explaining the measurement-constrained Hg0 levels and the life-time as well as demonstrated strong impact on Hg dispersion and deposition. The current study is focused on further evaluation of the reduction mechanism and its importance for Hg global cycling in the atmosphere. For this purpose a global chemical transport model (GLEMOS) is applied to perform a number of sensitivity runs with various configurations of the chemical scheme. The modelling results are evaluated against numerous Hg0 and HgII measurements. The analysis includes evaluation of different pathways the photoreduction mechanism and its effect on Hg concentration and deposition patterns, seasonal variation, long-range transport and deposition to various ecosystems.

M.P.1.3

ATMOSPHERIC MERCURY DAILY INTERCHANGE OF PLANTS IN ABSORPTION AND DESORPTION CYCLES.

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Mercury exchange at the plant leaf-atmosphere interface is an important issue when considering vegetation as a sink or source. The aim of this work was to clarify this process by studying Hg exchange under laboratory conditions with a plant model, Epipremnum aureum, under contrasting conditions of presence of gaseous mercury (both polluted and background environments), inducing in the plant a behaviour like sink or source of gaseous mercury. The experiment offer data about Hg exchange at the foliar surface, micrometeorological parameters and stomatal conductance, in order to a complete comprehension of the foliar mercury exchange. The results of the study showed different rhythms for the two processes, i.e., slower for desorption (14–196 ng m\(^{-2}\) d\(^{-1}\)) than for absorption (170–1341 ng m\(^{-2}\) d\(^{-1}\)). Desorption processes appeared to be more complex in a daily cycle, showing maximum desorption rates when stomatal conductance was high, but also during nocturnal hours and periods where Hg exchange values tended to absorption values in the mornings. Absorption processes seems to be the simplest, showing daily exchange values of absorption coincidental with positive values of stomatal conductance and null values during nocturnal hours. The main factors involved in desorption were stomatal conductance and temperature, but other factors may need to be considered. The absorption process only involves total gaseous mercury, stomatal conductance and relative humidity. A net balance of the two experiments offers data on the amount of Hg per unit leaf area (167 ng m\(^{-2}\) for desorption and 9213 ng m\(^{-2}\) for absorption), which supposes a total amount of 23 ng of mercury desorbed and 1280 ng (167 ng m\(^{-2}\) for desorption and 9213 ng m\(^{-2}\) for absorption), which supposes a total amount of 23 ng of mercury desorbed and 1280 ng absorbed during the whole experiment. Finally, the reversible/non-reversible characteristic of the Hg exchange process must be reconsidered bearing in mind that Hg within the leaf can be emitted if the changes in ambient conditions are appropriate to favour this process.

M.P.1.4

OBSERVATION AND SIMULATION OF GASEOUS OXIDIZED MERCURY (GOM) DRY DEPOSITION AT AN URBAN SITE IN NANJING, CHINA: INFLUENCE OF HETEROGENEOUS MERCURY OXIDATION

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Mercury (Hg) is regarded as a global pollutant with its notorious neurotoxicity, persistency and bioaccumulation effect. The three major forms of atmospheric Hg include gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate-bound mercury (PBM). The
oxidation process from GEM to GOM and the deposition process of GOM are crucial to the bioavailability of atmospheric Hg. In this study, we focus on GOM dry deposition at an urban site (NJU) in China. The surrogate surface (SS) method using cation exchange membrane (CEM) was adopted for the direct measurements of the GOM dry deposition fluxes from July 2018 to January 2019 with a time resolution of 1–2 weeks. The concentrations of GEM, GOM and PBM were simultaneously measured by TekranTM 2537X/1130/1135. Based on the GOM concentration we used the resistance model to simulate its dry deposition. Results from measurements show that the GOM dry deposition flux was significantly higher in winter than in summer and fall with an overall average of 0.302 ng m−2 h−1 in the observation period. Among the numerous parameters in the resistance model the two scaling factors (α and β) for the non-stomatal resistance components regarding the solubility and reactivity of the chemical species are the most sensitive ones. The large values for HNO3 (α=β=10) used to be applied in the model for GOM. However, recent studies found the values for HONO (α=β=2) are probably more suitable for GOM due to equivalent effective Henry’s Law constants (H*) between HONO and HgCl2. We used the latter configuration (α=β=2) for the resistance model and found good model performance except for three cases in summer, late fall, and winter, respectively. The O3 concentration at NJU was exceptionally high in the summer case, which could probably cause an underestimation of GOM using the TekranTM system. Therefore, we applied a correction scheme to the GOM concentration regarding the impacts of humidity and O3. The model performance was improved, especially for the summer case. The air quality at NJU was largely compromised in fall and winter because of polluted air masses from North China generated by coal combustion for residential heating. Heavy particulate matter (PM) pollution could result in heterogeneous Hg oxidation, followed by high Hg(NO3)2 or HgSO4 deposition in the presence of high NOx or SO2 concentrations. The two exceptional cases in cold season had elevated NOx and SO2, respectively, and could consequently induce GOM species with high deposition rates.

M.P.1.5

FIRST EDDY COVARIANCE FLUX MEASUREMENTS OF GASEOUS ELEMENTAL MERCURY OVER NATURAL SURFACES

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Direct measurements of the net ecosystem exchange (NEE) of gaseous elemental mercury (Hg0) are crucial to improve our understanding of global Hg cycling and ultimately Hg exposure in humans and wildlife. The lack of long-term, ecosystem-scale measurements causes large uncertainties in Hg0 flux estimates. Today it remains unclear whether terrestrial ecosystems are net sinks or sources of atmospheric Hg0. Here, we present the first successful eddy covariance (EC) NEE measurements of Hg0 over natural, low-Hg background soils (41 - 75 ng Hg g-1 topsoil [0-10 cm]) at a managed grassland site in Chamau, Switzerland. We present a detailed validation of the EC technique for Hg0 based on a Lumex mercury monitor RA-915AM and have derived a preliminary theoretical detection limit of ca. ±1 ng m-2 h-1. Based on our analysis we give suggestions to further improve the precision of the EC system and pinpoint challenges and interferences that occurred during the pilot measurement campaign. The measurements took place in summer 2018, which was characterized by extremely hot and dry meteorological conditions. We analyzed preliminary data from 25 days of measurements and estimated a net summertime grassland-atmosphere Hg0 flux in the range of -2.6 to 4.1 ng m-2 h-1 (95% confidence interval). The measurements revealed a distinct diel pattern with significantly lower nighttime fluxes. The median of the concurrent preliminary CO2 flux measurements was -4 μmol m-2 s-1. This indicates a net CO2 uptake by the grassland despite very dry conditions. Our results demonstrate a breakthrough in mercury science to measure the NEE of Hg0 because the system is available as a standard feature, relatively simple to deploy in the field, needs no carrier and zero gases and requires low maintenance. The system seems suitable to complement existing research infrastructures such as ICOS RI in Europe or NOAA Observing Systems in the US built to calculate greenhouse gas balances with direct Hg0 deposition and re-emission measurements. We anticipate our EC-Hg0 flux system to improve knowledge about mercury cycling between ecosystems and the atmosphere and to challenge model simulations on a regional and global scale.

M.P.1.6

USE OF BACK TRAJECTORY TO TRACK HIGH GEM CONCENTRATION EPISODES

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The dominant form of the atmospheric mercury is the gaseous elemental mercury (GEM). It has a long-lifetime (0.5-2 years) in the atmosphere and it can be oxidized in the atmosphere to form divalent mercury forms, which occur in both gaseous phase i.e. reactive gaseous mercury (RGM) as part of aerosol particle (HgP). RGM and HgP are water-soluble compounds with short residence time – hours to days for RGM and days to weeks for HgP. The RGM and HgP can be converted to methylmercury which causes serious health effects. The source of GEM can stem from natural (geologic activities, volatilization in marine environment, emission from terrestrial environments) and anthropogenic (combustion, manufacturing) emission. It’s volatility and stability make possible that GEM can be easily transported for a long distance in the atmosphere.

GEM concentration is measured with Tekran Mercury Vapour Analysers Model 2537B on ground (4 m agl) and 240 m level of tall tower on the National Atmospheric Observatory in Kosetice (NAOK), the Czech Republic. The measured concentration values are validated through a web-based QA/QC system of the Global Mercury Observation System (GMOS). The GEM concentration is measured in 5 min resolution where the typical concentration value is about 1.5-3 ngm-3.

Short episodes of GEM higher concentration occur time to time during long term monitoring. By generation of air parcel back trajectories or by connection of concentration data with wind speed and wind direction measured parallel on the tower the probable source of this episodes can be tracked. In this study we present situation from 25th of October 2016 where values between 1.5 ngm-3 to 6.5 ngm-3 were measured for one hour. The analysis of trajectories for this period was performed. For this purpose, the back trajectories were calculated with the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory’s (ARL) Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYPLIT) using the Global Data Assimilation System (GDAS) with high resolution (0.5) as an input data.

This higher concentration episode was forerun by fire at the North Harbour of BASF chemical plant in Ludwigshafen, Germany 8 days before (17th of October). An ensemble of trajectories was integrated to visualise a most probably source area for measured higher GEM concentration, but it showed, that accident at Ludwigshafen likely was not the cause of this episode.

M.P.1.7

VERTICAL AND HORIZONTAL ATMOSPHERIC MERCURY PROFILES IN A MINING ENVIRONMENT

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Mercury flows in the environment involved many transfer pathways, i.e., soil-atmosphere, soil-plant, plant-atmosphere, water-atmosphere, among others. Mercury emitted from soils, waters or plants contribute to the increase of the atmospheric mercury pool, especially in the lower layers of the troposphere. The main objective of the work described...
here was to obtain and discuss information acquired from vertical and horizontal profiles of total gaseous mercury in an environment contaminated by decommissioned mercury mining facilities. Data acquisition was carried out over a complete year in order to identify relationships between TGM data and secular variations in local micrometeorological and topographical data. Vertical and horizontal profiles of total gaseous mercury (TGM) from September 2014 to August 2015 were acquired using a Tekran 2537B and a Lumex RA-915M devices respectively, in a village polluted with mercury related to decommissioned mining and metallurgical facilities (Almadenejos). The vertical profiles show that higher TGM concentrations are present at lower heights during nocturnal hours and at higher altitude at dawn and dusk. The soil to atmosphere mercury exchange were upward at the first hours of the day during spring and summer periods, being this mercury exchange restricted to the lower meters above the ground in the summer period and to the upper monitored meters in the spring period. Autumn and specially winter appear as seasons with low mercury exchange, only at the end of the day, and preferably at upper heights. Horizontal profiles show background values close to 6 ng m–3 in all seasons except in the spring months, when they rise to 13 ng m–3 and increase the area affected by mercury emissions to more than 4 km around the mining and metallurgical sites. Daily, the most important process involved in gaseous mercury movements is the mixing layer, created in the early morning and completed on nightfall. Vertical transfers are predominant when this process is active, while major sources act as constant suppliers of total gaseous mercury to the mixing cell, producing its fall at dusk. Conversely, horizontal transfers prevail during dark hours, and the main factors are major and minor sources, wind speed and topography. In terms of risk assessment, minor sources can represent the highest local risk factor in areas with important diffuse levels in summer followed by spring, fall and winter. In 2014, the wet deposition fluxes of HgT were in the order of spring > winter > fall > summer, while for the 2015 the largest wet deposition flux was observed in fall, due to the more abundant rainfall events, followed by winter, summer, and spring, respectively. In order to understand the potential mercury sources in precipitation during the period of this study, atmospheric pollutants (PM10, PM2.5, O3, NOx, SO2), local meteorological parameters, back trajectories (NOAA Hysplit) and satellite observation tools for wildfire/biomass burning events have been considered and their contribution was singled out. This work concerns Hg in wet deposition and an assessment of the occurrence and possible sources of rainwater HgT. This has been done using information that was not previously available to estimate the impact of mercury due to wet deposition in Southern Italy.

### M.P.1.8

**WET DEPOSITION OF TOTAL MERCURY AT A SUBURBAN SITE IN SOUTHERN ITALY (CALABRIA): CONCENTRATIONS, FLUXES AND ASSESSMENT OF SOURCE AREAS**

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Accurate measurements of total mercury (HgT) in wet precipitation samples, collected in the suburban area of Cosenza (Southern Italy), over a 2-year period, from November 2013 to February 2016, were performed to study the distribution of rainwater HgT concentrations and to evaluate the seasonal contribution of wet deposition to the Hg flux. Precipitation samples were collected using a wet-only collector at the sampling site (39°21’N, 16°13’E, 217 m a.s.l) inside the Campus of UniCa (University of Calabria) in Rende, Italy, following harmonized sampling procedures reported in the Standard Operating Procedures (SOPs) of the GMOS project. The volume weighted mean (VWM) of total mercury concentrations in 2014 and 2015 were 7.1 ± 3.9 ng L–1 and 15.1 ± 10.4 ng L–1 (mean ± SD), respectively, whilst the wet deposition flux of HgT in 2014 and 2015 were 6.1 µg m–2 y–1 and 17.1 µg m–2 y–1, respectively. Seasonal VWM HgT concentrations in 2014 shows highest values in spring followed by winter, summer, and fall. In 2015, VWM HgT concentrations were characterized by highest Hg levels in spring followed by spring, fall, and winter. In 2014, the wet deposition fluxes of HgT were in the order of spring > winter > fall > summer, while for the 2015 the largest wet deposition flux was observed in fall, due to the more abundant rainfall events, followed by winter, summer, and spring, respectively. In order to understand the potential mercury sources in precipitation during the period of this study, atmospheric pollutants (PM10, PM2.5, O3, NOx, SO2), local meteorological parameters, back trajectories (NOAA Hysplit) and satellite observation tools for wildfire/biomass burning events have been considered and their contribution was singled out. This work concerns Hg in wet deposition and an assessment of the occurrence and possible sources of rainwater HgT. This has been done using information that was not previously available to estimate the impact of mercury due to wet deposition in Southern Italy.

### M.P.1.9

**UNIVERSAL SCALING IN ATMOSPHERIC ELEMENTAL MERCURY CONCENTRATION EXTREMES, IS IT LINKED TO A LOCAL ATMOSPHERIC LARGE SCALE MOTION?**

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The probability density function (PDF) of the inter-occurrence times between subsequent extreme events in gaseous elemental mercury (Hg(0)) concentration data, measured at different latitudes has been investigated. Above a certain fixed threshold in the data, the PDFs of the inter-occurrence time of the Hg(0) data are well described by a Tsallis q-exponential function, exposing the a long-term memory of the transport process, highlighted by a power decay of the auto-correlation function, and the non-equilibrium behaviour of the overall process. This complex behaviour, characterised by strong fluctuations on different temporal scales, can be effectively described by a superposition of statistics, which act locally on different time scales. This “statistics of statistics” is called “superstatistics”.

The superstatistical nature of the process lies in the competition between different mesoscopic processes which influence the dynamics of large-scale transport, and, in addition, are the principal responsible for the extreme events in the concentration data.

An extensive parameter fluctuating on time scales larger than the characteristic relaxation times of the system, has been identified. This new parameter incorporates all the possible fluctuations which produce a sudden variation in the collective dynamics. Shuffling the data series destroys the long-term memory, and all distributions (PDFs) become independent of the threshold Q, collapsing on to the same exponential distribution.

The possibly central role of the local atmospheric dynamic on extreme events observed in the elemental Hg data series means what may seem to be an “outlier” may simply reflect a combination of mesoscopic processes resulting in an “extreme” value.
TRENDS OF ATMOSPHERIC MERCURY CONCENTRATIONS AT MACE HEAD ATLANTIC COAST

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Long-term monitoring of data of ambient mercury (Hg) on a global scale to assess its emission, transport, atmospheric chemistry, and fading processes is vital to understanding the trends and impact of Hg pollution on the environment. Here we will present trends of the atmospheric mercury concentrations recorded during 2017 and 2018 at the Mace Head Atmospheric Research Station on the Atlantic coast of Ireland. The Mace Head observations could give scientists and models some insight into baseline concentrations of Hg concentrations in air in a marine remote environment, with an overarching benefit which clearly consists in the advancement of knowledge about Hg processes on global scale. Basing on meteorological analysis and Hybrid Lagrangian Integrated Trajectory model, the hourly averaged mercury concentrations were attributed to different air mass types: baseline, local, European polluted, and sub-tropical maritime. Monthly median Hg concentrations of all types decreased in -0.02 ± 0.07 ng m⁻³ yr⁻¹ over the analyzed period with significant but small variance among air mass types. The period covered by the measurements endorse the current modelling statement of a decreasing in the global mercury concentration trends. Furthermore, tests for temporal change of the trends indicate that the downward trends of mercury concentrations are leveling off for all air masses.

TOTAL GASEOUS MERCURY AND MERCURY DEPOSITION MEASUREMENTS IN FINLAND

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Total gaseous mercury (TGM) and mercury in deposition have been measured since 1996 and 2001, respectively, in Finland. Currently TGM and Hg deposition are measured at three stations Pallas, Virolahti and Hyytiälä. In addition, deposition is measured at Kotinen station. These stations belong to many international programs such as GMOS, WMO/GAW, EMEP, AMAP and IM. The results are reported e.g. to European Environment Agency. TGM is measured with automatic Tekran 2537A/B/X mercury analyzers at all stations, and in addition, a manual method is employed in parallel at Pallas by Swedish IVL. Deposition samples are collected with NILU type fallout collector during the winter months with snow and the rest of the year with funnel-tube-bottle combination, and the monthly samples are later analyzed in the laboratory with ICP-MS (until 2015, with CVAFS). Deposition results show a clear south-to-north decreasing gradient in Finland with an annual average of 2.9 µg/m² in the south (Virolahti) and 1.6 µg/m² in the north (Pallas) during 2009-2017. This is due to minor domestic emissions in the sub-arctic Pallas area and longer distance to the large European source areas compared to the southern stations. A clear seasonal cycle with higher deposition in the summer is also evident in the data largely as a result of higher relative humidity. The reactivity varied significantly between different salts, decreasing in the series sodium sulfate > sodium chloride > ammonium sulfate > ammonium nitrate. Uptake on ammonium nitrate was nearly reversible, with small values of the initial (3.6e-3) and steady state (3.3e-4) uptake coefficients and a rapid loss in the surface reactivity. Sodium sulfate was most reactive (initial and steady state uptake coefficient of 3.1e-2 and 1.7e-3, respectively), with the slowest loss in the surface reactivity. The lifetime of HgCl₂ with respect to its removal by dry marine and urban aerosols is estimated to be 2 days and 2 hours, respectively.

TREND OF ATMOSPHERIC MERCURY CONCENTRATIONS AT MACE HEAD ATLANTIC COAST

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Gaseous oxidized mercury (GOM) from oxidation of gaseous elemental mercury is thought to be responsible for the atmospheric mercury deposition, but the interaction of GOM with environmental surfaces is not well understood. To address this knowledge gap, we investigated the reaction of gaseous mercury (II) chloride (HgCl₂) with inorganic salts representative of aerosol surfaces in the marine (sodium chloride and sodium sulfate) and urban (ammonium sulfate and ammonium nitrate) atmosphere. The gas-surface reaction was studied in a fast flow reactor coupled to an ion drift - chemical ionization mass spectrometer (ID-CIMS). Mercury (II) chloride was quantitatively detected as HgCl₂NO₃⁻, using the HNO₃-N̄O⁻ reagent ion. Uptake curves showed a common behavior, where upon exposure of the salt to gas-phase HgCl₂ the concentration of the latter dropped rapidly and then recovered gradually. The initial drop and the rate of recovery varied significantly between different salts. The gas-surface uptake followed the Langmuir-Hinshelwood mechanism, showing the presence two types of reactive sites and one type of adsorptive sites. The reaction was confined to the solid salt surface, decreasing significantly when the surface coverage reached 0.5%. However, the reactivity of salts could be recovered nearly fully by cycling the surface through high relative humidity. The reactivity varied significantly between different salts, decreasing in the series sodium sulfate > sodium chloride > ammonium sulfate > ammonium nitrate. Uptake on ammonium nitrate was nearly reversible, with small values of the initial (3.6e-3) and steady state (3.3e-4) uptake coefficients and a rapid loss in the surface reactivity. Sodium sulfate was most reactive (initial and steady state uptake coefficient of 3.1e-2 and 1.7e-3, respectively), with the slowest loss in the surface reactivity. The lifetime of HgCl₂ with respect to its removal by dry marine and urban aerosols is estimated to be 2 days and 2 hours, respectively.

TOTAL GASEOUS MERCURY (TGM) AND OZONE (O3) OVER SPRING - SUMMER 2018 AND WINTER 2019 AT THE COL MARGHERITA ATMOSPHERIC OBSERVATORY (2543 M A.S.L.)

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Measurements of Hg and O3 in alpine environments are pivotal when evaluating air quality in natural ecosystems as well as when trying to understand regional and synoptic atmospheric transport regimes and advection of air pollutant to the Alps. This study is crucial for the evaluation of Hg exchange processes between soil and atmosphere in a high-altitude alpine environment, where increasing Hg snowpack con-
centrations occur during winter time, followed by Hg release to the overlying atmosphere during spring and summer time snowmelt. In this context, evaluating the gas phase reaction between elemental mercury and ozone is essential. All the experimental activities were performed at the CNR-IDPA atmospheric observatory at Col Margherita (CMA) that located in the Italian South Eastern Alps, a UNESCO protected region far from anthropogenic and natural sources of air pollutants (altitude 2543 m a.s.l., 46°22′0.6″ N, 11°47′30.9″ E). Local meteorological conditions, ozone and Total Gaseous Mercury (TGM) has been measured from March 2018 to present. The TGM was monitored using a Tekran 2537B (Tekran Inc.) using the same protocols as used for the GMOS project. Near-surface O3 measurements were taken with a Thermo 49c UV photometric analyzer (Thermo Corp.), following WMO/GAW guidelines. In the present study, daily and monthly levels of hourly Hg and O3 concentrations were assessed and compared the meteorological parameters (i.e., T, RH, P, WS, WD, Solar Radiation, Snowpack).

These mercury results obtained during the IGOSP ERA-Planet project were then compared with data taken during GMOS covering the same periods in 2014 and 2015. Notable events were investigated by performing back trajectory atmospheric reanalysis using HYSPLIT. The results showed that Hg concentrations increase, on average, from spring to summer, with some episodes of rapid daytime increase or decrease forming back trajectory atmospheric reanalysis during spring and summer time snowmelt. In this context, evaluating the gas phase reaction between elemental mercury and ozone is essential. All the experimental activities were performed at the CNR-IDPA atmospheric observatory at Col Margherita (CMA) that located in the Italian South Eastern Alps, a UNESCO protected region far from anthropogenic and natural sources of air pollutants (altitude 2543 m a.s.l., 46°22′0.6″ N, 11°47′30.9″ E). Local meteorological conditions, ozone and Total Gaseous Mercury (TGM) has been measured from March 2018 to present. The TGM was monitored using a Tekran 2537B (Tekran Inc.) using the same protocols as used for the GMOS project. Near-surface O3 measurements were taken with a Thermo 49c UV photometric analyzer (Thermo Corp.), following WMO/GAW guidelines. In the present study, daily and monthly levels of hourly Hg and O3 concentrations were assessed and compared the meteorological parameters (i.e., T, RH, P, WS, WD, Solar Radiation, Snowpack).

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The research is supported by the Russian Foundation for Basic Research, project 17-29-05044.

THE FIRST AIR MERCURY MONITORING OVER LAKE BAIKAL

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Lake Baikal, Siberia contains 22–23% of the world’s fresh water reserves. The max length and width of the lake are 636 and 79.5 km, respectively. Baikal is the world’s deepest lake with a maximum depth of 1642 m. Within the GMOS project, air mercury monitoring has been running at the Listvyanka station located at the SW shore of the lake. So far, there is no data on the air mercury distribution over the vast Baikal basin. In July 2018, for the first time, the air mercury survey was carried out throughout all Baikal area during cruise of the research vessel “Akademik Koptyug”. The continuous survey was made using the RA-915M mercury analyzer; the overall route covered 1800 km. The average mercury concentration of 1.09 ng/m3 over Lake Baikal is notably less in comparison with the average value of 1.60 ng/m3 obtained at the onshore Listvyanka station during the same days of cruise. The mercury anomalies of 3-5 ng/m3 can be explained by the long-distance mercury transfer from the coal-fired power plants of industrial cities (Irkutsk, Angarsk) and the emission sources of towns located along the lake shore. The mercury concentration over the gas-hydrate pools and oil seepages to the lake surface, up to 1.55 ng/m3, is slightly elevated as compared with the background level. A comparison of the average air mercury concentration at the terrestrial Listvyanka station and of the lake surface layer can lead to the conclusion that Baikal is a significant sink of the atmospheric mercury.

The research is supported by the Russian Foundation for Basic Research, project 17-29-05044.

SEASONAL AND ANNUAL CHANGES IN HG CONCENTRATIONS IN ATMOSPHERIC PRECIPITATION FOR ASSESSING THE LEVEL OF AIR POLLUTION WITHIN AN URBAN CENTER (BARNUAL CITY, RUSSIA)

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Wet scavenging by precipitation events is one of the principal mechanisms of the Hg deposition from the atmosphere. Hg concentration level in precipitations of the industrial centre is mainly influenced by the regional anthropogenic emissions of fuel combustion as well as long-range atmospheric transport of contaminants. Wet precipitation samples were collected for 5 years (from 2014 till present) at the monitoring station of the Institute for Water and Environmental Problems SB RAS within Barnaul city. Clean handling and analysis procedure have been realized to avoid contamination problems. Total Hg concentrations were determined in filtered and unfiltered sample (for each precipitation event) using Mercur Duo Plus analyzer according to the US EPA Method 1631e.

In general, both the range of THg concentrations in precipitation and volume-weighted mean (VWM) (15.3 ng/L) in Barnaul are comparable with other urban places, like the Boston area (0.73 – 24.6 ng/L), Pretoria (15.8 ng/L (VWM)), etc. THg concentration varied both inter-annually and seasonally, for example the ranges of observed concentration (without outlets) were 7.0 - 13.8 ng/L and 14.3 - 17.2 ng/L for 2016 and 2018, respectively, showing an increasing trend in recent years. Although inter-annual differences in THg wet deposition are mostly linked with differences in precipitation volume. Seasonal changes demonstrated elevated THg concentrations in cold periods comparing with warm period, so, in warm period of 2016 THg concentration ranged from 3.6 to 10.4 ng/L, whereas in the winter period 2016-2017 it ranges from 6.6 to 20.9 ng/L, that is in agreement with the seasonal variability of THg concentration has been reported at the GMOS monitoring sites in the Northern Hemisphere (i.e., Chinese sites). This is probably due to the fact that Hg, like some other elements, enters to the atmosphere with fly ash produced during the combustion of coal at Thermal Power Plants.

Hg fluxes based on the volume-weighted mean (VWM) calculation were calculated for an objective quantitative assessment and comparison with other regions. HYSPLIT back trajectories were used to explain Hg emissions (extremely high Hg concentrations) and reveal the sources of Hg deposition.

With an atmospheric residence time of up to 24 months, gaseous elemental Mercury (GEM, Hg0) is the primary form of Hg subjected to long range and global transport. In open ocean systems, formation and deposition of oxidized Hg forms from GEM has been identified as an important source of Hg to surface waters where it after bacterial mediated methylation can enter marine food webs as monomethylmercury. Long-range transport of Hg from industrial centres (e.g. Siberia, China) to remote areas, especially over the North Pacific Ocean, is well documented. However, not much is known about its regional and biogeochemical cycling.

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omethylmercury. Quantification of GEM concentrations and enhanced understanding of atmospheric Hg depletion events (AMDE) in marine boundary layers is therefore of interest. Here, we present shipborne measurements of total gaseous mercury (TGM), mainly consisting of GEM (presumably >98 % of TGM), collected onboard the Swedish icebreaker Oden during the Arctic Ocean 2018 expedition. Data were collected during the expedition from Svalbard to the North Pole and back between 1st of August and 21st of September, as well as during the transect of Oden from Svalbard to Helsingborg (Sweden) between 22 th of September and 5 th of October. Continuous measurements were performed using a Tekran 2537A automatic Hg analyzer with an air inlet installed approximately 10 m above the sea surface. During the expedition, continuous measurements of black carbon, aerosol particles and ozone were also conducted and here used to evaluate potential contamination of Hg from Oden's exhaust-plume and to understand elevated TGM concentrations and observed AMDE. Average concentrations of TGM detected were in agreement with previously reported concentrations.

M.P.1.17

SOURCE CHARACTERIZATION FOR MERCURY WET DEPOSITION OVER FIVE CITIES IN SOUTH KOREA

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We measured concentrations of mercury (Hg) and major ions (Na+, K+, Mg2+, Ca2+, NH4+, Cl-, SO42-, and NO3-) in rainwater collected from Seoul, Incheon, Taean, Gwangju and Jeju in South Korea to confirm the seasonal and spatial trends of rainwater Hg concentration as well as the major factors affecting these trends. The concentrations of major ions were measured from 2013 to 2017 in each city, while Hg was measured from 2015 to 2016 in Seoul, Incheon, Taean and Jeju, and from 2016 to 2018 in Gwangju. The monthly volume-weighted mean concentration (VWC) of Hg showed the highest value (28 ng L-1) in Seoul, followed by Incheon (16.03 ng L-1), Taean (10.99 ng L-1), Gwangju (7.18 ng L-1), and Jeju (6.09 ng L-1). A negative correlation was commonly found between VWC of Hg and precipitation depth with a particularly strong dilution during early rain event. We also found a strong positive correlation between the wet deposition flux of Hg and precipitation depth with a decreasing regression slope in the order of Seoul > Incheon > Taean > Gwangju > Jeju, which is in agreement with the order of air mass Hg pollution. When principal component analysis (PCA) with Varimax rotation was applied to identify main factors affecting the distribution of Hg and ions, 71 to 88% of overall data variance was explained by the two factors (73% in Seoul, 71% in Incheon, 88% in Taean, 80% in Gwangju, and 86% in Jeju). The PCA results further revealed that Hg distribution in Seoul was attributed to the dust transport as it showed highest loading on factor 2 affected by Ca2+ and Mg2+. The sources of Hg in Incheon seemed to be mixed with anthropogenic aerosols, as its distribution was affected by SO42-, NO3- and NH4+, as well as Ca2+ and Mg2+. The Hg variation in Taean and Gwangju was solely ascribed to the anthropogenic source, similar to that of SO42-, NO32- and NH4+. The Hg variation in Jeju was distinctly affected by marine aerosols, as it was mostly comparable to the variation of Na+ and Cl-. These results are consistent with an increased importance of coal combustion as a source of Hg and fine dust over mainland Korea. We will use the air mass back trajectory model (HYSPLIT) in future studies to provide clarification on the sources of air mass in each city.

M.P.1.18

SOURCE IDENTIFICATION AND TRENDS IN ATMOSPHERIC Hg AND Pb IN PM2.5 AT THE URBAN AND RURAL SITES ACROSS SOUTH KOREA

NOH, Seam¹; PARK, Kwang-Su¹; YU, Seok-Min¹; KIM, Hyuk¹; SEOK, Kwang-Seol¹; PARK, Jae Seon¹; CHOI, Jongwoo¹; KIM, Younghee¹
(1)Chemicals Research Division, Environmental Health Research Department, National Institute of Environmental Research, Republic of Korea

In this study, PM2.5-bound mercury (PBM) and lead (Pb) was collected at an urban and rural site in South Korea for three years (from 2014 to 2016). The average PBM and Pb levels in PM2.5 were 12±11 pg/m3 and 31±21 µg/m3 for rural and 36±34 pg/m3 and 26±18 µg/m3 for urban, respectively. PBM were pronounced with concentrations being highest in winter due to local meteorological conditions as well as seasonal factors, such as coal combustion for heating purposes in China. Results of 208Pb/204Pb isotope ratios show a minimum in summer, thereafter increasing progressively to fall to winter and reaching a maximum in spring. 206Pb/207Pb ratio as a function of Pb concentration converged to 1.16–1.17. In winter, no correlation of PBM with PM2.5, air pollutants, and heavy metals was seen in urban. Furthermore, urban showed higher PBM/PM2.5 and Pb/PM2.5 ratios in winter due to the strong atmospheric oxidation-reduction reaction conditions as well as local and regional PBM sources. We conclude that immediate attention must be given to addressing PBM levels in Korea, including considering it as a key component of future air quality monitoring activities and mitigation measures.

M.P.1.20

SPATIAL AND TEMPORAL TRENDS IN MERCURY DEPOSITION AND EMISSIONS IN THE US MIDWEST

KENSKI, Donna¹
(1)Lake Michigan Air Directors Consortium

This study examines recent spatial and temporal changes in mercury deposition in the US Midwest, where 32% of US stationary source emissions are located. USEPA’s Mercury and Air Toxics Standards rule (MATS) was designed to reduce emissions of mercury from power plants. The rule was promulgated in 2012 and fully implemented in 2016. This paper looks at the following indicators for evidence of the impact of MATS on atmospheric mercury: 1. Temporal trends in wet deposition, 2. temporal trends in litterfall deposition, and 3. Spatial changes in wet deposition. Emissions trends quantifying a decrease as a result of the MATS legislation and energy market changes are presented through 2017. Finally, concentration-weighted back trajectories and incremental probability functions for GEM, OMI, and PBM are examined to evaluate source regions and seasonality for these species.

M.P.1.21

SAHARAN DUST AS A VECTOR FOR MERCURY TRANSPORT

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(1)University of Manitoba

Mercury is known to sorb to particulate matter, and its partitioning to particles has been modeled under various environmental conditions; however, no such investigations have been conducted on Saharan dust. The Sahara is the world’s single largest source of atmospheric dust, with an average estimated emission of 800 million tons per year, accounting for 55–70% of the global total dust emission. Saharan-origin dust plumes travel across the Atlantic Ocean and can extend as far
as the Americas. Given the magnitude of Sahara dust emissions, any mercury transported on dust particles may alter the mercury burden of ecosystems throughout the western hemisphere. Real-time measurements conducted at the Izana station, Tenerife, in the Canary Islands, which is located at ~350km west off the Sahara Desert, found increases in both gaseous elemental mercury and particulate-bound mercury during dust storm events. Analysis of samples from nearby Teide volcano has ruled it out as a mercury source, suggesting that the particulate mercury is carried in the Sahara dust itself. Dust samples were collected via filtration and directly analyzed for total mercury content, finding 82 ng/g Hg associated with PM2.5 particles. Using this data, we have estimated the total particle-bound mercury in Saharan dust and generated a function for overall mercury flux associated dust storm events; this result will be essential in future global mercury transport and cycling models.

M.P1.22

OBSERVATION OF TGM IN THE FREE TROPOSPHERE AT THE SUMMIT OF MOUNT FUJI DURING SUMMER FROM 2013

NAGAFUCHI, Osamu1; SHINOZUKA, Ken'ichi2; NAKAZAWA, Koyomi1; KINOSHITA, Hazumu1; HISHIDA, Naoko1; NISHIDA, Yuki2; KATO, Shungo3

(1)Visiting Professor
(2)Researcher
(3)Associate Professor

To clarify the characteristics of Total Gaseous Mercury (TGM) long-range transport, observing in the free troposphere is important. We observed not only TGM but also, other trace gases and meteorological data which include radiosonde dataset and back trajectory analysis. These datasets were observed at Mt. Fuji Research Station (MFRS) which is located at the summit of Mt. Fuji (3,776 m a.s.l., 35.4°N, 138.7°E) during July to August 2013 to 2015. The TGM concentration exceeded the background value (1.5ng/m3–1.7ng/m3) of the northern hemisphere were observed on July 24 - 29 and August 19 - 20. When the high concentrations of TGM were observed in July of 2013, the air mass passed through the mainland of China and reached at MFRS based on the back trajectory analysis. On the other hand, the high concentration of mercury observed at MFRS on August 19-20 may be the influence of Sakurajima volcano eruption (August 18 at 16:31) from the calculation results of back and forward trajectory analysis. The origin of mercury flux arriving at MFRS during the observation period was 92% in China, 2.3% in Philippine, 1.9% in Japan.

M.P1.23

MERCURY FRACTIONATION IN AEROSOLS OF THE SOUTHERN BALTIC COASTAL ZONE

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(2)Institute of Oceanography University of Gdańsk

Information on the form in which Hg occurs in the atmosphere is important to understand the toxicity and bioavailability of this metal. So far, research on mercury speciation in the atmosphere has mostly focused on its three forms: elemental gaseous mercury (GEM / Hg0), reactive gaseous mercury (RGM / Hg2+), and mercury bound in aerosols (TPM). However, these studies do not provide complete information on mercury compounds in aerosols. So far, only two publications on mercury fractionation in TPM have been published; but these have focused mainly on describing the method and have provided only a limited number of environmental results. Therefore, the aim of the research was to identify forms of mercury occurring in aerosols in the coastal zone of the Baltic Sea, as well as to determine factors affecting the temporal changes in the share of individual Hg fractions. Aerosol samples were collected at the research station located on the roof of the Institute of Oceanography University of Gdańsk (Poland) from May 2016 to January 2017. Two measuring sets were used for the collection. Each of them consisted of a Teflon filter holder, a vacuum pump and a gas meter. A thermo desorption technique was used for the determination of mercury (THg and Hg fractions) using a direct mercury analyser DMA-80. The obtained results showed that the main forms of mercury present in aerosols are labile fractions, related to, gaseous mercury, mercury halides, mercury nitrate, organic mercury and a stable fraction bound to Hg sulphide. The conducted research also allowed to determine the origin of mercury sources in the studied area. In the winter it was burning fossil fuels, and in the summer, biological activity and emissions from the sea.

M.P1.24

MERCURY WET DEPOSITION AND ATMOSPHERIC PARTICLE BOUND HG AT THE COASTAL, URBAN AND FOREST SITES IN POLAND

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Wet deposition and total particulate matter samples were collected during field campaigns in 2008 and 2013-2014 at three different sites in Poland, representing coastal (Gdynia, big port town), forest (Jezioiry, Ecological station in National Park) and urban (Poznań city) areas. Total mercury concentration in rainwater samples were quantitatively determined using CV-AFS (PSA Millennium Merlin mercury analyzer, UK) and AMA-254 analyzer was used to determine Hg in TPM samples. Results of Hg concentration were considered in terms of most important sources, spatial and seasonal variation.

Analysis showed that maximum Hg concentration in rainwater was observed at the urban site (22.1 ng/l-1) followed by forest (18.3 ng l-1) and coastal (14.8 ng l-1). The annual wet deposition of Hg in Gdynia and Poznań was quite similar, 4.0 µg m-2 and 3.94 µg m-2, respectively. Hg concentration in atmospheric samples showed clear seasonal pattern, i.e. peak concentration was observed during colder months (Nov-Feb) followed by evident shift towards lower Hg levels in rainwater and PM samples that typically occurred during late spring and summer. Results from three selected sites suggest relatively high contribution of coal combustion sources, including local and regional emission from residential (domestic heating), commercial and industrial sectors. Specifically, wintertime increase of coal combustion intensity in combination with other factors such as low precipitation height, low air temperature and high aerosol loadings led to high Hg in air samples.

The concentration of Hg in rainwater showed statistically significant correlations with anthropogenic tracers (SO42-, NO3-), suggesting that contribution from local coal combustion was important. Moreover, the observed seasonal profile of Hg concentrations in rainwater from central and northern Poland indicated that samples were also affected by transport of polluted air masses from highly industrially-impacted southern regions, such as Upper Silesia and Małopolska Province. The concentration of total particulate phase Hg at the urban site varied in combination with other factors such as low precipitation height, low air temperature and high aerosol loadings led to high Hg in air samples.
MEASUREMENT AND MODELING OF ATMOSPHERIC GASEOUS MERCURY DEPLETION IN A VOLCANIC PLUME OF PITON DE LA FOURNAISE, LA RÉUNION ISLAND

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3) CNRS, IRD, GET, Université Paul Sabatier–Toulouse III, Toulouse, France
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6) Guillaume, LAc, Université de La Réunion, Météo-France, Saint-Denis de La Réunion, France
7) Université de La Réunion, Météo-France, Saint-Denis de La Réunion, France
8) ILaMP, CNRS, Université Blaise Pascal, Clermont-Ferrand, France
9) Royal Belgian Institute for Space Aeronomy
10) CIORES, University of Boulder, Colorado
11) IGE, Univ Grenoble Alpes, CNRS, IRD, G-INP, France

Volcanoes are thought to represent a major natural source of Hg to the environment although there is a clear lack of understanding in atmospheric reaction sequences occurring in volcanic plumes – in particular the extent to which halogen chemistry within the plume can oxidise elemental Hg to more reactive forms. Following the second volcanic eruption of Piton La Fournaise in La Réunion Island (21°S) in 2018 (27th of April to 01st of June), we recorded a volcanic plume at the Atmospheric Observatory of Maïdo situated 100 km northeast of the volcano at an altitude of 2200m. As part of the OCTAVE field campaign (March to June 2018), gaseous elemental mercury (GEM), reactive mercury (passive sampling system), and Hg stable isotopes were continuously measured at Maïdo. GEM showed an abrupt depletion during a few hours inside this plume raising several questions regarding oxidation and reduction pathways that occurred during the transport and/or at this altitude. Using additional parameters that were measured at the Maïdo station during the OCTAVE campaign (reactive halogens, ozone, NOx, SO2), we investigate the potential reaction pathways through developing a chain of numerical models that simulate the volcanic plume chemistry. These cover a wide range scales, from the high-temperature reactions near the volcanic source, to low temperature chemical processing of the dispersed plume, and up to regional scales with the WRF-Chem model. We include bromine, chlorine, and mercury species and their reactions as well as volcanic SO2-sulfate. The modelled bromine chemistry includes the “bromine explosion”, which generates reactive bromine species from volcanic HBr. These have the potential to oxidise the mercury which is emitted by the volcano. We suggest how comparing model output with observational data can help towards resolving uncertainties in the halogen-Hg chemical reaction pathways in a volcanic plume.

INFLUENCE OF ATHABASCA OIL SANDS OPERATIONS ON MERCURY LEVELS IN AIR AND DEPOSITION IN NORTH-WEST CANADA

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A 3D process-based mercury model, Global Environmental Multiscale - Modelling Air quality and ChEmistry - Mercury (GEM-MACH-Hg), representing atmospheric transport, transformation and deposition of mercury species, is used to estimate the impact of Athabasca oil sands operations (Alberta, Canada) on geographical distributions of air concentrations and deposition of mercury from 2012 - 2015. The study responds to following questions. What is the level and geographical extent of the impact? How is the impact changing with time? What is the initial and ongoing change? How does the impact compare to influences of wild fires, and regional and global anthropogenic emissions of mercury in the region? Multiple source-specific controlled model simulations are performed at global, continental and local scales. Comprehensive model evaluation is performed against observed concentrations of mercury species in air and deposition in the Athabasca Oil Sands Region (AOSR).

Model-measurement agreement of mercury levels in air and snow is found to be within model and measurement uncertainties indicating industry reported mercury emissions from Athabasca oil sands facilities to be consistent. Gaseous elemental mercury (Hg0) concentrations in AOSR are at similar level as in Northern Canada owing to a dominant contribution of long-range transport of Hg0 from global Hg sources. Whereas, ambient oxidized mercury (Hg2+; gaseous and particulate) concentrations and mercury deposition are elevated in catchments around Athabasca oil sands facilities (up to 100% in 2012). Biomass burning is an important but highly spatiotemporally variable source of deposition in Northern Alberta. Although, mercury deposition is higher in summer months compared to winter, the impact of Athabasca oil sands emissions is notably larger in winter. Accumulated Hg in snow has the potential of being mobilized to aquatic systems during spring freshet; measured water concentrations of Hg in Athabasca River downstream of oil sands facilities are indeed shown to be elevated. Intermittent variations in snow amount and surface temperature lead to significant variations in seasonal snow mercury loadings. Mercury deposition in AOSR is found to be equally sensitive to both changes in meteorology and Athabasca oil sands emissions.

INDOOR MERCURY IN A MINING RELATED CONTEXT: SOURCES AND SOLUTIONS.

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The importance of indoor air quality in human health and comfort has been well recognized in the last 50 years, and many national and international organizations has promoted measures to improve indoor air quality. This work focusses its efforts in describing the process of mercury vapour intrusion in domestic buildings in a mining related environment. To accomplish this purpose, a monitoring of indoor total gaseous mercury in homes has been conducted in Almadén, Puertollano and Ciudad Real (South central Spain) and in Mexico DF (Mexico), in order to identify main factors involved in mercury dispersion in indoor environments. In addition to this, an experiment has been carried out in a two-story building to study the relative importance of these factors in the process. Concentration of total gaseous mercury in Almadén homes has shown three contrasting levels: houses without suspected mercury source have in average 33 ng m-3 and can be considered as local background, while houses with indoor source has average concentrations of 315 ng m-3, houses with known underground sources have 236 ng m-3 and buildings with recent mercury spill in a laboratory in Mexico DF has shown average concentrations of 23840 ng m-3 during the first day, and during the whole period of the study the flow of gaseous mercury indoor levels in Almadén were higher than background levels measured in Puertollano (3 ng m-3 in average), probably due to the anomalous outdoor total gaseous mercury values in Almadén versus Puertollano, 27.4 and 1.8 ng m-3 respectively. The experiment in a two-story building offers data about indoor mercury accumulation speed and time needed to reach maximum level in different scenarios; maximum accumulation speed was measured isolating the building and...
adding a mercury source upstairs, while minimum was measured with
isolated building and air conditioned operating; the main factor involved
in mercury dispersion inside the building was the chimney effect of the
stairs, both in the case of accumulation and during dilution.
As main conclusion, indoor mercury presence can be temporary dimin-
ished with dilution actions but only the elimination of the active source
of gaseous mercury can solve the problem in terms of inhalation risk.

MEASUREMENT OF ATMOSPHERIC SPECIES IN QOMOLANGMA NATURAL NATURE PRESERVE, TI-
BETAN PLATEAU

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(5)University of Wisconsin
(6)Saint Louis University

Located in the world’s “third pole” and a remote region connecting the
Indian plate and the Eurasian plate, the southern region of Tibetan
Plateau is an ideal region to study the long-range transport of atmos-
pheric Mercury. Atmospheric species Hg monitoring was conducted on
Mt. Qomolangma (4276 m.a.s.l) during the Indian monsoon transition
period (from 15 April 2016 to 14 August 2016).The GEM, GOM
and PBM concentrations at the sampling site were 1.42±0.37 ng m−3,
21.4±13.4 pg m−3 and 25.6±19.1 pg m−3 respectively, during the
whole study period. And a slight increase in the GEM concentration
was observed from the period preceding the Indian summer monsoon
to the Indian summer monsoon period, while significant decreases were
observed in the GOM and PBM concentrations. A unique daily
pattern was observed with a peak value before sunrise and a low value
at noon. Due to the special local terrain condition, there is a large area
covered in glaciers in Tibetan Plateau, local glacier winds could increase
the transboundary transport of pollutants and transport polluted air
masses to the Tibetan Plateau. The atmospheric Hg concentration in
QNPN in the Indian summer monsoon period was influenced by trans-
boundary Hg flows. This highlights the need for a more specific iden-
tification of Hg sources impacting QNPN and underscores the impor-
tance of international cooperation regarding global Hg controls. This
study could help researchers and governments to better understand
global Hg cycling processes and the potential impacts from the rapidly
developing countries in South Asia.

MERCURY DEPOSITION IN YAKUSHIMA ISLAND THE
WORLD NATURAL HERITAGE SITE, JAPAN

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KA, Ken’ichi2; TETSUKA, Kenshi1; TETSUKA, Tatsuko6
(1)Fukuoka Institute of Technology
(2)NIC
(3)ISM
(4)Ken’ichi, Fukuoka Institute of Technology
(5)Kanshi,
(6)Tatsuko,

To clarify the characteristics of mercury deposition in Yakushima, Island,
the world natural heritage, we observed mercury concentration in pre-
cipitation since 2013. The observation site is located in mountainous
area which have 1,300 m a.s.l elevation and has about 10,000 mm pre-
cipitation/year. Precipitation sampler which is able to collect precipita-
tion every 10 mm (once the program started, it can collect precipitation
samples until 120 mm, automatically) is installed. Average concentration
of total Hg is 4.1 ng/L (range 0.24-44 ng/L). Result from the characteris-
tics of weather, total Hg concentration tend to be high when deep con-
vective cloud was observed. This suggest that the atmospheric Hg may
entrainment from boundary layer to the cloud. Comparison between
850 hPa (usually, it is about 1,500 m elevation) upper-level weather
chart and Hg concentration, when the experimental site was covered
by the wet area, the Hg concentration in precipitation tend to be lower
than the timing when the wet area was not covered. In addition, result
from the back trajectory analysis, when the air mass came from China
continent, the Hg concentration in the precipitation become high.

BIOGEOCHEMICAL CYCLE OF MERCURY IN THE IM-
PACT ZONE OF PULP AND PAPER MILLS AT THE MOUTH
OF THE NORTHERN DVINA RIVER, RUSSIA

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The researchers noted that in areas of intense economic activity in the
Arctic zone of the Russian Federation environmentally “hot spots” are
exist, in which the magnitude of the environmental degradation reached
dangerous levels, and pollution levels greatly exceed acceptable norms.
In particular, at present, the Arkhangelsk city and its surrounding area are
included in a priority list of environmentally “hot spots”.
It is known that the object of study - mouth area of the Northern Dvina
River, for a long time exposed to wastewater discharges and air emis-
sions of large pulp and paper mills in the process cycle which includ-
ed the mercury. Various researchers periodically noted here in water,
bottom sediments and some other objects of natural environment the
concentrations of mercury above background.
A study of the diurnal dynamics of contaminants in the environment,
and in particular, the substances of the first class of hazard - mercury in
water bodies is becoming increasingly important. This is due to the fact
that it makes it possible to predict the distribution and transformation
of various forms of mercury, depending on the specific conditions of the
aquatic ecosystem, the presence of tidal activity, temperature, charac-
teristics of pH, Eh and color of water of bottom sediments, the intensity
of the hydrodynamic processes, species diversity ecosystems and etc. All
this makes it possible to assess the extent of dispersion, accumulation
of mercury in the components of the aquatic ecosystem. To the study
of the topic dedicated work of various scientists who researched the
diurnal dynamics of mercury in the air, snow cover, water of the lakes
and revealed the relationship between solar activity, temperature of air
and water, and also pointed to the insufficiently known role of photolytic
gaseous elemental mercury production . The study of diurnal dynamics
of mercury makes it possible to simulate and predict the behaviour of
the time characteristics of the metal and its compounds. This knowledge
will allow to develop recommendations for optimization of the network
of water intakes to ensure household needs of the population of the region,
and minimize the possible negative effects on human health.
In Amazon, studies on the mercury (Hg) dynamics have been developed in the last years in both the environmental compartments and the organisms that inhabit this region. In this, mercury is known to present a natural occurrence that is intensified by anthropogenic factors, such as its use in small-scale mining. For contribute to the understanding of the Hg biogeochemistry in the Amazon, the present study sought to evaluate the levels of total mercury (HgT) in the bottom sediment and in the fish muscle of the Solimões River, analyzing the influence of seasonality and between the matrices evaluated. The Solimões river presents an equatorial climate, an Amazonian rainforest with fertile plains with seasonal flooding pulses resulting from the high rainfall of the first semester. Among the traditional communities there are indigenous and riverine people whose diet consists mainly of fish. The samples were collected in May and November of 2017 and were analyzed according to the methodology of Akagi et al (2004). The results obtained from the sediments were submitted to analysis of variance (ANOVA) and did not show seasonal variation in the regional levels of uncontaminated sites. Fish caught from different dietary habits, carnivorous, piscivorous, omnivorous, detritivorous and herbivorous presented a variation in HgT (Kruskal-Wallis test) between species in May and November, but the highest concentrations occurred in November 2017, suggesting that the flood pulses of the Amazonian rivers influence indirectly the concentrations of the metal. In both periods, carnivorous and piscivorous fish presented higher concentrations of HgT (Kruskal-Wallis test) followed by omnivorous, detritivorous and herbivorous indicating that factors related to the animal’s habit can influence in the variation of HgT. The concentrations in some carnivorous fish exceeded the limits proposed by the World Health Organization (WHO) and the Sanitary Surveillance Agency (ANVISA) for human consumption in November, giving special attention to the human consumption of these species. Therefore seasonality may influence the concentrations of HgT in fish, but for sediment this influence was not significant.

M.1.34
INORGANIC AND METHYLMERCURY BIOACCUMULATION, DISTRIBUTION AND TRANSFORMATION IN PHYTOPLANKTON SPECIES

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Phytoplankton could influence aquatic biogeochemical cycle of mercury directly through uptake and biotic transformations, and indirectly through the excretion of ligands influencing different abiotic and biotic transformations. Opposite to the substantial work performed with bacteria, the role of phytoplankton, such as green algae and cyanobacteria, in Hg transformation is poorly understood.

The goal of the study is to get insights on the role of phytoplankton in biotic Hg transformations in the freshwaters systems. Since the biotic transformations are essentially intracellular, the accumulation of inorganic (IHg) and monomethylmercury (MeHg, CH3Hg+), their cellular distribution and transformation in green alga Chlamydomonas reinhardtii, and cyanobacterium Synechocystis sp. were studied. Phytoplankton species were harvested at exponential and stationary growth phases and exposed to 1nM of 199Hg or 100 pM 201Hg for 24h. The cellular accumulation of IHg or MeHg was determined following isolation from the exposure medium by gentle centrifugation. To get an information about cellular compartments involved in the possible transformations, the cells were further separated to membrane and cytosol fractions. Hg analyses were carried out by isotopic dilution analysis gas chromatography coupled to inductively coupled plasma mass spectrometry. The changes in the ratio between the difference of control isotope concentration after and before incubation and the measured isotope concentration before incubation in the whole cells and the cellular fractions were used to determine the Hg transformations.

Results showed that both species accumulated significant amounts of IHg and MeHg, but the cellular concentrations were species- and growth phase- dependent. Under comparable exposure conditions, Synechocystis sp. accumulated about twice more IHg than C. reinhardtii. No difference in the whole cell IHg concentrations was found for Synechocystis sp. harvested in exponential and stationary growth phases. In green algae, both IHg and MeHg were mainly accumulated in the membrane fraction, thus their percentage in the cytosol varied between i.e. 10-15% in exponential and 35-40% in stationary phase. In cyanobacteria, about 50% of IHg and MeHg was found in the cytosol in Synechocystis sp. harvested in both exponential and stationary phases. Fluctuations in mercury concentration in each cellular fraction shown that there are mercury transfers between membrane fraction and cytosolic fraction. These variations also show that phytoplankton can carry out some mercury transformations (methylation and demethylation) and should be counted as a full participant in the biogeochemical cycle of mercury in aquatic systems.

M.1.33
INFLUENCE OF INVASIVE MACROPHYTES AND GUT MICROBIOTA ON MERCURY CONTAMINATION IN FISH: A MICROCOSMS STUDY

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The South western France aquatic lakes are temperate ecosystems subjected to the development of invasive macrophytes and with a recent problem related to mercury (Hg) contamination. It has been demonstrated that aquatic plant rhizosphere/periphyton is a favorable ecological niche for Hg methylation. Methylmercury (MeHg) formed in the periphyton could participate significantly to the food web contamination. Since aquatic plants are often considered as an important food source. The aim of this study was to determine the bioavailability of MeHg produced by plants roots in aquatic ecosystems. A microcosm experiment has been realized using isotopically enriched inorganic Hg at environmental concentrations (1 μg 199Hg/l). Three conditions have been tested (“sediment + fish”; “plant + fish”; “sediment + plant + fish”); plant model: Ludwigia sp; animal grazer: Pseudancistrus sp.). For all conditions, total Hg in fishes as well as MeHg associated with different compartments (water, sediments, roots macrophyte, fish) were analyzed by GC/ICP-MS. In addition sediment, plants, and fishes gut microbiota (end of the experiment) have been studied through MISEQ in all the conditions tested. The results revealed accumulation of the added Hg in both the plants periphyton and the sediments depending on the conditions. Me199Hg production in plants roots and the presence of this form in fishes (tissues and gut) highlighted a MeHg trophic transfer. Moreover, methylator bacteria were identified from the gut contents of the fishes when they were in the presence of plants by a high-through output cultivation method and by MISEQ sequencing. Some of them were related to bacteria found in the roots of Ludwigia sp. Based on these results, both the transfer of MeHg (and bacteria) from plants to fishes is highlighted but also Hg methylation is strongly suspected in the fish gut, potentially increasing the Hg bioaccumulation.
METHYLMERCURY PRODUCTION AND DEGRADATION UNDER LIGHT AND DARK CONDITIONS IN THE WATER COLUMN OF WESTERN US RESERVOIRS

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Previous studies have identified that reservoirs tend to have elevated fish methylmercury (MeHg) concentrations relative to natural lakes and free flowing rivers. There are several factors that contribute to this phenomenon, such as a shift from a lotic to lentic foodweb, increased sedimentation of mercury (Hg) and organic carbon, thermal stratification/development of an anoxic hypolimnion, among other processes. This study focuses on understanding one aspect of Hg cycling in a reservoir/lake: the production and degradation of methylmercury (MeHg) in the water column. The primary study location is the Hells Canyon Complex of three reservoirs on the Snake River along the Idaho-Oregon (USA) border. The degradation of MeHg was assessed as a biotic and abiotic process as well as under light and dark conditions. The study utilized stable isotope tracers of both inorganic Hg and MeHg in short-term (<50 hours) incubation experiments to assess MeHg production and degradation rates. The results showed that despite relatively high MeHg concentrations observed in the hypolimnion (at times >3 ng/L and >60% of the total-Hg present), the methylation rates in the anoxic hypolimnion of the water column were relatively low (on average 0.1%/hour), but were significantly higher compared to time-zero incubations and samples collected from the oxic epilimnetic waters. Water-column methylation also varied seasonally, between reservoirs, and locations within the reservoirs. This variation was mostly driven by the presence of anoxic conditions, which varied between years depending on snowmelt and other climatological conditions. Biotic demethylation rates in the dark were typically low and mostly below detection, whereas abiotic photodemethylation rates were much higher (around 1%/hour) but were significantly higher compared to time-zero incubations. The equilibrium concentrations with both Hg+2 and MeHg, as well as for different size-classes of particles. These results, along with binding isotherm data (Langmuir and Freundlich plots), are providing insight into sorption characteristics of mercury species with environmentally relevant microplastics.

PATTERNS IN MERCURY AND SELENIUM CONCENTRATIONS IN WATER, SEDIMENT, BIOFILM, AND INVERTEBRATE IN STREAMS DRAINING MOUNTAIN-TOP COAL MINING

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While both mercury (Hg) and selenium (Se) can bioaccumulate within aquatic ecosystems and are individually toxic to organisms. Se may protect against Hg bioaccumulation. Many studies thus propose that increased environmental concentrations and consumption of Se could reduce Hg toxicity in organisms. Yet, little is understood about the biogeochemical processes that potentially leads to this putative relationship. In this study, we seek to better understand the relationship between environmental Se concentrations and methylmercury (MeHg) production and accumulation. We measured concentrations of total Hg and MeHg in water, sediment, biofilm, stream macroinvertebrates, and riparian web-building spiders collected across a Se gradient (BDL-70 ug/L) due to mountaintop-mining of coal in Central Appalachia, USA. Our results show that Hg, MeHg, and Se all bioaccumulate through the food chain, with the highest concentrations found in macroinvertebrates. However, whereas Se bioaccumulation is enhanced in mined watersheds, Hg concentrations are lower in mined watershed compared to unmined watersheds. We also found limited evidence for an antagonistic relationship between Hg and Se at the microbial level. The interaction between these two elements is less conclusive in invertebrates; while MeHg and Se are negatively correlated in cranefly larvae, there is no correlation in spiders that prey on adult aquatic insects.

INTERACTIONS OF MERCURY SPECIES WITH WEATHERED MICROPLASTICS

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Heightening concern over microplastic pollution is their ability to serve as carriers of pollutants that are either part of the plastic (e.g. additives) or that are accumulated from the environment. For example, microplastics have been shown to adsorb some persistent organic pollutants, such as polyaromatic hydrocarbons, which are known to be taken up and accumulated by organisms. Certain plastics have also been shown to adsorb inorganic mercury (Hg+2) but the role microplastics play in transport and accumulation of this toxic heavy metal pollutant in aquatic ecosystems is not known. Given that both microplastics and Hg impact water quality and ecosystem health worldwide, determining sorption behavior between microplastics and Hg species (Hg+2 and MeHg) deserves scrutiny. In this study, we prepared microplastics by cryomilling weathered plastics found in the environment. Weathered plastics have different surface characteristics and pore structure compared to microplastics generated from raw virgin plastics. We have begun to examine the sorption characteristics between Hg-species and the small plastic particles. We spiked filtered natural (lake and river) water with known concentrations of mercury and allowed the mixture to equilibrate for at least 24 hours. We then added microplastics and observed uptake of the Hg onto the microplastic particles over time. For initial experiments, we determined total-Hg using a direct mercury analyzer (DMA). Preliminary results for high density polyethylene (HDPE) indicate rapid Hg+2 sorption to the microplastics, followed by a slower phase of equilibration lasting about 24 hours. The equilibrium sorption coefficient (Kd), determined by dividing the concentration of adsorbed mercury by the concentration of Hg remaining in the aqueous phase after equilibration, was 43 ml/g. This is significantly less than mercury sorption to natural sediments, however such sediments typically contain organic matter which Hg has a strong affinity to. We are completing experiments with different types of microplastics (e.g., polypropylene, polystyrene, polycarbonate, polyactic acid) at varying concentrations with both Hg+2 and MeHg, as well as for different size-classes of particles. These results, along with binding isotherm data (Langmuir and Freundlich plots), are providing insight into sorption characteristics of mercury species with environmentally relevant microplastics.
INVESTIGATING SEASONAL VARIATIONS IN CONCENTRATIONS OF MERCURY LEVELS IN TWO RECENTLY RESTORED URBAN WETLANDS

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As ubiquitous features of the urban landscape, wetlands have been recognized for their importance in habitat provision and the plethora of ecosystem services they can provide. In many cities they are useful solutions for storm water management, contaminant mitigation, and flood control. Previous studies have shown that constructed urban wetlands have the potential to increase aqueous methylmercury (MeHg) concentrations in the areas in which they are installed thus potentially contaminating aquatic systems and food webs that occur in close proximity. Despite the possible risk, created urban wetland systems have been severely under-studied and there is a lack of understanding regarding the seasonality of MeHg production and degradation, as well as the temporal changes that occur as the constructed wetland matures. The urban campus of the University of North Carolina at Greensboro (UNCG), restored two on-campus sites in March 2017 (also known as “The Wetlands Project”, both the wooded and open site are roughly 232 m² each in surface area). This restoration has resulted in significant increases in biodiversity, such as bat species, but a lack of knowledge about alterations in Hg cycling and how MeHg concentrations in sediment, water, and aquatic macroinvertebrates may vary over time in these systems. Monthly water samples from each site, as well as nearby streams have been collected since the first year of installation. These samples are analyzed for filtered (< 0.7 μm) total mercury (THg), MeHg, nutrients (phosphate), anions (sulfate), dissolved organic carbon, and total dissolved nitrogen concentrations; THg and MeHg concentrations are quantified using cold vapor atomic fluorescence spectroscopy (CVAFS). Seasonal sediment samples and some biota samples have also been collected and analyzed for THg and MeHg. So far, data has shown that the observed summer peaks in aqueous MeHg levels in the wooded site can be up to 200% higher than those observed in the open site and coincide with the more anoxic conditions (dissolved oxygen concentrations as low as 0.10 mg/L in surface water) during the dry summer. Preliminary sediment data has supported higher THg concentrations in the wooded site, likely as Hg is derived from surrounding urban forest. Surrounding land features (e.g. trees vs. lawns) could be contributing to the discrepancies observed between the campus sites by influencing the extent of production and degradation of MeHg.

MANAGING BEAVERS TO IMPROVE WATER QUALITY: EFFECTS ON MERCURY IN BIOTA

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The Eurasian beaver (Castor fiber L.) had been extirpated in many European countries during the 19th century. In the early 20th century beavers were however successfully re-introduced in areas of their former distribution range. Beavers as true ecosystem engineers have the potential to alter hydrological regimes and change biogeochemical pathways. The cycling of mercury (Hg), and specifically the transformation of Hg to its more bioavailable form, methyl-Hg (MeHg), may be influenced by beaver activity. The ability of beavers to build dams and hence to transform streams into series of wetlands and/or ponds with locally stagnant water, can cause elevated concentrations of MeHg in downstream water and biota. In the EU Interreg project WAMBAF (Water Management in Baltic Forests), we investigated if removal of beaver dams could mitigate the risk of elevated MeHg concentrations downstream. Different taxa of stream organisms covering a wide range of trophic levels, e.g. snails, blackfly larvae, and small predatory fishes, were sampled upstream and downstream of beaver dams in Poland, Lithuania, Latvia and Sweden. Sampling was conducted on six occasions during a 3-yrs period, three times before and three times after beaver dam removal. Analysis of sediment samples collected before dam removal identified higher MeHg concentrations in sediments within the beaver ponds and/or in the downstream compared to upstream sampling points, indicating that the beaver ponds acted as a source of MeHg. Preliminary results indicate that after removing the beaver dam and re-transforming the system to a stream, concentrations of Hg in biota decreased to the level of reference (upstream) values. The former sediments, now transformed to terrestrial and exposed soil were, however, still high in MeHg.
In a Hg laden environment, beaver dam removal could be a tool to help mitigate Hg burden downstream. However, dam removal without managing beaver density risks to translocate the problem since the affected beaver family will likely build a new dam at a different site. It should also be noted that beaver activities often have other positive environmental effects such as buffering of stream flow, increasing habitat and landscape heterogeneity, and functioning as a sediment trap with beneficial effects on biota diversity. As earlier research found higher MeHg concentrations in water downstream of young pioneer beaver ponds compared to old recolonized beaver ponds, we suggest that the removal of beaver dams would be more efficient in decreasing Hg burden downstream in young pioneer systems compared to old recolonized systems.

M.P.1.41

SPATIAL AND TEMPORAL MERCURY EXPORT DYNAMICS FROM WETLAND-DOMINATED HEADWATER CATCHMENTS IN THE BOREAL PLAIN, CANADA

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Wetland-dominated headwater catchments are known sources of methylmercury (MeHg), a bioaccumulative toxin, to downstream aquatic ecosystems. In the Western Boreal Plain there is a dearth of knowledge on the export dynamics of mercury from headwater catchments. To learn more about mercury cycling in the region, total mercury (THg), MeHg, major ions, and dissolved organic carbon concentrations were measured in surface water and hillslope runoff within the Stony Mountain Headwater Catchment Observatory (SMHCO) south of Fort McMurray, Alberta, Canada between July and October 2018. SMHCO comprises five wetland-dominated catchments with different dominant wetlands (northern ribbed fen, tamarack fen, poor fen, channel fen, and thicket swamp). The percentage of THg as MeHg in outflow waters typically increased over the growing season in all sites, peaking in August between 12-22%, though aqueous concentrations remained low. Over the study period, concentrations of MeHg increased and THg decreased at the outlets of the catchments. However, an increase in MeHg concentration was observed along the length of the channel fen, which was not observed in the other catchments. Unlike the fen dominated catchments, both THg and MeHg decreased along the length of the thicket swamp, concomitant with increased pH and proportion of particulate (>0.7 µm) bound mercury. This study highlights how different wetland-dominated headwater catchments in the region can affect downstream mercury loads. The possible MeHg sink function of the thicket swamp is particularly interesting as other recent research has shown swamps (e.g., alder swamps) to also be responsible for net decreases in MeHg in the landscape.

M.P.1.43

MERCURY (Hg2+) BIOACCUMULATION IN PICO-, NANO-, AND MICROPLANKTONIC SPECIES OF THE MICROBIAL FOOD WEB OF ULTRAOLIGOTROPHIC ANDEAN PATAGONIAN LAKES

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Dissolved inorganic mercury (Hg2+) is the most common chemical species in aquatic environments. In both marine and freshwater ecosystems, the incorporation of Hg2+ at the base of the pelagic food web can be an important pathway to trophic webs. Basal organisms comprising bacteria and phytoplankton may accumulate up to 105 times more Hg from the aqueous phase than the organisms at higher trophic levels. Then, to understand the incorporation of Hg2+ at the base of pelagic food webs is essential to delineate the pathway of Hg in aquatic ecosystems. Microbial assemblages are typical of deep ultraoligotrophic Andean Patagonian lakes and comprise pico-, nano-, and microplanktonic protists like picocyanobacteria, photoflagellates and mixotrophic ciliates. These species have a central role in the carbon cycle, primary production, and also in the incorporation of Hg2+ into lake food webs. In this study we evaluated experimentally the incorporation of Hg2+ in different species representative of the picoplankton fraction (Synechococcus sp., 0.2–2 µm), the nanoplanктon (Cryptomonas erosa, 2–20 µm), and the microplankton (the dinoflagellate Gymnodinium paradoxum and the mixotrophic ciliates, Stentor arauanus and Ophrydium naumannii, 20–200 µm). The radioisotope 197Hg was used to trace the Hg2+ incorporation in microbiota. The specific Hg2+ uptake was assessed considering the morphology and size of the different species. Hg uptake was analyzed as a function of cell surface (SCF: surface concentration factor) and cell volume (VCF: volume concentration factor), as proxies of adsorption and internalization, respectively. These organisms incorporate substantial amounts of dissolved Hg2+, displaying different Hg internalization and therefore, varying potential for Hg transfer. The SCF and VCF ranged between 38 and 1660 µL µm⁻², and

M.P.1.42

PERiphyton IS A HEAVEN FOR MERCURY ACCUMULATION AND ALGAL DIVERSITY AT HIGH ALTITUDE ENVIRONMENTS

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Inorganic mercury and its more toxic methylmercury form are subject to photo-reduction and photo-demethylation under UV light exposure in natural waters. Photo-reduction is known to be a significant process for the removal of Hg(II) and MeHg from surface waters. At the same time, high radiation inhibits photosynthesis and limits diversity and abundance of phytoplankton. However, little is known about the effect of radiation on mercury concentrations and algae diversity of periphyton. Extremely high-altitude environments such as Lake Titicaca (> 3800 m a.s.l.) allow performing natural experiments with light related effects on biota and biogeochemical cycles. Here we investigated the covariance between light penetration, algae diversity and mercury concentration in periphyton. Periphyton was cultivated in situ on artificial substrates at different depths (0.5, 1, 2.5, 3 and 3.5 m) in the water column. A significant effect of light attenuation was observed with depth. UV-B radiation penetrated only between 2.6 and 3.0 m, and UV-A penetrated between 4.9 and 7.2 m during the incubation (April to June). Unlike light attenuation, no significant differences in algae diversity and total mercury concentrations were observed with depth. Algae diversity varied more among replicates than among different depths. High variability on total Hg concentration in periphyton was also observed (2.8 to 37.9 ng g⁻¹). However, again differences among replicates were more significant than between depths (p > 0.05). A complementary analysis of algal diversity in natural periphyton at the more eutrophicaced area of Lake Titicaca shows higher light attenuation but still no significant effect on algal diversity. We then discuss the possible roles of periphyton on the fixation and chemical transformations of mercury. We also discuss potential ecological implications and propose two mechanisms for the possible protection of algae and mercury from light effects.
from 2 to 324 pL µm-3, respectively. In both cases, the values were highest for the dinoflagellate, followed by O. naumanni in SCF and by Synecococcus sp. in VCF. The high bioconcentration of Gymnodinium may be due to the adsorption on its external mucus sheath. In addition to surface area and quality, surface/volume ratio may likely control Hg2+ uptake in microplanktonic organisms. Hg bioaccumulated by pelagic protists can be transferred to higher trophic levels, regenerated to the dissolved phase by excretion, and/or transferred to the bottom sediments by particle sinking. Overall, in ultratropical oligotrophic Andean lakes, picoplankton and planktonic protists are key components of lake food webs, linking the pelagic and benthic Hg pathways, and thereby playing a central role in Hg trophodynamics.

**M.P.1.44**

**MERCURY IN RIVER AND FLOODPLAIN OF THE SOLIMÕES AND NEGRO BASINS (BRAZILIAN AMAZON)**

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River floodplains are known as important sites of mercury methylation. In Amazon lowland basins, floodplains vary in space, time and in the water quality of the overflowing rivers. This natural variability in extensive preserved areas makes Amazonian rivers interesting sites for studying the natural mercury cycle. Our objective was to investigate how spatio-temporal variations of Amazonian wetlands affect the mercury dynamics in Negro (acid and humic black-waters) and Solimões (muddy white-waters) basins. Sampling occurred in Negro (n = 52) and Solimões (n = 48) basins during low (November 2016) and high-water (June 2017) seasons. Total mercury (THg) and methylmercury (MeHg) concentrations were assessed in water and substrate (soil and sediment) samples of different environments of the floodplains (river, bare soil, under macrophytes bank and forest). Dissolved oxygen concentrations were higher in low-water compared to high-water season in both basins. Suspended solids concentrations, pH and electric conductivity varied between basins. THg concentrations in filtered (< 0.4 µm) black-waters were similar to those in unfiltered water. In white-waters, THg concentrations in filtered water were up to ~50% of the unfiltered water. Therefore, in white-waters, much of the mercury is associated with the suspended solids while in black-water it is dissolved. MeHg concentrations in unfiltered water were from 0.01 to 0.10 ng·L-1 in low-water season, and from 0.02 to 0.41 ng·L-1 in high-water season. During this last season, highest MeHg levels were observed in lake channels and vegetated flooded habitats, demonstrating the importance of floodplain as MeHg providers to the rivers. Organic matter represented between 0 and 56% of total substrate (soil and sediment) weight and had a weak correlation with THg concentrations. These were lower in Solimões basin (37±14 µg·kg-1 dry weight) than in Negro basin (79±33 µg·kg-1 dry weight), evidencing the naturally elevated mercury concentrations of substrates of the Negro basin. Within each basin, THg concentrations in substrate did not vary spatially neither temporally. Therefore, the habitat coverage and the flooding had no influence on substrate THg concentrations. We observed that the spatio-temporal variability was important for MeHg in water since flooded and vegetated areas were important MeHg contributors to the basin. However, neither the flood nor the spatial variability were important to soil THg concentrations. Considering that the Negro basin had the highest THg concentrations in substrates and that the physico-chemical properties of the basin is favorable for methylation it may have also high MeHg concentrations (currently under assessment).

**M.P.1.45**

**TRACING SOURCES OF MERCURY CONTAMINATION IN FRESHWATER FISHERIES ACROSS SPACE AND TIME**

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Inorganic mercury (Hg) and its conversion to the bioaccumulative organic methylmercury (MeHg), is responsible for most fish consumption advisories worldwide. Though the nutritional benefits of consuming fish are widely celebrated, in severe instances, cognitive impairment arising from high dietary Hg can offset the nutritional gains. Despite decades of recognition of the health threat posed by Hg, few ecosystems are studied in developing countries where individuals are highly reliant on fisheries. Therefore, we know little about the key sources of Hg to most major subsistence freshwater fisheries. Intensifying the concern, many regions of the world that rely on freshwater fisheries also rely on unregulated artisanal scale gold mining (ASGM) for income. Often, these fisheries and the adjacent watershed(s) surrounding them have become severely Hg contaminated and yet the exact locations of mining are frequently unknown. Identifying these mining hotspots and understanding the timing and degree of Hg enrichment requires baseline measurements and is requisite to managing and mitigating this Hg pollution.

Environmental chemists have commonly used inorganic media to reconstruct temporal trajectories of contamination. Previously we have demonstrated that in dynamic freshwater systems, fish Hg content does not trend with the Hg input history determined from sediment cores. To directly reconstruct Hg bioaccumulation trends, we have begun to explore the impact museum preservation processes have on Hg concentrations and stable isotope ratios of Hg, carbon and nitrogen. Preliminary results demonstrate that no significant fractionation of these isotopes occurs during museum preservation with formalin and ethanol, suggesting museum collected fish are viable for reconstructing historical trends and quickly capturing broad spatial ranges. Subsequent work will address whether severely Hg contaminated preservation reagents will impact fish Hg isotope composition.

Museum specimens collectively encompass pre- (n = 15,000) and post-industrial collections (n = 24 million) of fish from most of the largestl lakes (e.g. African Rift) and river fisheries (e.g. Mekong and Amazon) in the world. The resulting spatiotemporal coverage will offer unparalleled insights into the geography and timing of anthropogenic inputs of mercury to inland waters, the variation in natural background inputs, and the resulting threats to the health of the hundreds of millions of people who depend on freshwater fisheries as source of nutrition.

**M.P.1.46**

**THE DISTRIBUTION OF MERCURY AROUND THE LAKE SENTANI, PAPUA, INDONESIA**

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Lake Sentani is located at the northeast extremity of the Jayapura Regency in the Indonesian province of Papua. Although the lake is part of the Cyclops Strict Nature Reserve, there are some gold mining activity are there around Lake Sentani. The muddy water occurred by the min-
ing activity, flows into the Lake through creeks. The use of mercury was not reported by the mining activity but some case the tailings include heavy metals. Thus the impact of the tailing flowing into the Lake on ecosystems was concern. In this study, the mercury concentration in air, creek water and fish samples taken on the shore of Lake Sentani, Papua, Indonesia, was investigated. The samplings were conducted in April 2015. Twenty six fish samples which included Glossolepis incisus (f, m), Glossogobius sentaniensis, , Oxyeleotris heterodon, Amphiliopus labiatus, Oreochromis mossambicus were caught by local fishermen. Atmospheric mercury was collected on mercury collector tube as gold amalgam by sucking the air with air pump and measured by cold vapor atomic absorption spectrometry (CVAAS). The creek water samples were collected into Teflon bottles and brought back to the laboratory. The water samples were filtered through a membrane filter (pore size of 0.45 µm) and dissolved total mercury concentration in the filtered water was measured by CVAAS after BrCl digestion. Fish samples were freeze-dried and total mercury concentration was measured by CVAAS after wet digestion using HNO3-HClO4-H2SO4 at 230°C. The Hg concentration in fish samples was converted to wet weight basis by using the water content measured separately. Atmospheric mercury concentration ranged from 17 – 192 ng m-3 (avg. 78 ng m-3, n=5). The dissolved total mercury concentration in river water ranged from 0.58 – 15.3 ng L-1 (avg. 3.5 ng L-1, n=13). The higher values of these were observed near a mining site. Among the fish species, Glossolepis incisus (f) showed the highest mercury concentration of 0.198 – 0.584 mg kg-1 (avg. 0.289 mg kg-1, n = 4). The value was 20 times higher than the lowest concentration, 0.005 – 0.025 mg kg-1 (avg. 0.013 mg kg-1, n=3), observed for Oreochromis mossambicus. Among 26 fish samples, one sample contained mercury higher than the Indonesia National Standardization for mercury level in fish of 0.5 mg kg-1. The fact suggests that the inflow of mercury contained in the waste from the mining site gives a burden on ecosystems of Lake Sentani. The continuous survey will be required.

THE DISTRIBUTION OF MERCURY DISCHARGED BY ASGM ACTIVITY ALONG THE RIAU RIVER, RIAU, SUMATRA, INDONESIA

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Air, water, sediment, soil and epiphytic fern were collected at ten sampling locations set during 50 km of middle stream of Riau River in May, September, 2017 and October, 2018. Width of the river was more than 100 m and many mining machines were operated in the river. Atmospheric mercury was collected on mercury collector tube as gold amalgam by sucking the air with air pump and measured by cold vapor atomic absorption spectrometry (CVAAS). In workplace of gold shop, onsite measurement with a mercury analyzer was conducted. The water samples were separated into suspended particulate matter (SPM) and filtered water by filtration with membrane filter (pore size 0.45 µm). The T-Hg in the filtered water was measured by CVAAS after BrCl digestion. T-Hg and MeHg in solid samples were measured by CVAAS and by HPLC-CL method, respectively, after freeze-dried. Atmospheric mercury concentration along the river ranged from 2.9 – 45.4 ng m-3 (avg. ± s.d. = 10.0 ± 11.4 ng m-3). T-Hg in river water was 40.5 ± 28.9 ng L-1 and more than 90% of which was particulate mercury. SPM plays important role for mercury transport in the river. The T-Hg in the SPM was 0.140 ± 0.051 mg kg-1, which was significantly higher than 0.095 ± 0.071 mg kg-1 in sediment. T-Hg in riverbank soil of 0.046 ± 0.022 mg kg-1 tended to be lower than that in sediment, but the difference was not significant. The SPM may deposit on the riverbank soil at flood events. The T-Hg in fish samples (n=5) was 0.10 – 3.3 mg kg-1 and almost all the mercury was MeHg. The discharged mercury may be methylated and accumulated through the ecosystems in the river. Three gold shops were found in the urban area. The workplace of the shop has no ventilation equipment or the equipment did not work efficiently. During the burning process of gold amalgam, mercury concentration in the atmosphere rose sharply and exceeded the upper limit of the measurement range (> 1 mg m-3). Although the mercury concentration lowered gradually after the burning, the value kept > 0.01 mg m-3. The atmospheric mercury concentration of 0.01 – 0.13 mg m-3 was observed at the outside of a shop. Health impact for not only gold shop workers but also residents around the shop is concerned.

THE DYNAMICS OF MERCURY AROUND THE ARTISANAL AND SMALL-SCALE GOLD MINING AREA, CAMARINES NORTE, PHILIPPINES

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The distribution of total mercury (T-Hg) and organic mercury (org-Hg) in the environmental samples collected around the artisanal and small-scale gold mining (ASGM) area along the sea shore of Mambalao Bay, Camarines Norte, Philippines, was investigated. The samplings were conducted in Aug. 2017 and Sep. 2018. At each site, the soil samples were collected every 2 cm from the surface up to a depth of 10 cm. Marine sediment samples were collected with acrylic tubes. The obtained core samples were cut at every 2 cm. River sediment was collected with scoop. The samples were freeze-dried, ground withagate mortar, and used for determination of T-Hg and org-Hg concentrations, total organic carbon (TOC), and chemical composition. The atmospheric mercury concentration of east shore side, 6.1 - 25.8 ng/m3, was significantly higher than the value of 1.4 - 9.9 ng/m3 observed in west shore side, which suggested that the ASGM using mercury to extract gold from ore are there in east shore side. The average concentration of T-Hg in the forest soils of west shore side and those of east shore side were 0.081±0.028 mg kg-1 and 0.496±0.439 mg kg-1, respectively. In the vertical distribution of T-Hg in soil of the east shore side, the higher concentration was observed near the surface. These observations suggested that the mercury discharged into atmosphere by ASGM activity deposited and caused the increase in Hg concentration at the soil surface. The T-Hg, org-Hg and TOC showed a significant relationship, which suggested that the deposited mercury was adsorbed on organic matter and under high content of organic matter the mercury was subjected to methylmercury formation. The T-Hg concentration in river sediment in east shore side was significantly higher than that in marine sediment suggesting that the river transport of waste discharged from ASGM activity can become primary mercury source of the bay. In the vertical variations of T-Hg in the marine sediment, the higher values were observed near the estuary, and the vertical variations in core samples showed the increase in mercury concentration toward the surface. The highest concentration of T-Hg, 9.5 mg kg-1, was 2 orders of magnitude higher than the background levels of this area. If the ASGM activity continues, the inflow of contaminated waste will continue to raise the mercury levels in sediment, which will give a burden on ecosystems of the bay.
MULTI-YEAR RECORD OF ATMOSPHERIC MERCURY SPECIES AT A BACKGROUND MOUNTAIN STATION IN ANDEAN PATAGONIA (ARGENTINA): TEMPORAL TRENDS AND METEOROLOGICAL INFLUENCE

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 Nahuel Huapi National Park (NHNP) is a natural reserve of Patagonia (Argentina) limiting at its western stretch with several active volcanoes of the Andean volcanic belt (Southern Volcanic Zone of South America). The prevailing Pacific winds and the presence of the Andes determines a sharp precipitation and deposition gradient resulting in high mercury levels in western sectors of the Park. The EMMA station (Global Mercury Observation System, GMOS) is the southernmost Hg monitoring site of the continent and was set up within NHNP. This work provides continuous records of Gaseous Elemental Mercury (GEM) concentrations observed between 0.21 and 1.47 ng m^-3 (mean 0.86 ± 0.16 ng m^-3) and seasonal variation characterized by higher spring and summer levels (0.95 ± 0.13 ng m^-3 and 0.88 ± 0.15 ng m^-3, respectively) compared to winter and autumn concentrations (0.85 ± 0.16 ng m^-3 and 0.80 ± 0.15 ng m^-3). Day-time GEM levels were higher year-round. GEM varied between 0.42 and 37.2 ng m^-3 (mean 4.61 ± 4.00 ng m^-3) and PBM ranged from 0.42 to 20.1 pg m^-3 (mean 3.74 ± 3.41 pg m^-3) showing similarly marked seasonal trends with higher concentrations in the dry season (GOM: autumn=5.47 ± 4.39 pg m^-3; summer=4.64 ± 3.63 pg m^-3; PBM: autumn=6.32 ± 3.41 pg m^-3; summer=21.27 ± 21.71 pg m^-3). GEM levels at EMMA are in the lowest range within the concentration bounds reported for the Northern-Southern hemispheric gradient. PBM and GOM levels are moderate compared with other southern monitoring sites and varied more widely than GEM levels. Westerly winds, temperature and relative humidity showed up as the variables driving GEM, GOM and PBM levels at the EMMA Station. Backward Trajectory Analysis performed at different times showed up: i- the influence of long range transport determining low GEM, GOM and PBM levels brought by clean oceanic air masses from the free troposphere coming from the west (W) and southwest (SW) and, ii- the influence of short-range transport and low elevation air masses from the NNW and SW causing eventual increases in GOM and PBM levels at GEM levels, coinciding with the local influences of forest fires and volcanic activity upwind the EMMA station.
MERCURY FRACTIONATION IN CONTAMINATED SOILS FROM THE OAK RIDGE SITE, TENNESSEE (U.S.)

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The Y-12 National Security Facility is located near the city of Oak Ridge, Tennessee, USA that was built to produce components for various nuclear weapons systems. Mercury (Hg) was significantly used as a key element in the production enriched lithium isotopes for nuclear weapons. After the accident of 1958, large amounts of Hg was released to the environment causing severe contamination in soil, sediment, surface water, ground waters and the downstream environment along the East Fork Poplar Creek that originates from the Y-12 Security Complex. Most of the Hg contamination around Y-12 Complex occurred in the upper 10 feet of soils and fill. Remediation efforts have been made since then to alleviate the amount of mercury contamination that impacts the soil, water and wildlife at the Y-12 complex and surrounding areas. However, mercury levels in the water still exceed both the regulatory limits (51 ng/L) and the remediation goal (200 μg/L). The goal of this study was to investigate the mercury distribution in the top soils collected from the impacted areas in Oak Ridge TN, and its relation to other heavy metals, such as As, Pb, Cu and Zn. Sequential extraction was applied to determine Hg, As, Pb, Cu and Zn in nine different fractions of soils. Preliminary studies were conducted with artificially spiked and incubated soils as well as soils contaminated with enriched 200Hg isotope. Total digested was performed prior sequential extraction with HNO3 and HF mixture. The concentrations for total Hg (THg) varied between 5.3 mg/kg (for Bank samples) to 90 mg/kg for bottom layer soil samples. Fractionations measurements showed that the organic matter associated fraction contained most of Hg (organically bound Hg) ranging from 20 to 70% of THg, followed by amorphous Fe-oxide associated fraction (10 to 30% of total Hg) and residual fraction (3 to 15% of total Hg). Levels of soluble and exchangeable Hg species were not significant. Distribution of other heavy metals did not show any clear correlation with Hg in analyzed soil fractions (R2 = 0.03-0.40). A strong positive correlation however was noticed between Hg and As in several soils (R2 = 0.96). Most As was associated with amorphous Fe-oxides. Cu and Pb were dominant both in organic matter and amorphous oxide fractions. Zn was mostly bound to amorphous Fe-oxide but significant amount of Zn was also found to be associated with organic matter and crystalline Fe-oxides.

NEW INSIGHTS ON HG-SE INTERACTION IN SOIL-RICE SYSTEM: THE ROLE OF GEM

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Hg uptake by rice can be inhibited by Se in soil has been widely reported and demonstrated recent years. However, no matter the field study or the pot study that reported in the past, the effect of GEM (gaseous elemental Hg, usually occupy 95% of total gaseous Hg in air) on Hg-Se interaction in soil-rice system is poorly investigated and understood. One paper published in Environment Science and Technology speculated that deposition of Hg in air may inhibit Se uptake by rice. Although the model it provided seems to be reasonable, while persuasion is lacked due to the absence of systematic data. Here, we investigated the rice plants, that grown in Wanshan Hg mining area, with gradients of different mercury concentrations in soil and air. We found that Se in soil can only significantly inhibit Hg uptake by rice grown away from anthropogenic sources of mercury (no artificial smelting activities). Both the BAFs of Hg in rice tissues and TFs of Hg in root, stems leaves to rice grains were inhibited by Se in soil. However, inhibitive effect of Hg uptake by rice is greatly weakened in high background area of GEM, no matter the BAFs or TFs. This may be caused by much more proportion of Hg contributions originated from Hg in air, which disturbed and concealed the fact of inhibitive effect of Se on Hg comparing to low atmospheric Hg sites. Only significant positive correlation between GEM and Hg in polished rice was found indicate that high atmospheric Hg contributions in rice than in no artificial affected sites and Se is difficult to greatly inhibit Hg uptake from air and translocation to grain. We also observed that both soil Hg and atmospheric Hg inhibited Se uptake by rice, however, soil Hg and atmospheric Hg were positively with BAFs of Se in rice tissues, this may indicate that more Se is translocated to rice to antagonize toxicity of Hg in rice.

METHYLMERCURY IN THE OXIC WATER COLUMN OF A DEEP PERI-ALPINE LAKE

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Among the mercury species, the most hazardous for human and wildlife is methymercury (MeHg), a potent liposoluble neurotoxin, which is mainly produced by microbial activity in aquatic reduced environments, and has the property to biomagnify along the food chain. Several factors such as temperature, redox conditions, organic carbon, and sulphate availability impact the Hg(II) bioavailability in the biotic methylation process. Despite the well-established importance of the bottom sediments as a privileged site of biotic Hg methylation, growing evidences show that in marine environments a non-negligible fraction of MeHg is produced within the water column in layers with low dissolved oxygen and high organic particulate carbon concentrations. Methylation occurs also in the anoxic hypolimnion of lakes, and in 2016, our group established the potential role of settling particles in the Hg methylation in an oxic environment, with concentrations of MeHg in settling particles varying seasonally between 0.4 and 13 ng/g. Following this evidence, we currently develop a project to assess the presence of Hg methylation inside suspended particles in Lake Geneva. Continuous flow centrifugation was used to collect suspended particles from the main tributaries, and continuous flow filtration to sample lake suspended matter. Vertical profiles of ancillary parameters (temperature, pH, DO, turbidity, conductivity, fluorescence) to characterised water column conditions were measured using a “Seabird” multiprobe. Total mercury and methymercury concentrations were determined by standard CVAFS and CVAAAS analyses. Preliminary results show the presence of MeHg in suspended particles at 10 m depth (1.8±0.09 ng/g) and 50 m depth (2.04±0.31 ng/g), on a site located in the center of the lake, a few kilometres from the shore, and at a 309 m depth maximum depth. These results are comparable to those previously obtained on settling particles collected by sediment traps at the same period of the year, and are significantly higher than concentrations measured on suspended particles from the main tributaries (Rhone River: 0.12±0.02 ng/g; Aubonne River: 0.15±0.01 ng/g; Venoge River: 0.15±0.01 ng/g). These results are the first evidences of the presence of MeHg in the Lake Geneva suspended particles, they confirm the previous observations on settling particles and the likely production of MeHg in the oxic water column.

PRIMARY FACTORS INFLUENCING DISTRIBUTION OF METHYLMERCURY IN LAKES AND RIVERS: A PILOT STUDY FOR NATIONAL MERCURY MONITORING NETWORK IN SOUTH KOREA

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(1) GIST
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In order to setup a national Hg monitoring network in South Korea to estimate the annual mercury sedimentation flux into lakes in China, this study attempts to determine the concentrations of total mercury (THg) and methylmercury (MeHg) in lake sediments, as well as mercury deposits in the sediment. Investigations on individual lakes have been conducted, while regional research on various lakes around the country. 

M.P.1.58

**MERCURY CONCENTRATION AND SPECIATION IN MINE WASTES IN TONGREN MERCURY MINING AREA, SOUTHWEST CHINA AND ENVIRONMENTAL EFFECTS**

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Mercury mines are considered typical mercury (Hg) contaminated areas. Huge quantities of mine wastes were produced during long history of large scale Hg mining activities. Mine waste calcines are important mercury pollution sources to local environment. This study investigated Hg concentrations and speciation in mine wastes collected from Tongren Hg mine and their impacts on the surrounding environment with different remediation measures. Total Hg (THg) concentrations in the mine wastes varied widely from 4.15 to 825 mg/kg, and Hg0 was the dominant form in the wastes. No obvious deformations were observed in mineral boundaries of mine wastes by TEM analysis, indicating that the smelting processes were insufficient. Additionally, nanometer scale Hg compounds were observed in the mine wastes coupled with EDS microtopography analysis, which may pose potential risks to the local environment. Total soluble Hg (TSHg) concentrations in leachates of mine wastes averaged at 11.27 μg/L. THg concentrations in surrounding surface waters varied from 0.038 to 10.6 μg/L, and 21.1% of THg concentrations exceeded the level V of national standard (1 μg/L). The THg concentrations and pH in the surface water were significantly negatively correlated, indicating that Hg was more active under acidic conditions. Total gaseous mercury (TGM) concentrations above the mine waste heaps ranged from 13.5 to 309 ng/m3, which were significantly lower than previous studies. These data demonstrated the effects from restoration projects and proper treatment methods were needed in different mine waste heaps.

M.P.1.57

**SEDIMENT MERCURY AND METHYLMERCURY IN 35 CHINESE LAKES: CONCENTRATION LEVELS AND SEDIMENTATION FLUX**

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Lake sediments are key materials for mercury deposition and methylatation. Natural atmosphere deposition, soil erosion, river discharge and human activities release mercury into the water column, and finally the mercury deposits in the sediment. Investigations on individual lakes have been conducted, while regional research on various lakes around China has not been carried out. To better understand the mercury levels in lake sediments in China, a field survey on 35 lakes was conducted from June to October, 2014. Samples of lake sediment were collected from 100 sites at various lakes. All the large lakes in China were taken into account, such as Qinghai Lake, Poyang Lake, Dongting Lake, Xingkai Lake, along with some urban lakes, like West Lake in Hangzhou, East Lake in Wuhan, Xuanwu Lake in Nanjing. Samples were freeze-dried and sieved immediately after collection. Following the U.S.EPA method, this study attempts to determine the concentrations of total mercury (THg) and methylmercury (MeHg) in lake sediments, as well as to estimate the potential release of THg and MeHg flux. The THg concentrations in lake sediment vary from 13.6 ng/g (dry weight) to 1488 ng/g, with a median value of 85.0 ng/g, and the MeHg values vary between 0.05 ng/g and 1.70 ng/g, with a median value of 0.26 ng/g. Sediments from 5 urban lakes rank the top 5 of THg levels, with the THg concentrations from 353 ng/g to 1488 ng/g, indicating high human-source mercury release. Totally, more than 10 tons of THg deposited into the lake sediments in China in the year 2014, and due to the high sedimentation rate, Dongting Lake contributed an overwhelming majority of the total mercury sedimentation flux.

M.P.1.59

**SPATIAL AND TEMPORAL STATUS OF MERCURY IN THE POLLUTED URBAN RIVER ‘MITHI’ OF MUMBAI, INDIA**

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Total mercury (THg) levels were investigated in sediment and river water collected from Mithi river in Mumbai, India. Mithi river originates from the overflow of Vihar Lake and then receives the overflows from the Powai Lake. Mithi river flows for 15 kms and meets the Arabian Sea at Mahim Creek flowing through the populated areas consisting of under developed residential and unorganised and small industrial units such as scrap dealer, garages etc of the city. The samples were collected and analysed for THg with Milestone make DMA-1. THg levels in river water ranged from 0.19 to 137.04 μg kg-1 with a mean of 4.7 μg kg-1 and a 95% confidence interval for the mean of 1.21 to 8.19 μg kg-1. Sediment THg ranged from 49.96 to 472.98 μg kg-1 with a mean of 206.69 μg kg-1 and a 95% confidence interval for the mean of 158.89 to 254.49 μg kg-1. High temporal and spatial variation were observed with only six out of ninety-six samples showing THg concentration in river water above 5 μg kg-1. Statistical relationship...
between THg concentration and physicochemical parameters such as pH, chemical oxygen demand (COD), total suspended solids (TSS) were determined. Pearson correlation coefficient analysis showed no correlation between THg content and physico-chemical parameters. No correlation was observed between THg concentration in sediments and river water. Mumbai is a coastal area and fish is a staple food of populace. Literature review has revealed high THg levels in fishes and Mithi river may pose a point source of mercury pollution.

SEASONALITY OF DIPTERAN-MEDIATED METHYL-MERCURY FLUX FROM PONDS

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Methylmercury (MeHg) is an aquatic contaminant that can be transferred to terrestrial predators by emergent aquatic insects. We assessed the effects of month and pond permanence on dipteran-mediated MeHg flux (calculated as emergent dipteran biomass × dipteran MeHg concentration) in 10 experimental ponds. Emergent dipterans were collected weekly from permanent ponds with bluegill (Lepomis macrochirus; n = 5) and semipermanent ponds without fish (n = 5) over a 7-mo period (February–August, 2015). We detected a significant effect of month on MeHg flux from 6 dipteran taxa and aggregate MeHg flux, with the highest MeHg flux from herbivorous/detrivorous chironomid midges and predatory midges in March; biting midges, phan- tom midges and herbivorous/detrivorous orthodad midges in April; and mosquitoes in August. Aggregate dipteran-mediated MeHg flux peaked in April and then declined throughout the remainder of the summer. We did not detect a significant main effect of pond permanence or a significant month × pond permanence interaction effect on MeHg flux for any of the taxa examined in the present study or for aggregate MeHg flux. Given their ubiquity in aquatic systems and their importance in food webs at the land–water interface, dipterans are important taxa that should not be overlooked as a part of the Hg cycle.

LANDSCAPE AND WATER CHEMISTRY CONTROLS OF METHYLMERCURY LEVELS IN STREAMS OF A FORESTED WATERSHED IN NEW HAMPSHIRE, USA

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Forested watersheds in the Northeast U.S. are frequently hotspots for the formation and mobilization of methylmercury (MeHg). While inorganic mercury (Hg) levels and organic matter in these watersheds are strongly correlated, factors controlling levels of the toxic species, MeHg, require better understanding, particularly as these environments are under increased stress from climate change and anthropogenic pressures. We conducted a study of Hg speciation, dissolved organic carbon (DOC) quantity and quality, and landscape parameters across 12 tributaries of Lake Sunapee, New Hampshire, a watershed which is a hotspot for MeHg production and bioavailability. To examine the controls on MeHg levels in streams, water samples were collected from 27 sites in early spring and late summer, with more frequent sampling of 3 streams. Large variation in water MeHg levels (between 0.002 and 2.2 ng/L) and DOC concentrations (2 to 36 mg/L) was observed across sites. Levels of MeHg tracked water temperature over time within streams, but peak MeHg concentrations varied substantially between tributaries with different landscape characteristics. Landscape parameters (particularly wetlands and open water), stream water chemistry, and DOC quality could be used to predict MeHg levels across the watershed. Higher levels of MeHg, DOC, and terres- trial organic carbon quality were found in tributaries with greater % wetland in the catchment, whereas tributaries downstream of small lakes had lower MeHg and DOC concentrations, as well as more la- bile DOC fractions. Soluble iron was strongly associated with dissolved MeHg both spatially and temporally, suggesting reducing conditions in headwaters and wetlands were associated with MeHg production and release. These findings suggest that increases in precipitation and land disturbances, which support terrestrial organic matter dissolution and reducing conditions in soils and wetlands, will increase MeHg levels in streams in this region.

EFFECTS OF ENVIRONMENTAL DRIVERS ON PAST, PRESENT, AND FUTURE MERCURY CONCENTRA- TIONS IN FISH FROM BOREAL AND SUBARCTIC SCANDINAVIA

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The Mackenzie River, with a catchment >1 million km^2 and a mean water discharge of 10,000 m^3/s, is the largest conduit for freshwater and sediment delivery to the Beaufort Sea. During peak flow, the Mackenzie and its main tributaries have some of the highest Hg levels in freshwaters of the Canadian Arctic and subarctic (> 10 ng/L). An unknown fraction of this Hg is derived from thawing permafrost soils in the northern reaches of the Mackenzie basin. This contribution is likely to increase as NW Canada warms up over the next decades at nearly twice the mean rate of the whole country. To better anticipate the future impact of warming on riverine Hg transfer to the Beaufort Sea marine ecosystem, a Swedish-Canadian research project was initiated to identify and quantify the terrestrial sources of Hg in streams of the Mackenzie basin. Water was sampled from the Mackenzie itself and selected tributaries during spring peak flow in 2018, and will also be sampled during the base flow period in 2019. Water samples are being analysed for isotopic ratios of O and H in water, C and Hg (dissolved and particulate), as well as the optical properties of dissolved organic matter, to help in the source apportionment of Hg between various terrestrial pools such as rocks and organic soils. These data will be used to constrain a mixing model of water properties, including Hg loads, created for the Mackenzie drainage system. The mixing model will be used to simulate future riverine Hg transfer rates to the Beaufort Sea under varying scenarios of Hg release from the different terrestrial reservoirs, such as permafrost soils. The study design, methods, and preliminary findings will be presented.
Data on mercury (Hg) in freshwater fish from boreal and subarctic regions show an overall pattern of declining concentrations the last 50 years, in both Europe and North America. However, the last two decades, concentrations appear to be neutral or even increasing some places, despite reduced atmospheric emissions of Hg in these regions of the world. Further reduced emissions of Hg are expected in the near future as Hg reduction measures are implemented as part of the international agreement Minamata Convention on Mercury. How potential Hg reduction measures are influenced and potentially counteracted by other factors such as climate change and increasedrowning in catchments with different characteristics are largely unknown.

Since absence of data from the same lakes over time can lead to confusing temporal patterns drawn from spatial variation, we designed a sampling campaign to revisit lakes with historical data on Hg in fish along a north-south gradient in Norway and Sweden, from 59.0°N to 69.5° N. The lakes (n=25), although located in three different climatic regions, had similar gradients in dissolved organic carbon (DOC), and aqueous total Hg: South-boreal (n=9, 6.3±2.7 mg C L-1, 1.6±1.0 ng Hg L-1 – Mid-boreal (n=10, 6.5±7.3 mg C L-1, 1.9±1.3 ng Hg L-1) and Subarctic (n=7, 8.3±5.7 mg C L-1, 1.6±0.7 ng Hg L-1). Organic methyl-Hg (MeHg) were higher in the Mid-Boreal region (0.16±0.11 ng MeHg L-1) compared to the South-Boreal (0.06±0.06 ng MeHg L-1) and Subarctic regions (0.06±0.05 ng MeHg L-1). Perch (Perca fluviatilis) Hg concentrations were significantly higher in the Mid-Boreal region (0.44±0.38 mg kg-1) compared to South-Boreal (0.21±0.13 mg kg-1) and Subarctic regions (0.19±0.09 mg kg-1). The fish Hg concentrations were significantly positively correlated to the zooplankton MeHg concentrations, but there were no differences in biomagnification factors between the three regions (BMffish: concentrations in fish divided on concentrations in zooplankton, BMfzoopl: concentrations in zooplankton divided on concentrations in water), suggesting that the uptake at the base of the foodweb is of importance to the top predator Hg concentrations. We tested hypotheses on the main drivers of spatial patterns and temporal trends of Hg in fish in these lakes by collecting data on catchment characteristics (area, landuse, water chemistry (nutrients), gridded downscaled weather data (temperature, precipitation), and reconstructed DOC trends based on monitoring data and process-understanding of drivers.

**Effect of Body Size on Mercury Concentration in Shoreline Spiders**

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Recently, terrestrial shoreline spiders have been proposed as bioindicators of bioaccumulative aquatic contaminants such as mercury (Hg). Terrestrial shoreline spiders become contaminated with Hg when they feed on Hg-contaminated emergent aquatic insects. Although the effect of body size on contaminant bioaccumulation in other bioindicators, such as fish, has been thoroughly examined, there has been much less research on the effect of body size on concentrations of Hg in shoreline spiders. In this study, we determined the effect of body size on THg concentration explained by spider body size and found that spider THg concentration increased significantly with spider body size for Araneidae, Tetragnathidae, Salticidae and Pardosa spp. The percent of variation in THg concentration explained by spider body size ranged from 16% to 40% for Pardosa spp. and Salticidae, respectively. This study indicates that concentrations of Hg in shoreline spiders differ between spider taxa and within taxa by spider size. We recommend that future studies of Hg in shoreline spiders assess spider size.

**Placing HG Flux from Migrating Pacific Salmon in Context: Estimating Marine-Derived Inputs to Freshwater Ecosystems**

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MERCURY SPECIATION AT THE OXYCLINE OF A MERO-MICTIC LAKE (LAKE PAVIN, MASSIF CENTRAL, FRANCE)

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Mercury (Hg) speciation and partition are mainly governed by associations with sulfur (S), organic matter (OM), and iron (Fe). The oxyclines of aquatic environments, engendered by OM microbial degradation, shelter redox reactions of Fe and S, some of them involving phase changes. In the meantime, many Hg transformations, including methylation and reduction, are dictated by microbial activity especially in suboxic milieus. Lake Pavin, the unique meromictic maar lake in France, offers a unique natural laboratory where such Hg transformations can be observed in details. This 92-m deep lake has an aerobic upper layer (the mixolimnion) from the surface to mid-depth, overlaying the anaerobic monolimnion where sulfide concentrations reach 15 μM. The oxycline occupies a gradient over more than 10-m water layer (52-65 m), including a turbidity layer with high iron oxyhydroxide content. Despite an early rough description of Hg distribution in the water column (COSSA et al., 1994), no study focused on detailed Hg speciation and partition at the Pavin oxycline. We conducted several field campaigns in the last ten years, which combined the analysis of redox sensitive elements with Hg speciation both in aqueous and solid phases. In 2018, a 1-m resolution sampling has been performed at the oxycline for determining dissolved, particulate and colloidal concentrations of total mercury (HgT) and methylmercury (MeHg), and ancillary parameter (temperature, conductivity, pH, O2, FeII, SO4, HS-, etc.). Total particulate Hg, particulate MeHg, and colloidal HgT were low in the mixolimnion and peaked abruptly just above the oxycline; dissolved HgT and MeHg maxima were just below. Concentrations of Hg species decreased gradually deeper in the monolimnion, an increased again, but slightly, near the bottom. Reductive dissolution and precipitation of Fe appear to have a major role in these distributions. The layer where MeHg increases coincided with sulfate reducing zone.

TERRESTRIAL ORGANIC MATTER DRIVES INCREASED MEHg AND REDUCED ESSENTIAL FATTY ACID CONTENT IN ZOOPLANKTON FROM BOREAL AND SUBARCTIC SCANDINAVIAN LAKES

POSTE, Amanda1; KIDD, Karen; VEITEBERG BRAATEN, Hans Fredrik; BORGÅ, Katrine; AKERBLÖM, Staffan; ARTS, Michael; DE WIT, Heleen

1)NIWA

The objective of this work was to evaluate the Hg levels in target organs of one species of kingfisher, Chloroceryle amazona, in three South American rivers in Brazilian Amazonia and Pantanal. We determined Hg in liver, muscle, feathers and, in relation to size, weight and age of the birds, and Hg in the river water, and in relation to the deforestation dynamics of the areas, reconstructed in a time series of 40 years. The highest Hg were measured in the suspended particulate (8.6 ± 3.7 ng/L) and filtered portions (0.9 ± 0.4 ng/L) of the Teles Pires River in comparison with Juruena River (4.1 ± 3.6 and 0.8 ± 0.2 ng/L, respectively). The highest Hg among tissues was in the following order: feathers (4.97 ± 0.86 ng/L) > liver (0.80 ± 0.018 ng/L) > muscle (0.41 ± 0.11 ng/L). The highest levels in the feathers and muscle were found in the Teles Pires River samples (F=7.78, p=0.03; F=17.16, p=0.01 respectively). On the other hand, liver showed the highest Hg concentration in the samples of the Juruena River (F=3.83; p=0.04). There is a significant correlation between THg concentrations in feathers and muscle (R²=0.76, p=0.01) in both rivers. Likewise, we found a significant positive correlation between the animal’s length and Hg concentrations in liver (R²=0.10, p=0.04) and feathers (R²=0.13; p=0.02). The satellite images showed severe changes in the landscape, with the withdrawal of native vegetation for agriculture or livestock. Considering the total area of buffers, created within the collection area in each river, the Teles Pires River (cerrado-Amazonian transition area) lost about 25% of its original coverage, whereas the Juruena river (Amazon forest) lost is 18% and the Paraguay (cerrado) / humid zone / shrub vegetation) around 35.92%, between the years of 1988-2018. Our results suggest C. amazona as a potential sentinel species for the monitoring of environmental Hg contamination in Amazonia and Pantanal. In addition, our data point to a possible relationship between deforestation and Hg values in river water and biota.
Increases in terrestrial organic matter (tOM) transport from catchments to boreal lakes can affect methyl mercury (MeHg) accumulation in aquatic biota both directly by increasing concentrations of aqueous MeHg, and indirectly through effects on MeHg bioavailability and on energy pathways in the lower food web. We carried out a detailed study of water chemistry, zooplankton diet and fatty acid (FA) composition and MeHg accumulation in zooplankton in 25 Scandinavian lakes. The selected lakes were clustered in three latitudinally-distinct sampling regions (south boreal: 59–60.7° N; mid-Scandinavian: 63.1–65.7° N; and subarctic: 68.8–69.5° N), and covered a range of tOM concentrations within each of the three sampling regions. Higher tOM was correlated with higher aqueous Hg concentrations, lower estimated areal pelagic primary productivity, and evidence of increased contribution of terrestrial particles to pelagic particulate organic matter. Based on dietary marker analysis (d13C, d15N, and fatty acid [FA] composition), zooplankton diet was strongly linked to feeding mechanism, with dietary reliance on phytoplankton highest in the selective-feeding calanoid copepods, and lowest in filter feeding cladocerans. Zooplankton dietary reliance on phytoplankton and their concentrations of high-quality lipids, including polyunsaturated fatty acids such as EPA and DHA, were higher in the clear-water lakes than in the brown-water lakes, where bacterial and terrestrial food sources were more prevalent. MeHg was highest in zooplankton from the brown-water lakes, likely reflecting the higher aqueous MeHg concentrations. We also calculated the ratio of MeHg in zooplankton relative to the essential fatty acid DHA, in order to assess the relative nutritional quality (i.e. MeHg contamination vs. essential fatty acid content) of zooplankton as prey for higher trophic levels, and found that this ratio was significantly higher for brown vs. clear water lakes across all study regions. Our results suggest that, overall, higher tOM results in higher MeHg concentrations in water and zooplankton, and reduces zooplankton dietary reliance on phytoplankton. Increased tOM thus leads to a decrease in the nutritional quality of zooplankton (i.e. higher MeHg concentrations, and lower concentrations of essential fatty acids), which may cascade up the food web with negative implications for higher trophic levels.

M.P.1.73

ANOMALOUS MULTIPLE-MERCURY ISOTOPE FRACTIONATION DURING UVC-PHOTOLYTIC OXIDATION OF GASEOUS HGO IN THE ATMOSPHERE

SUN, Guangyi; SOMMAR, Jonas; FENG, Xinbin; ZHAO, Huifang; LI, Kai

The composition of mercury (Hg) isotopes in foremost atmospheric samples, including considerable isotopic anomalies for the even-mass-number 200Hg and 204Hg, have so far defied any stringent explanation. Here we report the triggering of large odd- and even-MIF during the reaction of UVC photolytically excited Hg atoms with synthetic air for a span of experimental temperatures and pressures relevant to the atmosphere. With 202Hg/198Hg ratio chosen for describing MIF following Blum & Bergquist, irrespective of temperature and pressure, the isotope composition of remaining HgO becomes mass-independently enriched in 199Hg in 199Hg > 201Hg > 203Hg and depleted in 200Hg. The extent of MIF triggered by UVC photo-oxidation decreased in the order of 204Hg > 199Hg > 201Hg > 203Hg, and increases with temperature. Regressions of ∆200Hg vs. ∆204Hg and 199Hg/198Hg vs. ∆201Hg yield slopes of −0.08 and 2.0 and about −0.2 and 1.5 at 298 and 233 K, respectively. In between the two higher temperatures investigated, there is a transition from normal MDF kinetic isotope fractionation (the lighter isotope 198Hg reacts faster than the heavier 200Hg) at 298 K to an inverse MDF effect (202Hg reacts faster than 199Hg) at 253 K. In the atmosphere, the generation of highly reactive Hg as electronically excited atoms (Hg0) may only take place in the upper stratosphere due to the attenuation of UVC-light by O2 and O3 molecular absorption underneath. We predict that a replenishment of Hg0 is sustained from photo-dissociation of gaseous oxidized mercury (GOM) compounds by radiation from 190 to 210 nm penetrating deep into the stratosphere, which would make the studied photo-oxidation a viable source of anomalous multiple-mercury isotope fractionation in GOM product formed. MIF will be inherited in stratospheric GOM that eventually descends into troposphere by deep/shallow stratosphere-troposphere exchange and dry deposits, including via aggregation on settling aerosols or through scavenging by convective clouds which become part of precipitation. The triggering of discernible even-MIF has partially been linked to photochemical self-shielding, an abundance-dependent line saturation process, operating during photolysis of molecules/atoms that have line-type absorption spectra with isotopically separated bands. Together with other effects (e.g., mutual shielding), self-shielding may cause massive isotope fractionation and may explain the non-MDF pattern in the atmospheric and cosmo-chemistry of O, N, S and plausibly Hg.

M.P.1.74

COMBINING MERCURY ISOTOPE AND SPECIES ANALYSES FOR THE INVESTIGATION OF CREEK SEDIMENTS DOWNSTREAM OF A HG(II) CHLORIDE CONTAMINATED INDUSTRIAL LEGACY SITE

SCHWAB, Lorenz; ROTHE, Florian; MCLAGAN, David S.; KRAEMER, Stephan M.; BIESTER, Harald; WIEDERHOLD, Jan G.

Mercury (Hg) release from former industrial sites can represent a significant local and regional environmental threat long after the initial contamination. Understanding the fate, mobility and bioavailability of Hg is essential for risk assessment and site management. In this study, we present Hg isotope and speciation data from creek sediments collected downstream of a former kyanisation facility (Black For-
est, SW Germany) where timber was preserved by Hg(II) chloride (HgCl2) treatment. Several tons of Hg have been released to local soils (which were not removed but overbuilt) and groundwater during the time of operation. Exfiltration of contaminated groundwater (Hg concentrations up to 700 µg/L) into the adjacent creek is leading to contamination of sediments and fish. This site serves as a natural laboratory to study Hg fate and biogeochemical processes at a HgCl2 contaminated site. Total Hg concentrations in the creek sediments (<2 mm) ranged from 19 µg kg⁻¹ at background locations to 77 mg/kg near the exfiltration of contaminated groundwater. The fine fraction (<125 µm) was consistently enriched in Hg (75µg/kg to 340 mg/kg). XRF data indicated weak correlations of Hg concentrations with major elements (Fe, S). A five-step sequential extraction indicated changes in Hg speciation of the sediments along the riverbed. Close to the exfiltration of contaminated groundwater, Hg was predominantly present in the F4 extract (12M HNO3), while in samples further downstream Hg was mostly present in the F3 extract (1M KOH). Pyrolytic thermo-desorption analysis confirmed the Hg speciation change from highly contaminated to less contaminated sediment samples by a shift in the maximum Hg release temperature from +250°C to 300°C. Isotope analyses by CV- MC- ICP-MS revealed significant δ202Hg-NIST-3133 variations between contaminated and background samples. Samples with highest Hg concentrations exhibited δ202Hg of +0.01‰ to -0.98‰. Samples with lower concentrations further downstream were isotopically lighter (-1.23‰ to 3.09‰). Only small isotopic differences between the fine fraction and bulk samples were observed. A conservative end-member mixing model used to estimate the extent of Hg contribution from the Kyanisation facility in sediments indicated differences between the fine fraction and bulk samples were observed. In a parallel study, also presented in this session, we address Hg isotopic signatures in sequential extracts will provide further insight into a decreasing influence with distance from the industrial source and a shift in the maximum Hg release temperature. Total Hg concentrations in the creek sediments (<2 mm) ranged from 0.17 µg/kg to 4.24 mg/kg. Sediments (101.6 ± 71.0 ng g⁻¹ and 0.3 ± 0.2 ng g⁻¹ respectively) were observed between canyon and continental shelf sediments. However, a reverse trend, suggesting a higher MeHg potential production in coastal sediments, was observed. A fine particulate matter enrichment, the MeHg proportion showed a decrease and those concentrations increased with the distance to the coast due to potential atmospheric transformation processes. Precipitation and atmospheric total suspended particulates (TSP) were collected from urban, suburban, and rural sites in Xiamen, southeast China during August 2017 – July 2018. All precipitation samples and TSP samples were analyzed for mercury isotopes compositions. Most precipitation samples were characterized by negative mass-dependent fractionation (MDF) (δ202Hg = -1.9‰ to 0.11‰), positive mass-independent fractionation (MIF) of odd isotopes (Δ199Hg = 0.01‰ to 0.43‰ and Δ201Hg = -0.01‰ to 0.45‰), and slightly positive MIF of even isotopes (Δ200Hg = 0.04‰ to 0.25‰). Most TSP-bound mercury (PBM) displayed negative MDF (δ202Hg = -2.24‰ to 0.27‰) and odd-MIF (Δ199Hg = -0.50‰ to 0.07‰ and Δ201Hg = -0.49‰ to -0.06‰), and positive even-MIF (Δ200Hg = 0.01‰ to 0.14‰). The δ202Hg values of precipitation were comparable to that of atmospheric PBM, which indicates that PBM was a major contribution to wet deposited Hg. The δ202Hg values of precipitation were consistent with those of coal-fired flue gas, suggesting that coal-fired power plant was an important source of wet deposited Hg. Larger MIF of 199Hg in atmospheric PBM in rural site than in urban site may result from the extended in-aerosol photoreduction during long-range transportation. The opposite Δ199Hg values of PBM and precipitation suggests the occurrence of aqueous photoreduction in water droplets. Backward air mass trajectory analysis showed that the δ202Hg value of PBM during short-range terrestrial air mass flow was relatively low. The Δ199Hg and Δ201Hg values of PBM during marine air mass flow were elevated, while the δ202Hg value was more positive. This study suggests that Hg isotope is a powerful tool for identifying the effects in deposited Hg from local and long-range transport sources and for exploring the potential atmospheric transformation processes.

Mercury (Hg) isotopic composition analysis is a useful tool to accurately identify the Hg sources and transformation mechanism of Hg. Specially, determination of mass-dependent (MDF) and -independent (MIF) fractionation of Hg isotope provides important information on the management of bio-accessible Hg. In this study, we characterized the stable isotopic composition of ambient air, sediment, and fish by coupling the both MDF and MIF values for Hg isotopes with a back-trajectory model in areas impacted by Hg contamination. All particle bound Hg (PBM) and total gaseous Hg (TGM) samples defined a straight line with a Δ199Hg/Δ201Hg slope of about 0.96, almost consistent with the results of the Hg2+ photo-reduction experiment, suggesting a possible effect of photochemical reduction during TGM-PBM transform. Potentially, the enrichment of TGM in urban area during these processes can explain the abundant PBM in summer. Paro Lake has high Hg in sediment that has three end-members Hg isotope composition by metal smelting (Pb, Zn), mining tail, and background soil in δ202Hg. Comparison of MDF and MIF signatures in fish reveals that bioaccumulated Hg is partially similar to atmospherically derived Hg stable isotopic composition than other input sources. This study investigated that Hg stable isotopic composition could serve as quantity and quality tool for tracing Hg sources in environment.

**ISOTOPIC COMPOSITION OF ATOMIC MERCURY AT URBAN AND RURAL SITES IN KOREA: SOURCES AND TRANSPORT PATHWAYS**

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Mercury (Hg) isotopic composition analysis is a useful tool to accurately identify the Hg sources and transformation mechanism of Hg. Specially, determination of mass-dependent (MDF) and -independent (MIF) fractionation of Hg isotope provides important information on the management of bio-accessible Hg. In this study, we characterized the stable isotopic composition of ambient air, sediment, and fish by coupling the both MDF and MIF values for Hg isotopes with a back-trajectory model in areas impacted by Hg contamination. All particle bound Hg (PBM) and total gaseous Hg (TGM) samples defined a straight line with a Δ199Hg/Δ201Hg slope of about 0.96, almost consistent with the results of the Hg2+ photo-reduction experiment, suggesting a possible effect of photochemical reduction during TGM-PBM transform. Potentially, the enrichment of TGM in urban area during these processes can explain the abundant PBM in summer. Paro Lake has high Hg in sediment that has three end-members Hg isotope composition by metal smelting (Pb, Zn), mining tail, and background soil in δ202Hg. Comparison of MDF and MIF signatures in fish reveals that bioaccumulated Hg is partially similar to atmospherically derived Hg stable isotopic composition than other input sources. This study investigated that Hg stable isotopic composition could serve as quantity and quality tool for tracing Hg sources in environment.

**MERCURY AND CARBON ISOTOPES EVIDENCE FOR BIOGEOCHEMICAL CYCLE OF Hg IN CABRETON SUBMARINE CANYON SEDIMENTS (ATLANTIC OCEAN, SW FRANCE)**

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Sediments are an integrative compartment for mercury (Hg) originating from both anthropogenic and natural sources. The measurement of spatial variations of Hg isotope ratios in sediments may enable source identification and tracking of environmental processes. In this study, the distribution of mercury species concentrations (inorganic mercury (Hg(II)) and methylmercury (MeHg)) and isotopic composition of Hg and carbon (δ13C) in surface sediments of a transect along the Cabreton Canyon were analysed. Higher Hg(II) and MeHg average concentrations were observed in canyon sediments (344.3 ± 317.2 ng g⁻¹ and 1.0 ± 0.6 ng g⁻¹, respectively) than in continental shelf sediments (101.6 ± 71.0 ng g⁻¹ and 0.3 ± 0.2 ng g⁻¹, respectively). Although these concentrations increased with the distance to the coast due to a fine particulate matter enrichment, the MeHg proportion showed a reverse trend, suggesting a higher MeHg potential production in coastal sediments. No distinct differences in Hg isotopic composition were observed between canyon and continental shelf sediments. However
isotopic ratios varied according Hg concentrations levels with an increase of δ202Hg and δ199Hg from the coast to the deep ocean. The coastal sediments (first 10 km) showed more negative δ202Hg values ranging from -0.94 to -0.48 ‰. In contrast, the furthest stations exhibited δ202Hg values from -0.62 to 0.27 ‰. The results suggest that coastal stations were impacted by different Hg sources than deep sea stations. Isotope ratios found in the coastal sediments were very similar than those detected in the adjacent Adour estuary, which suggests Hg terrestrial inputs as the dominating Hg source in near coastal regions. The different Hg origin in the canyon sediments is reinforced by a positive correlation between the δ²⁰²Hg and the δ13C. More positive values observed in the furthest stations may indicate Hg isotopic ratios altered by different natural geochemical processes (e.g., photoreduction and preferential adsorption processes).

M.P.1.78

MERCURY ISOTOPE FRACTIONATION AND SPECIATION IN SURFACE SOILS AND DRILLING CORES OF INDUSTRIAL LEGACY SITES CONTAMINATED BY TIMBER KIYANISATION WITH MERCURY(II) CHLORIDE.

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Mercury (Hg) kyanisation was patented by John Howard Kyan in 1832 and involves the preservation of timber via steeping it in ~0.66% Hg(II) chloride (HgCl2) solution. Leaks and ineffective storage and disposal has resulted in extensive environmental Hg contamination at these sites; compounded by the high solubility of HgCl2. These sites thus provide a unique opportunity to study Hg biogeochemical processes in situ without concerns of detection or quantification limits that can be problematic elsewhere. Here, we address Hg speciation and isotopic composition in undried drilling cores, topsoil and excavated waste materials (concentrations up to 50, 320, and 740 mg/kg, respectively) from two former kyanisation facilities in SW Germany. Hg stable isotope and pyrolytic thermo-desorption (PTD) measurements were used to distinguish Hg dispersion and transformation processes at these sites. Isotope analyses of a drill core showed some variability in MDF signatures (δ202HgNIST-3133) with negative values (down to -0.57%o) in the upper layers (above 4m), values close to 0% from 5 to 9 m, and slightly negative values of about -0.1 to -0.2‰ in the lowest layers (10 – 15m), which are in direct contact with groundwater. PTD analyses of topsoil and upper core layers showed that the majority of Hg was in the soil matrix-bound fraction (Hg release range: 200 – 300°C), although peaks were in the lower end of this range. These data suggest weakly bound HgCl2 associated with the original contamination is likely the dominant Hg species in these samples. PTD analyses from the aquifer zone of a drill core revealed the presence of Hg(0) (Hg release range: 200 – 300°C), suggesting Hg reduction processes may be occurring in the aquifers. Topsoil and waste materials from the same site showed variable MDF signatures (0.73% to 0.14%). In addition to matrix-bound Hg, waste materials also released some Hg in the 300 – 350°C range indicative of stronger complexed Hg species. Disturbances of this material during its removal and processing may have caused some Hg losses through volatilisation or dissolution enriching the substrate in heavier isotopes and less soluble, less volatile Hg species. All soil, core, or waste material samples measured so far exhibited very little MIF (±0.1% Δ199Hg). This work accompanies another study addressing Hg contamination in creek sediments downstream of one of the field sites (Schwab et al.).

M.P.1.79

PATHWAYS OF METHYLMERCURY UPTAKE INTO A HETEROOTRPHIC MARINE DINOFLAGELLATE

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Methylmercury (MeHg) predominantly enters the marine food chain through active and passive uptake into phytoplankton. This uptake can be inhibited by the strong binding of MeHg to dissolved organic matter (DOM), and this influence depends on both the quantity and quality of the DOM. In heterotrophic phytoplankton, such as the dinoflagellate Oxyrrhis marina, DOM is taken up as an energy resource. We therefore hypothesized that MeHg-DOM binding may enhance MeHg uptake by O. marina and other heterotrophic unicellular algae. This hypothesis is investigated via a series of controlled experiments using MeHg spikes, cultured heterotrophic dinoflagellate Oxyrrhis marina, and its prey, the autotrophic Haptophyte Isochrysis galbana. Three pathways were investigated: the passive uptake of MeHg into dead cells, uptake of MeHg bound to DOM, and consumption of prey exposed to MeHg. The results of these experiments will be presented and discussed in terms of the potential for heterotrophic organisms to enhance assimilation of MeHg at the base of the marine food chain in the presence of DOM. The role of DOM in mercury bioaccumulation is especially relevant in regards to future altered C loading in coastal systems.

M.P.1.81

SEDIMENT ARCHIVES OF HG CONCENTRATION AND ISOTOPIC COMPOSITION IN MOUNTAIN OLIGOTROPHIC LAKES OF THE CENTRAL PYRENEES (ARAGON, SPAIN)

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Mercury (Hg) isotopic composition offers new insights to Hg cycling processes in all environmental ecosystems, but very few studies have documented Hg cycling in pristine oligotrophic lakes. In this work, two sediment cores from Southern Central Pyrenean lakes have been investigated: Estanyà (karstic lake, 670m asl, core dated from ~2086 to 2001) and Marborè (alpine lake, 2612m asl, core dated from ~835 to 1969). The two study sites, located in a North-South alitudinal transect, show similarities with small surface lake areas and middle-sized watersheds made up mostly of carbonated bedrock. Nevertheless, bioclimatic conditions are substantially different with lower temperature and higher precipitations in the glacial Lake Marborè. In addition, catchment influences on the biogeochemical characteristics of Lake Estanyà are much more important because of the vegetation surrounding the lake and the hydrological balance mainly controlled by groundwater inputs. Determination of total Hg content by pyrolysis gold amalgamation-AAS provide a historical record of the Hg inputs. Besides, Hg stable isotope signatures (MC-ICP-MS) are used as tracers of Hg cycling (MIF-δ202Hg and odd MIF-δ199Hg), and Hg deposition pathway (even MIF-δ200Hg, wet vs dry Hg deposition). In sediment archives from Lake Estanyà and Lake Marborè, Hg concentrations show low level with mean values of respec-
the beginning of the Industrial Period (1750). A progressive increase of Hg concentrations is observed, mirroring the production in Almadén Hg mines (Southern Spain), exhibiting a maximum for Estanyà (97±2ng/g) and for Marboré (106±1 ng/g). Hg isotopic results highlight also this trend as the Industrial Period is characterized by higher odd MIF values (Mass Independent Fractionation, Δ199Hg). Indeed, before 1750, Δ199Hg = 0.03±0.07% for Estanyà and Δ199Hg = -0.07±0.07% for Marboré whereas Δ199Hg = 0.21±0.09% for Estanyà until 1976 and Δ199Hg = 0.20±0.14% for Marboré up to present day. This result is also well supported by a comparison with Estibere (2100m asl, Southern Central Pyrenees) peat record, in previous published work, which displays the same trend of MIF values than Marboré. Finally, the influence of the watershed is well demonstrated using even MIF - Δ200Hg which exhibits significant difference between the two lakes: Estanyà being more influenced by dry deposition (low Δ200Hg) than Marboré influenced by wet depositions (higher Δ200Hg, rain and snow).

M.P.1.83

USE OF STABLE MERCURY ISOTOPE TO ASSESS THE CONTRIBUTION OF DIFFUSE LEGACY SOURCES OF DISSOLVED MERCURY TO STREAM WATER.

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Historical and ongoing releases of mercury (Hg) have resulted in a legacy of Hg contamination in streambed sediment, streambanks, and floodplain soils downstream of the Y-12 National Security Complex (Y12), along the flow path of East Fork Poplar Creek (EFPC) near Oak Ridge, Tennessee, USA. Much of the Hg associated with streambed sediments, streambanks, and floodplain soils resides in relatively insoluble fractions, and has thus low anthropogenic legacy Hg (THg) concentrations. However, recent studies comparing hydrologic discharge and THg flux from Y12 and Lower EFPC suggest that additional dissolved Hg from hyporheic pore water or groundwater discharge may contribute as much as a third of downstream dissolved THg during baseflow. Thus, the over-arching goal of this project was to use natural Hg stable isotope signatures to gain a more comprehensive quantitative and mechanistic understanding of the processes that supply dissolved Hg to surface water and thus drive observations of watershed-scale Hg fluxes. To achieve this goal, we have undertaken an intensive multi-seasonal field study that couples the Hg isotopic composition of dissolved THg in stream water and in critical subsurface ecosystem compartments (i.e., hyporheic zone, riparian floodplains, and groundwater) with hydrologic flux measurements in four gauged reaches of EFPC. The release of dissolved THg into EFPC is highly variable, declining rapidly prior to export from Y-12. Outside of Y-12, dissolved THg fluxes variably increase along the flow path, likely due to inputs of diffuse legacy Hg. Inputs of diffuse legacy Hg are largest and most consistent within the upper reach of Lower EFPC, possibly related to high-Hg concentration Historic Release Deposits. Hyporheic pore water and riparian groundwater dissolved THg concentrations were also highly variable. Groundwater typically had lower dissolved THg than adjacent stream water. The riparian floodplain at one site (EFK18.0) had elevated dissolved THg, likely coinciding with Historic Release Deposits. Center-channel hyporheic pore water consistently had higher dissolved THg than overlying stream water. The hyporheic zone at our upstream-most site (EFK22.3), closest to Y12, appears to be a significant hotspot of diffuse legacy dissolved THg inputs to EFPC. By combining an isotope mass balance of stream water dissolved THg fluxes with an assessment of the relative importance of dissolved THg contributed to the stream across critical interfaces, we aim to directly link diffuse legacy source(s) of dissolved Hg in critical subsurface zones to changes in dissolved Hg flux observed at the watershed scale.

M.P.1.84

USING MERCURY STABLE ISOTOPE TO ASSESS RE-MOBILIZATION OF LEGACY MERCURY IN AN INDUSTRIAL CONTAMINATED STREAM

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The broad goal of this project is to better understand the role of anthropogenic legacy mercury deposits in the mercury biogeochemical cycle within stream ecosystems. While legacy mercury within streambed sediment largely resides in recalcitrant forms (e.g., mercury

THE DIFFERENTIAL TRANSPORT OF INORGANIC MERCURY DUE TO FORESTRY PRACTICES ON HILLSLOPES: A FIELD EXPERIMENT USING ENRICHED STABLE ISOTOPE TRACERS

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The movement of mercury within the landscape is an important component of regional mercury cycling; however, relative to other processes, such as methylation, mercury transport remains poorly understood. The high soil-water partitioning coefficients of inorganic mercury (Hg(II)) suggest that subsurface transport would likely occur as preferential flow, bound to colloids or dissolved organic matter. Furthermore, anthropogenic activities, such as forest harvesting, can greatly alter the hydrological pathways and geochemical conditions that affect Hg(II) transport. Limiting the removal of residual biomass from harvested hillslopes has been shown to decrease runoff post-harvest, which may alter the subsurface transport of Hg(II) from these disturbed systems. This study aimed to investigate the effect of post-harvest biomass removal on the transport of Hg(II) in a northern Minnesota mature aspen forest using enriched stable mercury isotope tracers. One uniform hillslope was divided into three treatment blocks (Reference, Biomass-Removed, and Biomass-Left) and two different isotope tracers applied pre-harvest (200Hg, 2011) and post-harvest (204Hg, 2012) to assess the difference in Hg(II) transport. Harvesting occurred between December 2011 and March of 2012 in the Biomass-Removed and Biomass-Left blocks, where the residual biomass was removed in the Biomass-Removed treatment but left on the ground in the Biomass-Left treatment. Between 15 – 23 μg/m2 of enriched Hg(II) tracer was applied to the three sites once snowmelt ended and measured throughout the summer using subsurface runoff collectors. Additionally, the hydrological conditions at each site and runoff volumes were recorded. During the study period (May – early August) 406 and 360 mm of precipitation fell during 2011 and 2012, respectively. Relative to the input, only 0.06 to 0.16% of the added 200Hg was recovered in 2011, resulting in Treatment:Reference ratios of 0.38 and 0.32 for the Biomass-Left and Biomass-Removed, respectively. Post-harvest, tracer recovery increased to between 0.48 and 1.12% and Treatment:Reference ratios were 1.86 and 3.34 for the Biomass-Left and Biomass-Removed, respectively. Under wet conditions (2012), a greater proportion of the soil water was available for exchange with precipitation, mobilizing a greater proportion of ambient mercury, which accounted for 89–96% of the total mercury measured. However, under drier conditions (2012), subsurface transport was likely relegated to preferential flow pathways, resulting in a lower proportion of ambient mercury relative to the tracer (77–84%). The differential nature of the subsurface mercury transport depending on the precipitation regimes illustrates that Hg(II) was primarily transported though preferential flow on hillslopes, regardless of the forestry practices.
sulfides), small portions may be more mobile and bioavailable. Re-mobilized legacy mercury has the potential to contribute to stream water mercury loads and/or may be more bioavailable for transformation into methylmercury and incorporation into the food web. In this study, we used mercury isotope ratios to determine whether legacy mercury in streambed sediment may contribute dissolved mercury to the surface water of East Fork Poplar Creek, a contaminated stream in Oak Ridge, Tennessee, USA. We performed mercury isotope analyses on five-step sequential extractions of streambed sediment collected from East Fork Poplar Creek, downstream of the historical point-source of mercury. Bulk sediment δ202Hg values ranged from -0.18‰ to 0.40‰ (±0.03‰, 2SD) and Δ199Hg values ranged from -0.12‰ to -0.06‰ (±0.02‰, 2SD). Isotopic analyses of the sequential extractions revealed that weak acid-soluble mercury had lower δ202Hg values (by 0.29 ± 0.10‰) and higher Δ199Hg values (by 0.08 ± 0.02‰), relative to the total mercury in the sediment. Organically-bound mercury also had higher Δ199Hg values (by 0.09 ± 0.02‰), while water-soluble mercury was isotopically similar to the recalcitrant forms. The similarity between the most soluble and the most recalcitrant pools of mercury suggests that the water-soluble pool may represent a “first flush” of re-mobilized recalcitrant legacy mercury. Ongoing isotopic analyses of surface water and hyporheic pore water will reveal whether there is a relationship between in situ dissolved mercury isotopic composition and potentially re-mobilized (extracted) sediment fractions. Thus far, hyporheic pore water with higher dissolved mercury concentrations appear to be most isotopically similar to the “first flush” and to the recalcitrant pools of mercury within the sediment. These data suggest potential re-mobilization of recalcitrant legacy mercury from streambed sediment to the hyporheic pore water, which may subsequently enter the surface flow or be incorporated into the food web.

M.P.1.85

USING MERCURY STABLE ISOTOPES TO DETERMINE SOURCES OF MERCURY IN THE FOOD WEB OF THE ST. LOUIS RIVER, MN, USA

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Mercury contamination in the Great Lakes region is a prevalent concern due to elevated Hg concentrations in fish in relation to human health and wildlife guidelines. While atmospheric deposition of Hg is ubiquitous, releases from legacy Hg point-sources have resulted in numerous Areas of Concern (AOCs) across the Great Lakes. One of these AOCs is the lower St. Louis River, which is the largest tributary to Lake Superior, and has fish Hg concentrations double that of the open lake. Despite these highly elevated concentrations, it is difficult to infer the sources of Hg to these fish due to different Hg inputs (e.g. precipitation, legacy, or upstream runoff) coupled to the complex ecology at river mouths.

The aim of this study was to utilize Hg stable isotopes to elucidate Hg sources across the different trophic levels of the St. Louis River food web including zooplankton, benthic invertebrates (mayfly larvae and dragonflies), riparian spiders, prey fish (shiners, Yellow Perch), and game fish (Walleye and Northern Pike). Invertebrates and prey fish from the St Louis River exhibited Hg isotopic fingerprints similar to the “first flush” and to the recalcitrant pools of mercury, indicating potential bioaccumulation of legacy Hg. Game fish displayed greater variability in isotope values, with some individuals exhibiting highly enriched signatures (δ202Hg = 0.8 to 1.2) in comparison to prey species. Precipitation in Lake Superior is a likely secondary source of Hg to game fish; this was confirmed with the additional Hg isotope tracers Δ199Hg and Δ200Hg, which displayed higher photochemical and atmospheric processing, respectively in these individuals. A reference site on the Bad River was also examined to confirm that the legacy signature observed in the lower St. Louis River food web was from industrial Hg sources and not from the natural transformation of upstream Hg. The Bad River, which has similar geomorphological characteristics and food web structure to the St Louis River, displayed a completely different Hg isotope signature in biota (δ202Hg = -1.0 to -0.8) more likely related to upstream watershed Hg and confirming the preservation of an industrial source across the food web in the lower St. Louis River.

M.P.1.86

MERCURY UPTAKE BY DESULFOVIBRIO DESULFURICANS ND132: PASSIVE OR ACTIVE?

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Methylmercury is produced predominantly by a small group of anaerobic microorganisms possessing a gene pair, hgcaB, that confers the ability to convert inorganic mercury (Hg(II)) to methylmercury. However, our understanding of the pathways and factors that control Hg(II) uptake by these organisms is limited, and it remains controversial whether they take up Hg(II) passively or actively. In this study, we used the sulfate-reducing bacterium Desulfovibrio desulfuricans ND132 as a model methylating organism and examined the dynamics of concurrent Hg(II) adsorption, uptake, and methylation by both viable and inactivated cells or spheroplasts in laboratory incubations. We present evidence for predominantly passive uptake of Hg(II) by ND132 cells and show that, in the absence of thiols, >60% of the added Hg(II) (25 nM) was taken up passively in 48 h by live and heat-killed cells and also by cells treated with the proton gradient uncoupler, carbonyl cyanide m-chlorophenyl hydrazone (CCCP). Heat treatment or CCCP treatment halted Hg(II) methylation, but did not stop cellular Hg(II) uptake, which is likely driven by competitive binding of Hg(II) by intracellular proteins or thiol-containing cellular components. As a result, the presence of 50 µM thioglutathione substantially decreased Hg(II) uptake by both the heat-killed and CCCP-treated cells due to competition between cells and glutathione for Hg(II) binding. Similarly, treatment with CCCP impaired the ability of spheroplasts to methylete Hg(II) but did not stop Hg(II) uptake. Spheroplasts also showed a greater capacity to adsorb Hg(II) than whole cells, and the level of cytoplasmic membrane-bound Hg(II) correlated well with methylmercury production, suggesting that Hg(II) methylation is associated with the cytoplasmic HgcaB proteins, as previously proposed. The results indicate that cellular Hg(II) uptake by ND132 cells is primarily controlled by Hg(II) speciation and ligand exchange and appears independent of active metabolic processes.

M.P.1.87

KINETICS OF MERCURY METHYLATION CATALYZED BY HGCAB

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Bioaccumulation of highly toxic methylmercury (MeHg) in the food web is a significant public health concern. MeHg typically accounts for at least 90% of the mercury in fish. The majority of MeHg in the environment originates from the conversion of mercuric mercury (Hg(III)) by an enzyme-catalyzed process associated with the activity of anaerobic bacteria and archaea carrying the hgcaB gene cluster. The two genes are predicted to encode a corrinoid-dependent membrane pro-
tein, HgcA, and a [4Fe-4S] ferredoxin, HgcB, consistent with roles as a methyl carrier and electron shuttle, respectively. Although microbial Hg methyltransferase activity has been characterized in vivo, the relationship between Hg methylation and cellular metabolism, specifically the roles of HgcA and HgcB are not well understood. Proteomics studies with the model Hg-methylating bacteria Geobacter sulfurreducens PCA and Desulfovibrio desulfituricans ND132 have demonstrated that HgcA and HgcB are exceptionally low in abundance. We determined the kinetics of enzymatic Hg methylation in cell lysates D. desulfituricans ND132 and demonstrated that the activity of the proteins HgcA and HgcB irreversibly converts mercuric mercury Hg(II) to MeHg. The enzymatic Hg methylation mediated by HgcAB is highly oxygen-sensitive, irreversible, and follows Michaelis-Menten kinetics with an apparent KM of 3.2 nM and Vmax of 19.7 fmol·min⁻¹·mg⁻¹ total protein for the substrate Hg(II). The chemical speciation of the Hg(II) substrate is an important factor to consider due to the high affinity of Hg(II) for biological thiols with stability constants of up to 45 for Hg(II)-bis-thiolate complexes, which may limit availability of Hg(II). We investigated the impact of thiol levels on MeHg formation by HgcA and HgcB and found that methylation activity is not impaired at high thiol/Hg(II) ratios. Furthermore, we explored the role of cellular metabolites, such as 5-methyltetrahydrofolate, pyruvate, ATP and S-adenosyl methionine (SAM), on Hg methylation activity in ND132 cell lysates and identified a correlation between S-adenosyl methionine levels and Hg methylation rates. The results provide new insights into the function of HgcA and HgcB and their interdependence with cellular carbon and energy metabolism. A comprehensive understanding of the various geochemical and biochemical factors culminating in the production of MeHg will facilitate the development of effective strategies to reduce exposure to this pervasive neurotoxin.

**IMPACT OF METABOLISM, THIOLS AND MERCURY CONCENTRATION ON MERCURY METHYLATION AND HGCA EXPRESSION IN PSEUDODESULFUVIBIO HYDRARGYRI BEROC1.**

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Methylmercury (MeHg) is the most toxic species of mercury (Hg) since it bioaccumulates in trophic chain, leading to human exposure. MeHg has mainly biotic origin and sulfate reducing bacteria (SRB) are the main contributors in most aquatic ecosystems. While SRB produce large amounts of sulfide when growing under sulfate reduction, their versatile metabolism leads them to grow under non sulfidogenic conditions. SRB, especially Geobacter sulfurreducens, Desulfovibrio desulfituricans and Desulfo bacterium Hildenborough are known to produce HgcA and HgcB which methylate Hg(II) to MeHg irreversibly. The enzymatic Hg methylation mediated by HgcAB is highly oxygen-sensitive, irreversible, and follows Michaelis-Menten kinetics with an apparent KM of 3.2 nM and Vmax of 19.7 fmol·min⁻¹·mg⁻¹ total protein for the substrate Hg(II). The chemical speciation of the Hg(II) substrate is an important factor to consider due to the high affinity of Hg(II) for biological thiols with stability constants of up to 45 for Hg(II)-bis-thiolate complexes, which may limit availability of Hg(II). We investigated the impact of thiol levels on MeHg formation by HgcA and HgcB and found that methylation activity is not impaired at high thiol/Hg(II) ratios. Furthermore, we explored the role of cellular metabolites, such as 5-methyltetrahydrofolate, pyruvate, ATP and S-adenosyl methionine (SAM), on Hg methylation activity in ND132 cell lysates and identified a correlation between S-adenosyl methionine levels and Hg methylation rates. The results provide new insights into the function of HgcA and HgcB and their interdependence with cellular carbon and energy metabolism. A comprehensive understanding of the various geochemical and biochemical factors culminating in the production of MeHg will facilitate the development of effective strategies to reduce exposure to this pervasive neurotoxin.

**TIME DYNAMICS OF LOW MOLECULAR MASS THIOL BIOSYNTHESIS BY ANAEROBIC MICROORGANISMS AND THEIR MULTIPLE ROLES ON MERCURY CELLULAR UPTAKE AND METHYLATION**

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The formation of the neurotoxin methylmercury (MeHg) is a biotic process where anaerobic bacteria methylate inorganic divalent Hg (Hg(II)) intracellularly. The cellular uptake mechanisms are still not identified, but low molecular mass (LMM) thiols play an important role together with thiol groups on the outer membrane in controlling the chemical speciation of Hg(II). For example, increased concentration of specific LMM thiols, especially cysteine, is known to enhance the formation of MeHg. A recent study showed that metabolically active anaerobic microorganisms produced LMM thiols in vivo and exported them to concentrations up to 100 nM in the assay medium. The concentration range was sufficient to significantly affect the chemical speciation, uptake and methylation of Hg(II) without any external addition of LMM thiols. At low mercury concentration (~50 nM) the chemical speciation was dominated by the Hg(Cys)₂ species. In this study we investigate the time dynamics of biosynthesis and cellular export of LMM thiols by Geobacter sulfurreducens and Desulfovibrio desulfituricans ND132 and the impact on the chemical speciation and methylation of Hg(II). LMM thiols were separated by liquid chromatography and determined by electrospray ionization tandem mass spectrometry (LC-ESI-MS/MS) and Hg(LMM-RS)₂ complexes were determined by thermodynamic modeling and by direct measurements using LC-Inductively coupled plasma MS (LC-ICPMS). Preliminary results will be presented for the production of LMM thiol compounds, formation of Hg(LMM-RS)₂ complexes and the Hg(II) methylation rate during typical time courses for bacterial Hg methylation assays. Characterizing the time-dependent molecular composition of LMM thiols associated with methylating microbes is important to further understand their multiple roles on Hg(II) uptake and MeHg formation in bacteria assays and in the environment.

**ABUNDANCE AND DIVERSITY OF HGCA+ MICROBES IN CHESAPEAKE SALT MARSH SOILS – RELATIONSHIPS TO MEHG AND SITE BIOGEOCHEMISTRY**

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We explored the abundance and diversity of Hg-methylating organisms in salt marsh soils along the US east coast, along with soil biogeochemistry including MeHg accumulation and gross MeHg production rates. Our goal was to evaluate the role of Hg methylator community structure, relative to biogeochemistry, in determining MeHg accumulation in soils. Soil cores were obtained from marsh sites with salinities ranging from 2 to 13 ppt and different dominant vegetation types, Soils averaged ~100 ng Hg/g and ranged 0.1 to 10% MeHg. The strongest biogeochemical parameters related to the accumulation of MeHg were dissolved Hg and dissolved sulfite, which correlated with Hg methylation activity in soils. In this study, the results helped to determine if the difference in MeHg production observed in cells growing in different metabolism conditions, was related to the complexation of Hg to sulfide/sulfur and/or related to the number of cells in the sample. Furthermore, the difference on MeHg production was related to hgcA gene expression under different growing conditions.
Our study indicated that Hg contamination is high within the vicinity of the mined area and reduces downhill away from the site. The maximum concentration of 1,111 ng/g exceeds the allowable Hg levels of 4100 ng/g for protection of ecosystem health and 1000 ng/g for protective of the water resource of the National Norms and Standards for the remediation of contaminated land and soil quality in South Africa, Notice 467 of 2013.

Key words: Mercury, methyl-mercury, thermo-desorption analysis, soils, South Africa

M.P.1.92

DETERMINATION OF THIOL COMPLEXES OF MERCURY SPECIES IN CULTURES OF METHYLATING BACTERIAL STRAINS

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Microorganisms play a central role in methylmercury (MeHg) production in aquatic systems, either directly by controlling inorganic mercury (Hg(II)) methylation and MeHg degradation either indirectly, by changing Hg speciation. The chemical speciation of Hg(II) plays a key role in uptake and MeHg formation and the chemical speciation of the formed MeHg controls also the export from the cell. Chemical forms of Hg(II) and MeHg which have been reported to be available for uptake/export in methylating bacteria include neutral sulfide complexes and complexes with specific low molecular mass (LMM) thiols. Accurate determination of the chemical speciation of Hg(II) and MeHg is thus crucial when elucidating the mechanism of MeHg formation.

In this work, a novel analytical method has been developed based on ultra-high performance liquid chromatography in combination with electrospray-ionization tandem mass spectrometry to analyze sulfides and LMM thiols including reduced and oxidized thiols and their corresponding Hg(II) and MeHg complexes. In a second step, experimentations with pure cultures of a methylating bacterium exposed to Hg(II) have been performed to determine the nature of MeHg and Hg(II) thiol complexes by the analysis of extra- and intracellular fractions.

M.P.2.1

ASSOCIATION OF ENERGY METABOLISM BIOMARKERS AND MERCURY EXPOSURE IN THE BRAZILIAN WESTERN AMAZON

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Exposure to mercury has been linked to disorders in the metabolism of lipids and glucose and may contribute to metabolic syndrome and insulin resistance. This study aimed to evaluate the association of biomarkers related to energy metabolism with the environmental mercury exposure in a city of the Purus river basin, Acre State, Brazil. A comparative study was carried out in Beja village, Pará river basin, Pará State (2,428 km between localities), An epidemiological survey was performed with blood and hair samples collection for total mercury analysis (Hg-T) and blood for serum lipoproteins analysis (total cholesterol, LDL, HDL, non-HDL cholesterol, triglycerides), glycemia, insulin, and leptin. T-Hg analyzes were performed by CVAAS. Lipoproteins and glycemia were analyzed by automated enzymatic method.
Insulin and leptin were analyzed by enzyme immunoassay. Geometric mean of T-Hg in Manoel Urbano city was 16.12 μg.l-1 in blood (95% CI 13.63 to 19.07) and 4.22 μg.g-1 in hair (95% CI 3.57 to 4.99). In Beja geometric mean was 4.29 μg.l-1 in blood (95% CI 3.66 to 5.03) and 0.82 μg.g-1 in hair (95% CI 0.70 to 0.97). In Manoel Urbano, the highest levels of T-Hg in blood were observed in participants aged 40 and older (p=0.007), men (p=0.027), normal weight (p=0.049), smokers (p=0.007) who consumed two or more fish meals per week (p<0.000), total cholesterol at or above 200 mg/dl (0.009), LDL equal to or above 130 mg/dl (p=0.030), non-HDL cholesterol equal to or above 160 mg/dl (p=0.004) and triglycerides equal to or above 150 mg/dl (p=0.017). Mercury levels in hair was associated with age over 40 years (p=0.003), overweight (p=0.031), consumption of two or more fish meals per week (p=0.000), total cholesterol equal to or above 200 mg/dl (0.013), LDL equal to or above 130 mg/dl (p=0.036), leptin outside the reference levels (p=0.025) and hypertension (p=0.024). In Beja Village T-Hg levels in blood were higher in the age group of 40 to 59 years old (p=0.046) and in smokers (p=0.026). T-Hg levels in hair were not associated with any analyzed variables. It was found a possible association between T-Hg levels and total cholesterol, non-HDL cholesterol, triglycerides and leptin, suggesting a possible interaction between the exposure and these biomarkers profile.

M.P.2.2

BURDEN OF MILD MENTAL RETARDATION ATTRIBUTED TO PRENATAL MERCURY EXPOSURE IN AMAZON: LOCAL AND REGIONAL ESTIMATES

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The gold rush in the Amazon Region caused an increase of mercury (Hg) levels in the environment, and, consequently, raised human exposure. Once released into aquatic systems, Hg could generate methylmercury (MeHg), an extremely toxic compound, which is accumulated through trophic chains. Several studies have provided evidences of the brain sensitivity to MeHg, as well as, of the fetus vulnerability during pregnancy. The main objective of this study was to estimate the Mild Mental Retardation (MMR) in Amazonian populations, caused by prenatal MeHg exposure and these biomarkers profile.

8-isoprostanes). ANCOVA with post-hoc comparison was used to assess the effect of consumption of fish with higher and lower doses of Hg on markers of inflammation and oxidative stress, while controlling for age, BMI and baseline biomarker status.

All participants were healthy females of childbearing age with a median (IQR) age of 23 (20, 30) years, and BMI of 22.7 (20.7, 26.4) kg/m2. Total Hg content of the tuna and sardines was 0.014mg and 0.004mg per 140g portion respectively. The median (IQR) Hg intake from fish per week for participants in the tuna group was 0.014 (0.014, 0.029), and for participants in the sardines group, Hg intake per week was 0.008 (0.004, 0.008mg). No significant effect of consuming fish with differing doses of Hg was observed for markers of inflammation or oxidative stress. In conclusion, the current study found that intervention with higher and lower Hg doses from fish did not have an effect on inflammatory or oxidative stress markers when compared to the no fish group. Further research is required to examine the effect of Hg from fish on such biomarkers.

M.P.2.4

METHYLMERCURY TOXIC EFFECTS ON HUMAN STEM CELLS FROM EXFOLIATED DECIDUOUS TEETH

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Methylmercury (MeHg) is a high toxicity global pollutant to environment and living beings. The main source of intoxication with MeHg is through ingestion of contaminated fish and oral cavity cells are targets to MeHg-induced toxicity. The human stem cells from exfoliated deciduous teeth (SHED) are a mixed population of highly proliferative, clonogenic cells with the ability of differentiating into a variety of cell types, including fibroblasts and odontoblasts. Since Hg blood levels in the Amazon population are around 0.3μM, in the present study, we aimed to show MeHg effect even on low concentrations. SHED cell lines were exposed to 0.1, 5 and 10μM of MeHg for 24h and analyzed through cell viability, metabolism and reduced glutathione levels as an indicative of oxidative stress. Our results showed that 5 and 10μM leads to a decrease on cell viability (54.61 ± 1.1% and 43.95 ± 2.3%, respectively) and metabolism (30.10 ± 3.6% and 20.91 ± 1.3%, respectively). However, the oxidative stress showed by glutathione levels decreases even on the lower concentration (80% ± 3.7%) as well as above 5 (20.78% ± 2.6%) and 10μM (21.13% ± 4.3%). Our study indicates that 0.1μM of MeHg are not able to induce primary endpoints of toxicity as cell death and changes on metabolism of SHED cells, however, this concentration alters the proper oxidative balance of SHED cells. As oxidative stress could lead to cell damage, chronic exposures over 0.1μM of MeHg could be harmful to human cells.
METHYLMERCURY EFFECTS ON HUMAN ORAL CAVITY CELLS

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Mercury exposure is primarily associated with ingestion of contaminated fish in its most toxic form, MeHg. Although its toxic effects are related to the nervous, cardiovascular and immune systems, oral cavity cells are directly (during food intake) and indirectly (through the presence of mercury in the blood) exposed to this metal. Among the cells existing in the oral cavity, periodontal ligament fibroblasts (FLP) are important cells responsible for the production of matrix and extracellular collagen, besides sustentation, renewal, repair and tissue regeneration. In the present study, FLP cell lines exposed to two distinct concentrations of MeHg for 24h were analyzed for toxic effects (metal accumulation, cell viability and metabolism) as well as parameters related to oxidative stress (DNA damage, lipid peroxidation and total antioxidant capacity). Concentrations were determined after LC50 definition (4.2 μM).

The first concentration is known to be higher and possible toxic (3 μM), while the second one is found in the blood of populations exposed to metal (0.3 μM), such as riverine communities from Amazon region with high consumption of fish. After FLP cells were exposed to MeHg, we observed the accumulation of mercury in 0.3 μM and 3 μM treatments (0.07 ± 0.008 μg/L and 0.45 ± 0.02 μg/L). This accumulation had as a linear-type saturation curve indicating that metal accumulated diffusively in the cells, typical of organic form of the metal (MeHg) and responsible for the higher toxicity. However, although mercury accumulated in both treatments, the cell viability and metabolism only decreased significantly in the highest concentration used (68.0 ± 1.4% and 33.9 ± 11.1%, respectively). The preliminary data of oxidative stress parameters showed an increase of DNA damage with 30% of fragmentation in FLP cells also exposed to 3 μM MeHg when compared to control. As a result, our study indicates that acute exposure to MeHg in FLP cell lines was toxic and preliminarily altered the oxidative state only in the highest concentration (3 μM). However, the lower concentration used (0.3 μM) require attention since mercury is a persistent substance, and can bioaccumulate, reaching toxic levels in chronic exposures.

NEW INSIGHTS FROM THE STUDY OF VULNERABLE POPULATIONS EXPOSED TO MERCURY: GENETIC SUSTEPPIBILITY, PERIPHERAL MARKERS OF NEUROTOXICITY AND THE IMPACT OF LARGE-SCALE PROJECTS IN AMAZON.

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Human exposure to mercury is a serious problem of public health in Amazon. Accompanying riverine Amazonian populations since 2006, we demonstrated that mercury is present in human populations (adults and children) under the influence of artisanal small-scale gold mining areas (ASGM), but also in those areas with no ASGM. We showed that riverine populations living at the areas of large-scale projects such as dams are also exposed to medium-to-high levels of methymercury, probably due to the mobilization of environmental mercury into the food chain. Exposed individuals present long-term deleterious problems such as lower antioxidant defenses, genotoxicity, classical symptoms of neurotoxicity, and high prevalence of non-communicable diseases. Central Nervous System is the target organ for methylmercury, the most toxic species of mercury. However, accurate measurement of early neurotoxicity is especially challenging due to confounding factors in neurobehavioral evaluations and the scarce literature about reliable peripheral markers in humans. In this scenario, S100B protein is a well-established biomarker of brain damage that can be detected in cerebrospinal liquid and blood. It was recently associated with mercury neurotoxicity. Due to the difficulty of adequate protein conservation in isolatedREMOTE populations, we used S100B mRNA levels in blood as a way to assay mercury neurotoxicity. Our recent results demonstrated that S100B mRNA expression in blood of exposed individuals is more than twice the expression in nonexposed individuals, supporting this peripheral marker as an useful tool for the early diagnosis of mercury-induced neurotoxicity.

Asessment of Major Anthropogenic Sources and Emissions of Mercury in India

MANDADI, Bhargavi

Mercury has caused widespread concern around world due to its great toxicity. Annual mercury emissions increased due to various uses of metals like industrial metals extraction, Artisanal gold production, FoSi fuel combustion and mercury production and use. The estimation of global Hg emissions between 2010 and 2015 has grown at a rate of 1.8% per year. Regionally, emissions decreased in the U.S, Europe and Canada, while they increased immensely in Central America, South Asia and Eastern Africa. Asia remained the largest emission region. Power and heating was largest single anthropogenic Hg emission occupy 45% of total anthropogenic emission amount. For this reason, the Mina-Mata convention on mercury was signed by 128 countries in 2013, calling for worldwide control of anthropogenic releases of Hg.

Due to its high volatility of Hg, it can stay in the atmosphere for 1618 months. There are four common forms of Hg in the environment, namely Hg0, Hg2+, Hg p and MeHg. The various forms determine its toxicity level. Hg0 can harm the human central nervous system through the respiratory tract, while inorganic Hg will affect the kidneys via gastrointestinal absorption. Organic mercury can be accumulated in fish and plants (most toxic). The world famous Mina-Mata disease in Japan was because the residents ate the fish contaminated by MeHg.

India is an industrial giant with one of the fastest growing major economies in world. One of the major concerns in developing countries like India is Alzheimer’s disease, a common neurodegenerative disorder that leads to dementia and death. According to statistics, China is first followed by US and India in country wise prevalence of dementia. As of 2015, there were an estimated 46.8 million people with dementia worldwide.
There is strong cultural pattern of fish consumption among coastal people (East, West and Southern coast of India). Several studies have shown that pesticide exposure in Indian population is much higher compared to western world. India may become “hot spot for mercury poisoning”. Development of new technologies to prevent mercury emissions into the air is mandatory, mostly concerning primary releases due to anthropogenic activities. General ways to reduce mercury emissions like substitution by non-mercury alternatives, waste to energy (WTE), and reducing consumption of products produce mercury emissions.

M.P.3.2

**MERCURY REMOVAL FROM HARD COAL INTENDED FOR THE NON-INDUSTRIAL COMBUSTION INSTALLATIONS WITH THE USE OF A METHOD COMBINING THE DRY DESHALING AND THERMAL PRETREATMENT PROCESSES**

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Mercury and its compounds are classified as very toxic and they are a real threat for human health. One of the main sources of mercury emission to the environment are the coal combustion processes. A special issue is the use of hard coal in the sector of non-industrial combustion installations (among others, the residential, commercial, institutional, agriculture sectors as well as other small-scale combustion installations). In contrast to the coal-fired power plants, users in this sector do not have systems to reduce emissions, including mercury. For this group of users, the solution may be use of hard coal with the lowest possible mercury content. However the availability of such coals is limited. In the paper, the solution for production hard coal with low mercury content with the use of a method combining the dry deshaling and thermal pretreatment processes was proposed. The proposed method allowed to reduce mercury content in analyzed coals in the range from 43 to even 92% with the average of 64% (in relation to the energy contained in coal, i.e. in relation to lower heating value). The obtained coals were characterized by relatively low mercury content from 1.5 to 4.8 µg/MJ with the average of 2.4 µg/MJ (from 44 to 94 µg/kg with the average of 58 µg/kg). The application of the proposed solution would allow to reduce the annual mercury emissions from the non-industrial combustion installations in Poland by 0.365 Mg, which is nearly 48%. It should be mentioned, that the proposed solution would allow to enhance the quality and calorific value of hard coal as well. Additionally, the preliminary mass and energy balances for the proposed method as well as the distribution of mercury between the obtained products were determined. The total energy demand for the proposed solution was estimated at the level of 1.3 to 3.4% in relation to the chemical enthalpy of feed coal (in relation to the lower heating value).

M.P.3.3

**SELENIUM AND MERCURY IN SOILS AND MINING WASTES FROM ARTISANAL SMALL-SCALE GOLD MINING AREAS ALONG THE PRA RIVER BASIN**

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Selenium is a natural element that is found in rocks and soils especially in minerals deposits. It is an essential micronutrient which plays a key role in detoxifying the body from environmental chemicals but can also be toxic in high quantities. Mercury is an environmental pollutant and highly toxic to human health even in small quantities. Twenty (20) composite soil and two (2) mining waste samples were sampled from Artisanal Small- scale Gold Mining (ASGM) areas in the Pra River Basin Ghana. The concentrations of THg and Se were determined in the soil and mining waste samples using kO-Instrumental Neutron Activation Analysis (kO-INAA) method. The concentrations of Se (mg/kg) in fifteen (15) of the soil samples were below the detection limit. Out of the five (5) soil samples with Se concentrations that were above detection limits, two (2) were obtained from Dunkwa-On-Offin site 1 and 2. Dunkwa-On-Offin site 1 gave both the highest Se (3.5±0.20 mg/kg, n = 5) and THg (80.5±2.80, n = 20) in the soil samples. Also, a maximum of 62.4±2.30 mg/kg of Se and 1.318±4.60 mg/kg of THg were found in one of the mining waste samples from Dunkwa-On-Offin site 1. A correlation of 0.92 (p-value = 0.03, n = 5) between Se and THg concentrations in the soils was established. The environment of Dunkwa-On-Offin has been exposed to high levels of Se and THg.

M.P.3.4

**UNDERSTANDING THE COMPLEX CHEMISTRY OF MERCURY IN AQUEOUS PHASE – THE ROLE OF MONOVALENT MERCURY**

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The chemistry of mercury species in aqueous phase is very complex, which renders the investigations of natural and technical systems demanding ones. On the other hand this offers also the possibilities of new technical approaches in the development of technological processes aimed to remove Hg from gases and solutions. Among these chemical properties the formation of huge variety of complexes should be mentioned with ligands encountered in aqueous solutions in the nature or in the technologies, e.g. halides, oxo-sulfur anions, carbonate etc. Two other properties should be mentioned in brief, i.e. the volatility of the element, together with it’s low solubility and the formation of monovalent Mercury species from divalent cation and the elemental Hg. The later reaction was not taken into account in almost any investigation. The reaction Hg0 + Hg2+= Hg22+ is shifted, according to the reaction equilibrium constant, far to the right, directing the interest to the chemistry of Hg22+. First of all, the dissolution of elemental Mercury from gaseous to the aqueous phase could be enhanced by fast removal of dissolved Hg0 from the solution. Secondly, the solubility of monovalent mercury compounds is relatively low, enabling the removal of Hg form the solution to the surface of solid phase. Hg2Cl2 is known as a compound that sticks to the solid surfaces available. These two steps could facilitate the transport of Hg0 from gaseous phase to the solids, including some intermediate reactions, specifically oxidation and complexation. The description of some experimental phenomena observed in our laboratory and pilot scale continuously running mercury removal process from gaseous phase under wet desulphurization process conditions is given. Theoretical calculations to explain the behaviour of the chemical system are presented. The results show that monovalent mercury should be taken into account in any modelling of the Mercury chemistry. The second obvious conclusion is that the analytical procedure(s) for the determination of Hg22+ in trace amounts in aqueous phase urgently needed to be developed to support such investigations.
M.P.3.5

GASEOUS ELEMENTAL MERCURY ADSORPTION AND RECOVERY BY ELECTROTHERMAL SWING SYSTEM WITH ACTIVATED CARBON FIBER CLOTH
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Mercury (Hg) is one of the most hazardous air pollutants. It has a wide range of effects on humans and natural organisms. In the past decades, efforts have been devoted to Hg usage reduction. However, with the huge amount of abandoned fluorescent lamps, it is important to carefully capture and recover the Hg(0) in the products in order to both cut down humans’ Hg demand from the environment and avoid the hazardous effect of Hg on the environment and human health. The work presented aims to develop a novel and sustainable approach to adsorb and recover the low-concentration Hg(0) in the tail gas of recycling processes for fluorescent lamps. Activated carbon fiber cloth (ACFC) is a material used for high-efficiency adsorption due to its high surface area and fiber structure. In this study, a series of experiments were carried out to determine ACFC and nitric acid treated ACFC (HNO3-ACFC) Hg(0) adsorption efficiency and regeneration efficiency. The purpose of nitric acid treatment is to examine the effect of different amount of oxygen functional groups on Hg(0) adsorption efficiency. The regeneration was done by an electrothermal process. The electrothermal regeneration was conducted with 20 W, 40 W and 60 W of regenerating electricity. Through excessive heat, adsorbed Hg(0) would be released rapidly from ACFC surface, resulting in high Hg(0) concentration in the effluent, nearly three times of the amount of initial concentration that could make condensation easier for the recycling plant to recover Hg(0). The effectiveness of regenerated ACFC and HNO3-ACFC for Hg(0) adsorption was also examined in this study. The experimental results showed that, with an initial Hg(0) concentration in a range of 260~300 µg/m³, ACFC had about 80% of Hg(0) adsorption efficiency. After electrothermal regeneration, ACFC and nitric acid treated ACFC (HNO3-ACFC) Hg(0) adsorption efficiency generally rose up to nearly 90% after 60 W electrothermal regeneration. After acid treatment, the content of oxygen functional groups on HNO3-ACFC increased and enhanced the adsorption kinetics, resulting in over 90% of adsorption efficiency before and after electrothermal regeneration. Both ACFC and HNO3-ACFC still had great adsorption efficiency after nine cycles of adsorption and regeneration. These results indicated that ACFC and HNO3-ACFC can be an effective and renewable adsorbent for low concentration Hg(0) adsorption and recovery.

M.P.3.6

NATURAL AND LOW-COST MANGANESE ORE SORBENTS FOR ELEMENTAL MERCURY REMOVAL FROM FLUE GAS
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Abstract: Sorbent injection is widely accepted as a promising method for controlling the mercury emissions. The traditional activated carbon sorbent is restricted by the high operating cost, sorbent recovery and reuse. Therefore, it is necessary to develop the high-efficiency, low-cost and regenerable sorbents for Hg0 removal from flue gas. Compared with activated carbon, natural mineral sorbents are promising candidates as cost-effective sorbents for mercury removal due to its low price and abundant reserves. However, the systematic study on Hg0 removal by natural manganese ore has not yet been reported. In this work, mercury removal performance of natural manganese ore sorbent was systematically investigated in the fixed bed reactor under the conditions of simulated flue gas. The physical and chemical properties of manganese ore sorbent were analyzed by Brunauer–Emmett–Teller (BET) surface area, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The natural and low-cost manganese ore sorbent was used to remove Hg0 in flue gas. The results indicated that the average Hg0 capture efficiency is much higher than 90% in the temperature window of 100-250 °C. Moreover, the effects of flue gas components on mercury removal and reaction mechanism were investigated. O2, NO and HOCl exhibit a promotive effect on mercury adsorption by natural manganese ore. H2O and SO2 exert a slight influence on Hg0 adsorption over the natural ore. Further, XPS and temperature programmed decomposition desorption (TPPD) results suggest that the adsorbed mercury compounds on the used sorbent surface are mainly ascribed to HgO, HgCl2, Hg(NO3)2 and HgSO4. Manganese ore sorbent shows excellent regeneration performance for Hg0 capture from flue gas. The regeneration process shows little effects on the pore structure and crystal structure of sorbents. Theoretical results obtained from density functional theory calculations show that chemisorption mechanism is responsible for Hg0 adsorption on manganese ore surface.

M.P.3.7

RECYCLABLE AND REGENERABLE COPPER-MANGANESE SPINEL-TYPE SORBENT FOR MERCURY CAPTURE FROM FLUE GAS
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Sorbent injection has been considered to be an effective and promising technology for mercury capture from flue gas. The wide application of the existing commercial mercury sorbents is restricted by its shortcomings, such as high cost, secondary pollution, no regenerability. In this work, a series of novel Cu-Mn spinel-type sorbents were developed using low-temperature sol-gel auto-combustion synthesis method. CuMn2O4 sorbent exhibited excellent mercury removal performance in a wide temperature window of 50-350 °C. The adsorbed mercury species exist in the forms of Cu-Hg amalgam and HgO on the sorbent surface. The pre-exponential factor and activation energy for Hg0 desorption are 1.06×104 s⁻¹ and 61.43 kJ/mol, respectively. The limiting mechanism in mercury removal process was identified. Mercury removal by CuMn2O4 sorbent is controlled by mass transfer process when the superficial velocity is large. The mercury removal results indicate that the average Hg0 capture efficiency is much higher than 90% in the temperature window of 100-250 °C. Moreover, the effects of flue gas components on mercury removal and reaction mechanism were investigated. O2, NO and HOCl exhibit a promotive effect on mercury adsorption by natural manganese ore. H2O and SO2 exert a slight influence on Hg0 adsorption over the natural ore. Further, XPS and temperature programmed decomposition desorption (TPPD) results suggest that the adsorbed mercury compounds on the used sorbent surface are mainly ascribed to HgO, HgCl2, Hg(NO3)2 and HgSO4. Manganese ore sorbent shows excellent regeneration performance for Hg0 capture from flue gas. The regeneration process shows little effects on the pore structure and crystal structure of sorbents. Theoretical results obtained from density functional theory calculations show that chemisorption mechanism is responsible for Hg0 adsorption on manganese ore surface.

M.P.3.8

SEVERAL APPROACHES ON THE USE OF REGENERABLE SORBENTS FOR THE RETENTION OF MERCURY IN THE GAS PHASE
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Most of the technologies proposed to reduce mercury emissions from different industrial activities involve the use of non-regenerable solid sorbents, such as activated carbons impregnated with sulphur and zeolites, thus generating waste that should be treated as toxic.
SOLUBILITY OF ELEMENTAL MERCURY IN DIFFERENT SOLVENTS AND MIXTURES FOR THE MODELING OF HG PARTITIONING THROUGHOUT OIL AND GAS PROCESSING

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Removal of mercury in the oil and gas processing is necessary for a number of health related and economic reasons. A range of different mercury species can be found in crude oil and natural gas. However, especially in the gas phase, elemental mercury is considered to be the predominant species. It is therefore necessary to analyse Hg quantitatively, also in their different species in oil and gas installations. One approach to estimate the elemental mercury mass balance throughout oil and gas processing is the use of modelling software. This can help to avoid the necessity of a laborious detailed analysis with sampling throughout the production. The prediction of partitioning and distribution in all involved phases allows for the optimisation of decontamination and waste minimisation plans. This provides important information on where to place mercury removal units in the process. However, data on the solubility of elemental mercury in various solvents over a wide temperature range are limited. In this project the solubilities of elemental mercury in a range of solvents used in oil and gas processing were determined at various temperatures. Investigated solvents include alcohols, glycols, hydrocarbons and amines. To achieve this, a method for the analysis of elemental mercury in different solvents using cold vapour atomic fluorescence spectrometry (CVAFS) was developed. The experimental setup for exact temperature control during the equilibration of the samples needed to be designed and manufactured. This method was compared to literature values of known Hg0 solubilities in water, hexane and methanol.

Especially for previously not investigated solvents, data can be used in the modelling of the mercury mass balance in oil and gas processing. In addition to the solubility of elemental mercury, the equilibrium between HgS and Hg0 is of major interest for modelling in oil and gas processing. The transformation of the mostly inactive Hg0 to the volatile Hg0 at higher temperatures can lead to higher levels of mercury contamination. Data on the equilibrium of this reaction at varying temperatures will be of enormous value and have not been reported in the literature yet.

THE REMOVAL AND RECOVERY OF HG0 FROM COAL-DERIVED FLUE GAS OVER NOVEL MOSS2-NANOHEETS CONTAINING MATERIALS

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There have been increasing concerns on the emission of mercury to the atmosphere due to its potent detrimental impacts on biological system, especially its potential lethal impacts on human being’s health. The largest anthropogenic source of mercury emission is associated with coal-utilization, which accounts for approximately 475 tonnes of mercury emission to the atmosphere per annum. In this study, the MoS2 nanosheets materials were prepared via incipient wetness impregnation (IWI) and sulfur-chemical vapour reaction (S-CVR) methods and tested in terms of their potential for Hg0 capture. It was found that the MoS2 nanosheets containing materials had good potential not only
for the removal of Hg0 from but also for the recovery of Hg0 from flue gas. The removal efficiency remained at almost 100% for 2000 min. Its theoretical capacity for Hg0 capture was found to be 18.95 mg/g based on the Elovich model. It is believed that these MoS2 nanosheets provided dense active sites for Hg0 capture. The removal of Hg0 at low temperatures was achieved via the binding of Hg0 with the chalcogen (S) atoms on the entire basal plane of the MoS2 nanosheets to form a stable compound. The regeneration of adsorbent was further conducted using conventional heating at 300, 250 and 200°C based on the temperature programmed decomposition desorption (TPDD) study. It was found that the ratio of desorption and adsorption reached 99.4% for the third test when the adsorbent was regenerated at 200°C. These results indicate that among the temperature studied, 200°C was the optimum temperature for the regeneration of adsorbent with the maximum efficiency for the recovery of Hg0.

M.P.3.12

INDUSTRIAL APPLICATION OF NON- THERMAL PLASMA FOR THE MERCURY AND DIOXINS REMOVAL IN FLUE GAS

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(2)State Environmental Protection Engineering Center for Mercury Pollution Prevention and Control

At present, there is an urgent demand for mercury and dioxins pollution control technology, internationally. It is necessary to find a solution other than the activated carbon adsorption process. In recent years, our self-developed Non-thermal plasma (NTP) coupling system has been applied for mercury and dioxins removal in the flue gas, the system is composed of corona discharge plasma reactor and ceramic nano-material adsorption tank. The parameters of the plasma are 35-40KV, 400-450A, 1000Hz. The saturated adsorption capacity of ceramic nano-materials for Hg2+ is more than 5156μg (Hg2+)/g. Mercury is oxidized in a plasma reactor and adsorbed by ceramic nanomaterials. This complex adsorbent material exploits both the gold selectivity to mercury and the titania photocatalytic properties to improve trapping performances. Such a system does not need carrier gas such as argon, helium, nitrogen, thereby cutting the running cost. Moreover, a low cost single board computer (e.g. Raspberry) board is used to control and record all the system functioning. The compact prototype (24x20x12 cm) works in automatic or manual sampling mode according to the user requirements. The power consumption is quite low, 50 W in, where n is the number of set measurements. Algorithms including automatic peak searching are employed to retrieve the mercury concentration. Experimental results (indoor) have shown that, for 30 minutes of sampling time, we have obtained peaks with a minimum signal to noise ratio of 10, measuring Hg0 at about 4 ng/m3 (simultaneously measured by commercial automated system, Tekran 2537). A preliminary calibration, showed that the instrument has a linear response in the range 10-2000 ng. Finally, the developed system exploits the photo catalytic properties of the titania to selectively desorb, assisted by UV light, some interfering compounds absorbed by the trap (e.g., SO2, BTEX) during the

M.P.3.14

MERCUERY GEOCHEMICAL PROSPECTION IN MEDIEVAL MONEY FORGERS UNDERHAND WORKSHOP IN KONĚPRUSKÉ CAVES

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(2)National Museum

The carst cave complex in Koněprusy, situated 20 km south west from Prague, (re)discovered in 1950, is popular touristic destination in the central Czech Republic. One of the caves in the upper part of Koněprusy complex was named Mincovna (Mint). In this area, a money forgers secret workshop was operated according to medieval legend. Indeed, archaeological research performed in 1958 in Mincovna revealed copper circles, mint copper semi-finished coins and pieces of equipment used for money forging. The mintage on counterfeit silver coins corresponded to period 1465-1470. One of the questions addressed by the archeological research was to identify technique used for silversmithing of the copper coin bases. It was speculated that the technique was based on evaporating metallic mercury from diluted silver amalgam spread on a surface of copper circles. We tested this hypothesis by geochemical prospection in Mincovna focused on mercury contamination. Cave materials including sinters, calcites and cave clays were sampled in various parts of Koneprusy cave complex. Total mercury content was analyzed on AMA 254 by conventional technique. Mincovna and its close surroundings were remarkably contaminated by mercury. The highest mercury identified concentration was 1944 ng Hg/g, while the median content was 324 ng Hg/g (over the whole cave). Natural Hg background, measured on samples collected in uncontaminated cave areas reached on average 10 ng Hg/g. Distribution of Hg contamination in the cave space was highly unequal, pointing to a movement of evaporated Hg0 with the air along chimney fissures upwards. Mercury contamination was predominantly associated with the clay materials but the cave sinters were practically uncontaminated. Up to date, it was possible to identify emanation of Hg0 from contaminated materials into the cave air. The highest Hg0 concentration in the Mincovna air was 8.0 ng/m3, while the background concentration was 1.9 ng/m3 (measured by Lumex). Contemporary geochemical research of the Mincovna cave shed light onto a real foundation of the medieval legend. Thus considerable amounts of mercury must have been manipulated in the cave area, causing legacy contamination preserved over period of 500 years. Our results further support the hypothesis of silverying by fire within the Mincovna area. In the carst cave environment, mercury was fixed to ambient clays and it is slowly released till recent.

M.P.3.13

COMPACT SYSTEM FOR THE MONITORING OF ELEMENTAL MERCURY EMPLOYING LOW-COST TECHNOLOGIES.

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A monitoring system for elemental mercury detection using a low-cost optical measurement method and a smart trap is presented. The optical measurement method is based on the Cold Vapor-Atomic Absorption (CVAAS) Spectrophotometry implemented with a compact measurement dual cell containing an UV source and a photodiode. The smart trap consisted of borosilicate beads covered by nanostructured titania nanoparticles functionalized with gold nanostructures. This complex ab-
M.P.3.15  
MERCURY DISTRIBUTION IN THE PROCESSING OF NON-FERROUS ORES  
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Non-ferrous metallurgy is one of the main sources of anthropogenic mercury emission. In the European Union, it is responsible for about 4% of mercury emissions. In the case of Poland, this share is around 9%, but it is still the second largest source of mercury emission. During the preparation of non-ferrous metal ores for smelting, the following processes are carried out: crushing, grinding, enrichment and drying of the concentrate. Enrichment has the greatest impact on the mercury content of the product to be smelted. It removes materials that impair the properties of the ore. One of the enrichment processes is flotation, the effect of which on the mercury content has been studied. Three types of non-ferrous metal ores were subjected to experiments. Two of them were zinc and lead ores and the third was copper ore. The concentration of mercury in the feed, product and waste was determined. The course of the flotation itself was also checked and on this basis the process balances for mass and mercury were drawn up. In the second part of the study, the differences in mercury concentration in individual grain classes of zinc and lead ore and cooper ore were determined.

M.P.3.16  
PRODUCTION OF ELECTRICITY, NON-FERROUS METALS AND CEMENT AS A SOURCE OF ANTHROPOGENIC MERCURY EMISSION IN POLAND  
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(1) AGH University of Science and Technology, Faculty of Energy and Fuels  
Due to its adverse impact, the emission of mercury into the atmosphere from industrial processes are subject to special monitoring. The largest sources of anthropogenic emission of mercury into the atmosphere are the production processes: electricity, cement, non-ferrous metallurgy or chemical industry. In the case of emissions in the European Union, the shares in 2016 are as follows: electricity production – 63.4%, cement production – 12.4%, non-ferrous metallurgy – 3.7% and chemical industry – 5.6%. In the case of emissions in Poland, the shares are different: electricity production – 77.8%, cement plants – 5.5%, non-ferrous metallurgy – 8.8% and chemical industry – 0.3%. Analyzing the aforementioned sources in Poland, the influence of the three most important industrial sectors on the total mercury emission was determined. On the basis of own researches, the values of emission factors from individual processes were determined. Using the production data, emissions from these sectors were calculated.

M.P.3.17  
GOLD CERTIFICATION AND SUSTAINABILITY IN BRAZILIAN ASGM  
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Gold certification from Artisanal and Small Scale Gold Mining (ASGM) is an attractive prospect to stimulate changes in the gold production, contributing to the development of clean and sustainable practices. There are some certified gold guarantee seal, such as Fairmined, which is backed by a certification system with traceability requirements, considering responsible socio-environmental practices, and promoting actions for the sustainability of the activity. The present study discusses the feasibility of certification of Fairmined gold in Brazilian ASGM areas taking into account the technological, social and legal features. This study addressed Brazilian legislation for the production of gold by ASGM, including the way to obtain a license for the production of legalized gold. The methodology to select ASGM study areas started by mapping legal ASGM areas and stakeholders in Brazil. After, the stakeholders were consulted and ASGM areas were selected based on their potential to accomplish the requirements described in the Fairmined Standard legal aspects, access, receptivity by goldminers and governmental and/or no governmental organizations supports. Twelve ASGM areas were studied: 2 in Amapá state and 10 in Mato Grosso state in partnership with governmental entities. Semi-structured questionnaires based on the Fairmined model with questions about environmental protection, legalization, decent work conditions and Human, Economic, Social and Cultural Rights. Based on all information collected from technical visits, surveys through questionnaire, meetings and interviews with stakeholders, a SWOT Matrix and a classification suggested by Alliance for Responsible Mining (ARM) were the project management tools used for analyzing ASGM results obtained and to support the recommendation of candidate areas with better chances, or fewer gaps, to start the process of certification according to Fairmined Standard. The ASGM communities studied were interested in participating in the certification process, if they were submitted to it, although some social and environmental difficulties were observed, which some of them depend on public policies. The results also showed that the Fairmined system has the potential to be implemented with great chances of success in 5 from the total of 12 ASGM areas visited, surveyed and/or analysed, which indicates the feasibility of implementation of the Fairmined in ASGM in Brazil. It is expected that the besides jewels consumer, financial market and technology segment, which are also direct consumers of gold, will support the certification processes.

M.P.3.18  
THE AMAZING SPIDER-MINE: WOLF SPIDERS (ARANEAE, LYCOSIDAE) AS BIOINDICATORS OF METAL CONTAMINANTS (HG, PB, AG) NEAR ARCTIC MINE SITES  
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Arctic is considered a hotspot for deposition of globally transported contaminants like heavy metals (e.g. Hg and Pb) and organic contaminants (e.g. POPs & PAHs). Although remote emissions are the dominant sources for most contaminants deposited in the Arctic, local sources such as mining or mineral processing also occur, often leading to a long-lasting imprint on the surrounding environment. Detailed environmental monitoring before, during, and after mining activities is thus essential to evaluate the contamination status of a mining area. Here, we therefore investigated the use of Arctic wolf spiders as a potential monitoring organism for heavy metal contamination (e.g. Hg, Cd, Pb). The rationale for choice of species was that spiders are the most abundant group of terrestrial predators in Arctic ecosystems, and have documented abilities to accumulate metals. In Greenland however, most contamination studies in relation to mining have targeted the marine environment, with less attention given to the terrestrial. Following a distance transect (0 – 40 km) near the former Black Angel Pb-Zn-mine, Maarmorilik, West-Greenland, we therefore collected samples of two species of wolf spiders (Pardosa glacialis and P. groenlandica), along with supporting samples from soil and lichen, and analyzed these for geochemical elements using Q-ICP-MS and DMA. Generally, metal concentrations in spiders were found to reflect the contamination status of the surrounding environment.

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trend of the area, i.e. decreasing concentrations with increasing distance from the old mine, yet large differences in bioaccumulation efficiency occurred between elements (Ag>Cd>Zn>Cu>Hg>Pb). We found larger differences in heavy metal concentrations between age groups (juvenile vs adult) than between species. That is, adults generally showed higher concentrations than juveniles, suggesting that distinguishing between age classes of spiders is critical in future assessments of the environmental contamination status using spiders as biomonitors. Further, bioaccumulation of Hg (130 - 1300 ng g⁻¹ d.w. measured on individual specimens) was evident in the area, yet the former mining activities could not be concluded as the main source of measured Hg in aquatic biota. Results showed that Hg concentrations found in soils (2.69 – 3.93 mg/kg), mine wastes (>100 mg/kg), river sediments (58.87 - >100 mg/kg) and marine sediments (3.37 – 6.79 mg/kg) were elevated compared to the global background of <60 μg/kg. These high concentrations of Hg in soils and river sediments were influenced by different pathways for release of Hg from its mine operations from 1953 to 1976 while Hg in marine sediments were caused soil erosion and the mine wastes (calcines) used to construct a jetty in nearby Honda Bay. Mine wastes represent the largest source of Hg in the area due to the low efficiency of the recovery process using calcination. Further works are recommended to determine if Hg is contaminating the surface water and groundwater in the area.

M.P.3.19

SOMETHING FORGOTTEN 30 YEAR-OLD MERCURY HOTSPOT IN CENTRAL EUROPE AND ITS IMPACTS ON AQUATIC BIOTA

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We examined The Kössein-Röslau river system (east Bavaria, Germany), a mercury (Hg) pollution hotspot originated from the production of Hg compounds in Chemical Factory Markredwitz (CFM). Although the factory is out of service for over 30 years, total mercury concentration in floodplain sediments is still 300 mg/kg and the rivers currently export suspended particulate matter (SPM) with mean Hg concentrations ca 20 mg/kg. Most of this suspended particulate matter is accumulated in the Skalka Dam Reservoir, where bioaccumulation occurs in aquatic biota and part is distributed further to the river system. The Hg discharge from CFM caused mercury concentrations in fish muscles up to 6 mg/kg, many times exceeding the actual safety limit (0.5 mg/kg). In addition, we estimated that in a 22 km long channel belt is approximately 13 t Hg deposited and in the Skalka Dam Reservoir further 15 t Hg. Part of this study was also devoted to macrophytes and periphyton biofilms, where markedly increased concentrations of Hg were found. We confirmed, that they play an important role in the entry of Hg into aquatic biota.

M.P.3.20

MERCURY CONCENTRATIONS IN SOILS AND SEDIMENTS IN THE VICINITY OF ABANDONED MERCURY MINE AREA IN PUERTO PRINCESA CITY, PHILIPPINES

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The abandoned mercury (Hg) mine area in Puerto Princesa City, Palawan is included in the list of abandoned and inactive mines in the Philippines that is characterized with high risk to human health and the environment and requires to be rehabilitated. The mine site, once operated by Palawan Quicksilver Mines, Inc. (PQMI), is located approximately 3 km inland from Honda Bay coast and within the catchment of the Tagbueros River which is a local fishery and recreational area. In this study, Hg levels in soils and sediments were measured to assess the possible release of Hg from the site to the surrounding natural environment. Results showed that Hg concentrations found in soils (2.69 – 3.93 mg/kg), mine wastes (>100 mg/kg), river sediments (58.87 - >100 mg/kg) and marine sediments (3.37 – 6.79 mg/kg) were elevated compared to the global background of <60 μg/kg. These high concentrations of Hg in soils and river sediments were influenced by different pathways for release of Hg from its mine operations from 1953 to 1976 while Hg in marine sediments were caused soil erosion and the mine wastes (calcines) used to construct a jetty in nearby Honda Bay. Mine wastes represent the largest source of Hg in the area due to the low efficiency of the recovery process using calcination. Further works are recommended to determine if Hg is contaminating the surface water and groundwater in the area.

M.P.3.21

MERCURY REMEDIATION OF CARBON STEEL FROM PRODUCTION AND PROCESS ASSETS

HUNTER, Lee

Even though it is just a ‘metal’, in industries where Mercury is a naturally occurring contaminant or even a required process component its dynamic and phenomenal cyclic characteristics are still not widely known or fully understood.

Global industry continues to drive forward with production, research, development, adaptation, mitigation, treatment and disposal of mercury, mercury compounds and mercury-contaminated products, but there are still large areas of the industrial process that have yet to be fully or properly addressed, although it could be argued that is mainly due to it being directly related to end-of-life on the process and containment infrastructure. The issue... is carbon steel.

Carbon steel acts as a scavenger, capturing any mercury and mercury compounds from within process streams and retainer, in various conditional states, along the surface of the steel, within layers of corrosion, areas of deposition and within the surface matrix of the steel substrate. In particular, Mercury contamination can cause problems to offshore processing platforms and other downstream hydrocarbon production facilities, as well as the intermediate infrastructure. The Oil & Gas industry is aware of the cycle phenomenon whereby Mercury is absorbed into the surface matrix of carbon steel pipelines during the process and transportation of contaminated hydrocarbon mediums and its subsequent ability to desorb back out from the steel surface and return to those same, or new uncontaminated, streams. However, the fate of the carbon steel pipelines, vessels and equipment falls under further limitations with lengthy, costly and typically unverifiable results... until now!

As a growing concern among operators and companies around the world the decommissioning, disassembly and disposal of contaminated assets, subsea pipelines, platforms and refineries has always had its limits with current legislation, and most commercial applications, only dealing with the decontamination of free (adsorbed) Mercury from system internals prior to its decommissioning.

It is now possible to fully remove mercury from the surface matrix of carbon steel, in a repeatable manner, which ensures that the decontaminated carbon steel sections meet the strict acceptance criteria for recycling purposes using a licensed steel smelter.

Understanding the contaminant and how it behaves under certain conditions has been key to developing a selection of decontamination methods and applications that can now be applied quickly and methodically in remote locations as well as sensitive and dynamic environments while also providing flexibility and certainty to meet limited, but licensed, final waste disposal routes and best practices.
M.P.3.22

MERCURY CONTAMINATION WITHIN FSO/FPSO MARINE VESSELS, CURRENT PRACTICES AND THE NEED FOR CORRECT ASSESSMENT & REMOVAL

HUNTER, Lee

Even though it is just a ‘metal’, in industries where Mercury is;
1. a naturally occurring contaminant (Oil & Gas, Mining)
2. a required process component (Mining, VCM and Chlorine plants)
3. a result of feed and logistic infrastructure (Petrochemical, Marine and Tank Storage)

...its dynamic and phenomenal cyclic characteristics are still not widely known or fully understood but it is the interaction with carbon steel that continues to allude most, compounded even further due to natural levels within SE Asia hydrocarbon reservoirs being up to 1000 times higher than other areas of the world.

Carbon steel captures mercury and mercury compounds from within process streams and retains it along the surface of the steel, within layers of corrosion and within the surface matrix of the steel substrate. As a growing concern the cleaning, decommissioning and disposal of contaminated assets or infrastructure has costly repercussions, financially, environmentally and physically, attributed to by poor legislation, regulations and policing as a direct result of a limited knowledge and understanding to these unique characteristics.

Current practices don’t provide for the determination of what is contaminated, how to deal with it or how to monitor and/or verify its removal which continues to increase the cases of hospitalization and death of workers across Asia.

With a simple revision of standard procedures, safety protocols and regulations these incidents can be eliminated not only from the cleaning activities and the ‘Green Recycling’ demolition of the vessels but also the lethal practice of recycling mercury-contaminated steel by smelter.

M.P.3.23

THE POTENTIAL OF MAGNETIC CELLULOSE NANOPARTICLES AS ECO-FRIENDLY SORBENT FOR MERCURY SPECIATION ANALYSIS

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Sample preparation including preconcentration and clean-up is usually a crucial step that is indispensable in most analytical procedures for mercury speciation analysis due to the low concentration of mercury species naturally occurring in environmental samples. Most of the methods traditionally used for this purpose, such as solid phase extraction, presents some operational limitations and/or are not environmentally friendly. Recent improvements are coming from the incorporation of nanomaterials as sorbents. In particular, the use of magnetic nanoparticles simplifies the extraction process due to the easy isolation of the species from the matrix by an external magnet and improve the efficiency due to the enhanced dispersion. However, magnetic solid phase extraction (MSPE) has been scarcely explored for trace metal speciation analysis. The few MSPE methods applied until now for the analysis of mercury species are based on conventional sorbents, which are environmentally unfriendly and expensive and usually need complex synthesis and functionalization. Thus, the development of fast and reliable MSPE methods using eco-friendly sorbents and simple analytical tools becomes an analytical challenge. Among the new renewable and biodegradable nanomaterials which have been explored in last years for other analytes, nanocellulose stands out as an interesting green alternative to traditional sorbents.

Therefore, the aim of this work has been to study the potential of magnetic nanocellulose nanoparticles as an eco-friendly sorbent for the simultaneous extraction and preconcentration of mercury species using MSPE. The conditions influencing the adsorption and desorption steps were carefully optimized. It is remarkable that the developed method enables to combine in a single step the preconcentration and the derivatization of mercury species for their further analysis by gas chromatography coupled to atomic fluorescence detection, which greatly simplifies the sample preparation process. This approach not only offers several advantages related to the use of an eco-friendly and renewable sorbent but also accomplishes the benefits of MSPE, as well as the analytical requirements of high selectivity, good anti-interference ability and very low detection limits. Hence, the proposed method, which has been applied for the first time for the simultaneous analysis of monomethylmercury and inorganic mercury in water samples, becomes a new interesting alternative for mercury speciation analysis in environmental applications. The advantages and disadvantages in comparison with other available options will be also discussed.

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M.P.3.24

MERCURY BEHAVIOR IN FLOWBACK FLUIDS AFTER WELL WORKOVER

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Natural gas and crude oil contain small amount of mercury, and it must be removed for stable production of oil and gas and environmental concerns. Especially in design phase of production facilities, it is important for optimization of Mercury Removal Unit (MRU) to assess accurately concentration and chemical form of mercury in production fluids based on mercury analysis during Drill Stem Test (DST). However, chemical form of mercury during DST may be different from that in steady production phase, because mercury might be oxidized by dissolved oxygen (DO) in brine. If an incorrect assessment on mercury analysis during DST is made, it is difficult to achieve efficient mercury removal and modify MRU after start of production especially in offshore facilities, because they have limited space for equipment and modification of MRU forces unscheduled production downtimes.

To investigate influences of fresh brine containing DO on mercury behavior in unsteady production phase like DST, mercury speciation analysis in flowback fluids were conducted during clean up flow at a natural gas well after acid washing.

As a result, particulate mercury concentration in filtered solids collected from condensate and flowback water reached a peak at the early phase of clean up flow, then decreased to around two orders of magnitude lower at the late phase when pH and total iron concentration in flowback water were close to those in steady production phase. Furthermore, mercury sulfide was identified in some filtered solids by X-Ray Diffraction analysis. Although the natural gas contains small amount of hydrogen sulfide (H2S), considering pH in flowback water and dissociation reaction of H2S, the direct reaction of elemental mercury and H2S cannot explain the sharp decline of particulate mercury concentration during clean up flow. Therefore, the result of the mercury speciation analysis indicates that mercury sulfide may be produced by the reaction of DO in workover fluid with H2S and elemental mercury in natural gas, and reveals that different chemical form of mercury is produced in unsteady production phase like just after well workover.

In a similar situation with well work over such as DST, this result will help to understand mercury behavior in flowback fluids.
ANALYSIS OF MERCURY CONTENT IN BIOMASS AND ITS THERMAL PROCESSING PRODUCTS

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Biomass is one of the basic renewable energy sources in Poland. In addition to the undisputed advantages, Biomass also has several disadvantages, ie high moisture content, and thus low heat of combustion, which makes it impossible to use it in some types of boilers. In this case, the use of partially processed – carbonized biomass in the form of biochar will be better. Biochar is devoid of all the disadvantages of biomass (high moisture content, low calorific value), and still has all its advantages. In addition, the biochar may also, thanks to adding it to the soil, contribute to the reduction of CO2 emissions to the atmosphere, and improve soil properties by increasing water retention. The content of mercury in biomass is lower than in coal, but for some types of biomass, its content can be significant, especially in the case of waste biomass. The mercury content in various types of biomass, forest type, agro type, and waste biomass was analyzed in the work. The content of mercury in pellets made from different types of biomass was also analyzed. The analysis was performed using the Lumex RA-915 + spectrometer with the RP-91C adapter. Then each of the biomass samples was carbonized. The process of coalification took place at selected temperatures of 300°C, 400°C, 500°C, and 600°C, at the stand of a special reactor for carbonizing coal. After coalification of each of the examined biomasses at the above-mentioned temperatures, the content of mercury in the product of the coalification - biocarbon process was re-examined.

The results presented in the article were obtained in research co-financed by the National Center for Research and Development under agreement No. BIOSTRATEG3 / 345940-7 / NCBR / 2017 titled: Water in the soil – satellite monitoring in improving water retention using biocarbon (acronym: SoilAqChar).

M.P.3.27

MERCURY REMOVAL SOLUTIONS FOR IONIC AND ORGANIC MERCURY IN PETROLEUM REFINERY AND WELLHEAD

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Mercury-contaminated oil and natural gas are widely produced over the world. In fact, the mercury concentration in these feedstocks is quite different on a case-by-case, but mercury shall be removed to protect health, safety, environment and process equipment. From the viewpoint of equipment protection, mercury damages plant facilities, such as heat exchanger made by aluminum alloy or rare metal-based catalyst for refinery. From these reasons, the mercury concentration as product specification is defined as lower than 1 wtppb for petroleum products and lower than 0.01 μg/Nm3 for natural gas. "Adsorption" is a typical process for removing mercury in petroleum refinery. This is a simple process, using only vessels with adsorbent. There are 2-types adsorbent, mainly used aluminum oxide-based and the other is activated carbon-based, and it is selected by considering throughput, mercury concentration and adsorbent life. By using aluminum oxide-based adsorbent, mercury is captured by converting to stable mercury compounds. Simple adsorption is not ultimate solution, sometimes mercury leaks after adsorbent. Main reasons, which affect performance of adsorbent, are 1) types of mercury and 2) adsorption inhibition. Mercury can be classified into three types, i.e. elemental, ionic and organic mercury compounds by using UOP method 938-10. Elemental mercury can be removed by adsorption easily, but ionic and organic mercury compounds are difficult to be removed. In addition to the above, adsorbent is sometimes inhibited by poisonous components contaminated feedstocks. For these problems, JGC has solutions by combination with typical adsorption process. For the problem by types of mercury, "Decomposition", our process is catalytic reaction without hydrogen, is effective to convert ionic and organic mercury compounds into elemental mercury. The elemental mercury that produced by catalytic decomposition are almost completely adsorbed by the adsorbent. For the problem by adsorption inhibition, "Stripping" is used for separating elemental mercury and poisonous compounds. By integration of decomposition, stripping and adsorption processes, any type of mercury can be removed to 1 ppb level.

M.P.4.2

MINERS, MINERALS AND MINAMATA: INTERDISCIPLINARY PERSPECTIVES ON ARTISANAL AND SMALL-SCALE GOLD MINING AND SUSTAINABLE DEVELOPMENT

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Due to its toxicity, persistence, and long-range mobility, mercury (Hg) has become a pollutant of global concern. Owing to its infinite persistence, Hg contamination is a legacy that transcends generations, geopolitical boundaries, environmental media, and trophic levels. The Minamata Convention came into force August 16th, 2017, with the ob-
Objective to protect human health and the environment from the adverse effects of Hg. As the world’s newest international treaty on chemicals and waste, Minamata it is not without its challenges. Due to the unique properties of mercury, it is widely used in industrial applications, medical instruments, and mineral commodities, namely artisanal gold, with complex supply chains and global trade dynamics. Debate as to whether international trade conflicts with environmental protection efforts remains controversial, and tensions have mounted during the Conference of the Parties (COP) on monitoring and effective evaluation. Policy dialogue indicates that pollution abatement initiatives for mercury; mercury storage and contaminated sites will require significant global coordination, innovation, political will, and enabling regulatory environment as well as enforcement conditions. Present in over 70 countries world-wide, Artisanal and Small-scale Gold Mining (ASGM) contributes nearly 38% of global emissions resulting from amalgamation processes used to extract gold from concentrated or whole ore (UNEP 2019). Minamata represents the only legally binding global instrument that directly targets ASGM (Article 7) through legislative reform, awareness raising, technology transfer, and capacity development at operational and strategic levels through National Action Plans (see Annex 7, Article C). Despite prospects for poverty reduction, public health and environmental impacts of mercury use and subsequent contamination are severe, and widespread informality remains a persistent issue for national governments. In 2015, an international roundtable of 60 leading science and policy experts on mercury convened to assess mercury use in ASGM, centering on interactions between miners (livelihoods), minerals (national resources) and Minamata (global) policy. Following science-policy expert interaction, perceptions on the relative importance of mercury in ASGM changed. These data suggest that while mercury serves as an entry point to raise awareness on ASGM, Hg is hardly the endpoint. Despite growing development spending, interventions trying to convince miners to adopt mercury-free methods for health or environmental considerations alone have proven ineffective. Within this context, we explore why science-policy integration is essential to transform the ASGM economy at local, national and global scales, and how the anthropology of artisanal gold mining can improve the policy-making and implementation process of Minamata.

M.P.4.3

THE “WICKED PROBLEM” OF MERCURY USE IN ARTISANAL AND SMALL-SCALE GOLD MINING: A CONCEPTUAL FRAMEWORK TO INFORM POLICY AND RESEARCH

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Mercury use in artisanal and small-scale gold mining (ASGM) has captured global concern for nearly fifty years. A number of well-intended policy and development schemes have been applied with the goal of promoting safer and cleaner mineral processing methods or eliminating mercury use altogether. However, the majority of these interventions have not achieved long-term success, and mercury use in ASGM continues to be widespread. In an attempt to understand why these efforts have been largely unsuccessful, this paper applies the wicked problem concept, first coined by Horst Rittel in 1973 with respect to urban planning challenges that proved to be too complex for conventional design applications because of their social underpinnings. Like the challenges that Rittel described in urban planning, mercury use in ASGM cannot be separated from the social context in which it takes place. Drawing from a review of mercury reduction and elimination interventions applied globally, as well as field research in Latin American countries, this paper explores the reasons why decades of interventions have resulted in a lack of significant progress in eliminating mercury use from ASGM and reducing global mercury emissions from the sector. Based on this analysis, a framework is proposed that situates ASGM within the full social and technical contexts in which it takes place and can contribute to a more comprehensive understanding of mercury use in ASGM operations. In line with the goals of the Minamata Convention, enacted in 2017, this approach allows us to identify opportunities for future research, policy, and development initiatives aimed at addressing mercury use and emissions from ASGM.

M.P.4.4

HEALTH AND RISK COMMUNICATION OF CONTAMINANTS IN THE DEHCHO AND SAHTÚ REGIONS OF THE NORTHWEST TERRITORIES, CANADA

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Public health strategies related to contaminant exposures in Indigenous communities in northern Canada need to balance the risks and benefits of consuming country foods. Elevated mercury concentrations in some fish species in some lakes in the Northwest Territories (NWT), Canada resulted in a series of fish consumption notices that suggested people limit their consumption of specific fish species. It is not known what level of awareness is and understanding of these consumption notices, whether they resulted in altered food behaviours, or the risks perceived with country food consumption. As part of a larger human biomonitoring study in nine Indigenous communities in the Dehcho and Sahtú Regions of the NWT, participants were invited to respond to a Health Messages Survey on health and risk communication for contaminants, with a focus on mercury and cadmium. Questions included the awareness and understanding of current health messages on country foods and contaminants, questions on risk perception related to contaminants, perspectives on health and country foods, how people usually heard about consumption notices and other information on health, foods and/or contaminants, and preferences for receiving messaging. Participants (n=87) indicated a high consumption of country foods (99%), preference to eat only country foods (38%), and heard that country foods had beneficial nutrients (90%). Seventy percent of respondents had heard or seen messages about fish with high levels of mercury and had heard this from researchers or scientists (52%), radio (44%), or a friend (44%). Since hearing the messages on mercury in fish in specific lakes, respondents reported that they were more concerned about the fish they ate (46%); decreased the amount of fish they ate (32%); and changed the location where they usually fish (29%). Most participants had access to the internet (68%), cell phone or land line (61%), and listened daily to local radio as a source of news (74%). Doctors were the most trusted source of information about contaminants (51% trusted “a lot”), followed by friends or relatives (45%), Elders (44%), and university researchers (43%). Collaboration between researchers, government, trusted sources and communities in the NWT, Canada is critical to develop cross-cultural, co-created communication strategies and build more knowledge around the complexity of risk perception and health messaging. The priority should continue to be carefully planned communication strategies, built through engagement with communities, which promote country food consumption while lowering contaminant exposures to maintain and improve health and well-being.

M.P.4.6

CURBING ILICIT MERCURY AND GOLD FLOWS IN WESTAFRICA: OPTIONS FOR A REGIONAL APPROACH

EIGENMANN, Gabi; HALLA, Grace; FERNANDEZ GARCIA, Rocio

West Africa is considered home to some of the richest gold-ore deposits and highly dependent on the artisanal and small-scale gold mining sector. Not only it provides a major source of employment and income for a substantial part of the population, but also, its gold production constitutes one of the major exports in the region. The widespread use of mercury in ASGM (mainly imported), along with
the challenges characteristic of this area (lack of reliable data, porous borders, high level of informality, presence of illegal activities and lack of coordination among the relevant stakeholders) highlighted the necessity of a regional response in order to reduce the use and emissions of mercury in an effective manner.

Based on the request of several countries in the Economic Community of Wester African States (ECOWAS) region, UNIDO, with the support of the Government of Switzerland and in cooperation with the Global Initiative Against Transnational Organized Crime, released a study that analyses mercury and gold trade flows, its regulation and taxation in 12 countries. This analysis aims to provide the basis for a future regional approach that will contribute to phase out of mercury in the ASGM sector and harmonization of the taxation and royalty rates in the region. Analyzing the situation resulted in the following recommendations aiming to achieve an effective and coordinated effort: (a) improve the knowledge of mercury flows; (b) standardize mercury-specific regulatory frameworks; (c) increase engagement with and capacity of customs organizations; (d) focus regional efforts on import and export hubs, particularly seaports; (e) reward miners who extract gold using mercury-free or environmentally friendly technologies; (f) harmonize gold-export regimes; and (g) strengthen regulatory oversight of gold imports in destination hubs. Based on the gathered data, further follow up actions focusing on three main areas below are currently under planning by UNIDO and other national and regional stakeholders: (i) Harmonization of gold and mercury related regulation at a national and a regional level; (ii) Development of a regional approach for the environmental sound management of mercury and other hazardous wastes; and (iii) Support of a coordinated approach to enhance the development and implementation of the National Action Plans for the ASGM sector and should continuously form a component of the management review and plan. This is because waste inclusive agricultural and industrial waste knows no boundary. The lack of integrated Minamata based technology waste management technique poses the most challenging aspect of prosperity offered by the quality, quantity, diversity and sustainability of our environmental resources. Therefore, this paper would discuss the content of an integrated environment code anchored on a sustainable integrated Minamata based science planning cycle. This approach could drive and sustain the harmony between man and the environment.

Keywords: Minamata; mercury; environment code

M.P.4.8

ARTISANAL AND SMALL-SCALE GOLD MINING IN THE PUNO REGION OF PERU: A CASE STUDY OF MERCURY USE IN FORMALIZED OPERATIONS

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Artisanal and small-scale gold mining (ASGM) is the largest source of global anthropogenic mercury emissions. Studies in Peru have highlighted the many environmental and human health issues surrounding ASGM and have particularly focused on the use of mercury during the gold recovery process and its impacts. The Peruvian government is aware of the problems associated with ASGM and mercury use but also recognizes the importance of ASGM activities for rural populations. In 2016, Peru ratified the Minamata Convention but has yet to release its national action plan. In the meantime, they have attempted to create mechanisms to move ASGM activities into the formal economy, which include provisions that require miners to reduce mercury use and implement safer mercury handling practices. These efforts have also included decentralizing formalization by giving authority to regional governments. In the Puno region of southeastern Peru, there are over 30,000 artisanal and small-scale miners, and in 2017, the region produced over 10,000 kg of gold. However, only about 3-4% of ASGM operations are formalized. When miners become formalized, they are supposed to receive technical assistance to improve their processes, yet these operations still use mercury as the preferred gold recovery method due to its low cost and easy access and continue to contribute to mercury emissions. This paper provides one of the first critical reviews of formalized ASGM operations and their role in mercury emissions. Through an analysis of formalized ASGM operations in Puno, it quantifies the amount of mercury used and lost to the environment. Furthermore, it highlights miners’ interests in being trained in efficient, mercury-free techniques to process their gold ores. It suggests that policy and formalization efforts are not enough to tackle mercury use and emissions in Puno and beyond, and without consistent follow-up, enforcement, technical support, and monitoring, even formalized ASGM operations will continue to contribute to mercury emissions.

M.P.4.7

TRANSITING CONVENTION TO AN INTEGRATED CODE FOR SUSTAINABLE DEVELOPMENT

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The Minamata Convention on Mercury is a global treaty to protect human health and the environment from the adverse effects of mercury. Communities recognize that the level of anthropogenic use and releases of mercury could lead to an increase in environmental pressure on critical areas. These adversely impact on the aquatic and terrestrial environment of the population and fragile ecosystems. Therefore, there is need for stakeholders to critically appraise principles, policies and practices of the Minamata Convention and incorporate them into existing and would be Regional and International Environment codes. This attitude could lead to sustainable environment that is driven by Minamata based principles and practices. The integrated Minamata based code could be useful in management of contaminant-free active environmental resources. This is for enhancing social, economic and environmental resource performance. The management of watersheds, industrial systems, agricultural systems and biodiversity could fail, in the absence of integrated and improved Minamata based techniques to environmental management. Therefore, sustainable organs need to handle legal instruments in a sustainable manner to encourage and support integrated programs of industrial and agricultural communities. The significant focus areas of sustainable agricultural development, industrial development, and management of the natural resources have suffered setback. These setbacks are due to the limited understanding of the role of an integrated Minamata based principles, policies, and practices in the management of the environment. There is minimal integrated Minamata based management system in developed and developing countries. In planning and attempting to manage man and the resources under his control, the ability to subdue waste using integrated Minamata based science approach is critical to stakeholder.

M.P.4.9

MERCURY CYCLING AND BIOAVAILABILITY AT TWO CONTAMINATED ESTUARINE SITES IN THE NORTHEAST U.S.

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Similar concentrations of methylmercury (MeHg) were found in fish (Pundulus sp) downstream of two contaminated estuarine sites in the Northeast US: the Penobsot River, a remote site contaminated by
historic inputs from a chemical plant in Orrington, Maine, and Berry’s Creek, which runs from a Superfund site of the same name to the Hackensack River, NJ, and is heavily impacted by industrial activity. Despite the similar levels of MeHg in fish near these sources of contamination, the sites vary substantially in Hg loading (THg was 14 mg/kg and 0.8 mg/kg at the Berry’s Creek and Penobscot sites, respectively). The sites also differ in their ecological setting and degree of anthropogenic impact, indicating biogeochemical factors other than sediment and water MeHg levels alone control bioavailability of MeHg to the food web. Concentrations of DOC and salinity gradients were comparable between sites, whereas DOC quality in Berry’s creek was significantly more degraded, based on δ13C and fluorescence measurements. Differences in particle composition were also evident between the two systems: levels of chlorophyll and phytoplankton counts in the suspended particle fraction were much higher at Berry’s Creek, especially during the spring phytoplankton bloom, than in the Penobscot. The distribution of MeHg between two size fractions of suspended particles was relatively similar in Berry’s Creek, whereas significantly higher MeHg was found in particles >20 µm in the Penobscot. In the Penobscot, calculated levels of expected MeHg in phytoplankton at the base of the foodweb, based on measured dissolved MeHg, DOC and chlorophyll-a, were in reasonable agreement with the concentrations of MeHg in suspended particles (which include phytoplankton), whereas in Berry’s Creek, predicted levels of MeHg in phytoplankton were much higher than observed concentrations. In addition, bioaccumulation factors between the suspended particulate and fish were much higher in the Penobscot. Together, these findings demonstrate much higher bioavailability of MeHg from the water column to the base of the food web, as well as higher bioaccumulation in fish at the less impacted site. The findings of this work imply that parameters such as carbon quality and land use affect bioavailability in near-shore environments, suggesting that more biogeochemical factors need to be included in contaminated site assessments.

M.P4.11

DEVELOPING TECHNICAL GUIDANCE FOR THE IMPLEMENTATION OF THE MINAMATA CONVENTION SECRETARIAT OF THE MINAMATA CONVENTION ON MERCURY

The Minamata Convention on Mercury requests the Conference of the Parties (COP) to develop technical documents to assist the parties in implementing specific provisions of the Convention. The guidance related to the supply sources and trade of mercury, the guidance on developing a national action plan on artisanal and small-scale gold mining and the guidance on best available techniques, best environmental practices and support for parties in relation to mercury emissions to air were adopted at COP 1 in 2017. The guidelines on the environmentally sound interim storage of mercury other than waste mercury were adopted at COP 2 in 2018. These documents are available on the Convention website.

COP 2 agreed on the intersessional work on a number of technical matters. Firstly, COP-2 started a process for controlling and reducing mercury release to land and water from relevant point sources not addressed in other provisions of the Convention. It established a technical expert group to work electronically to develop a report for COP-3 including a list of significant point sources, along with a suggested roadmap and structure for the development of draft guidance on methodologies for preparing its inventories.

Secondly, COP-2 established a technical expert group to work on the thresholds to determine whether certain waste falls under the definition of mercury waste covered by article 11 of the Convention. The expert group will meet in May to develop a report including a comprehensive list of waste consisting of mercury, an indicative list of waste containing or contaminated by mercury, and relevant approaches and methodologies for establishing thresholds for mercury waste. Thirdly, COP-2 reviewed the draft guidance on managing the contaminated sites, and requested the secretariat to revise the draft guidance and submit it to COP-3 in November 2019, by inviting comments and input from the parties and other stakeholders and consulting with experts involved in the development of the earlier draft. The guidance will be drafted in non-prescriptive language, providing general advice to parties taking into consideration the variety of national circumstances of parties. A framework and decision tree for the management of contaminated sites, which was not included in the draft for COP-2, will also be developed.

Comments and inputs for this intersessional work, received by mid-February, have been posted on the Convention website. The progress in the development of the COP-3 document will be presented orally.

M.P4.10

A HYBRID MODELLING/EMUULATION METHOD AND WEB-BASED SUPPORT TOOL TO AID IN THE IMPLEMENTATION OF THE MINAMATA CONVENTION

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Within the implementation of the Minamata Convention, all parties are required to “control, and where feasible, reduce” Hg emissions from a Convention-specific set of sources. However, the Convention does not specify the extent of the measures to be implemented, in terms of quantitative emission limits, reduction amounts, or control technologies. Each nation involved, however, is required to apply its own measures tailoring them to its individual economic and technological situation. Unfortunately, Hg pollution is a global concern, and facing it without a global coordinated strategy represents a significant challenge, from both scientific and technological perspectives.

The existing current scientific uncertainties regarding the full biogeochemical cycle, and its eventual response to global climate changes, are a challenge to the effective evaluation of any policy aimed to reduce Hg exposure over the medium to long term. The proposed methodology aims to establish the short-term effects on Hg deposition fluxes based on Hg emission perturbations in both speciation and reduction, therefore allowing the evaluation of BAT(s) available for a given region/country and/or single emission sector. The approach relies on the analysis of multiple, specifically designed global CTM simulation ensembles. The final aim is to build a statistical emulator that allows an interactive and real-time estimate of the effects of the measures chosen to be implemented. A bootstrap-based integrated variation evaluation within the ensembles provides a range of uncertainties regarding the Hg cycle. This permits an evaluation of the impact of BAT(s) both within and beyond national or regional boundaries.

The interactive features of the method presented are suitable for implementation in a web-based tools, released as a component of GeoInt, a Spatial Data Infrastructure (SDI) developed at CNR-IIA in order to manage geo-referenced data, that will constitute a core application of the activity of the Group on Earth Observation (GEO) and the Flagship Global Observation System for Mercury (GOS4M), which is part of the GEO Work Programme (2016-2025).

The method and the tool presented represent a first step towards a more comprehensive and integrated decision support system, with the capability to explicitly account for economic costs, which could eventually enable a Hg emissions trading system where countries with different technology levels can share credits.

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TRACING THE DEPOSITIONAL HISTORY OF MERCURY TO TWO COASTAL NATIONAL PARKS IN THE NORTHEAST UNITED STATES

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Establishing records of mercury (Hg) accumulation at sensitive sites provides an important means of assessing previous environmental conditions and historic Hg inputs from atmospheric deposition. Robust records of Hg deposition can also be important for evaluating legislation on atmospheric loading, and for predicting future needs. Lake sediment archives from undisturbed environments have been found to be the most reliable records of Hg accumulation rates. However, while sediment Hg records in some regions are well-established, the geographic distribution of deposition archives across the North American continent is sparse and coastal sites along the Eastern United States present an important data gap. In this work, we assess Hg accumulation in lake sediments at two coastal National Parks in the Northeast U.S. - Acadia National Park and Cape Cod National Seashore. Sediments from each site were collected using a Glew-type corer and sectioned in 0.5 cm increments. A short-lived radioisotope approach using 7Be measurement in recently deposited sediment was applied to improve the resolution of 210Pb dating measurements in surface sediments, and total Hg was measured in each core section. Accumulation records were interpreted relative to wet deposition records from each site, and to background Hg and sediment deposition rates measured in sections of the cores prior to human activity (pre-1850’s), to normalize changes in accumulation to each watershed. This work adds to the body of Hg deposition records, which provide a key measure of the effectiveness of Hg reduction policies.

MEASURING ATMOSPHERIC MERCURY ON A GLOBAL SCALE WITH PASSIVE SAMPLERS

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The Minamata Convention on Mercury has set out the requirement that an assessment of the effectiveness of the treaty is conducted 6 years following coming into force. One way to assess the success of global reductions of mercury is to observe the changes of mercury levels in the atmosphere on a large scale. Current active mercury measurement methodology has shown to be a very effective way to assess both spatial and temporal trends; however, cost and capacity of this method limit its effectiveness in many areas of the world. A new Canadian passive mercury air sampler (MER-PAS) has been developed and its use is growing around the world in regional monitoring networks and research studies. A full trial of how effective this sampler can be on a global scale, in order to meet the obligations of the Minamata Convention, has yet to be undertaken. Starting in 2019, Environment and Climate Change Canada (ECCC) will be initiating a global passive mercury pilot study to assess how feasible this method can be to meet the Convention objectives. By combining currently existing infrastructure and monitoring networks, the samplers will be deployed to collect spatial and temporal concentrations of atmospheric mercury. This project will combine data collected from passive mercury networks in place such as the Northern Contaminants Program (NCP) passive mercury project in Canada, the Latin American Passive Air sampling Network (LAPAN) in south America along with mercury networks that currently measure other media such as the Asia Pacific Mercury Monitoring Network (APMMN), the Atmospheric Mercury Measurement Network (AMM) in the USA and the ECCC-Atmospheric mercury Monitoring Network (ECCC-AMM) in Canada. This pilot study also plans to dovetail on other passive monitoring networks such as the Global Atmospheric Passive Sampling Network (GAPS) and air measurements in the Caribbean to deploy the mercury passive sampler. By combining the current infrastructure where existing mercury networks are available and fill in information gaps by using other non-mercury networks, the first step of this global picture can be created. The plans, structure and development of this pilot project will be presented.

REGIONAL COOPERATION TO MONITOR MERCURY WET DEPOSITION AND ATMOSPHERIC CONCENTRATIONS IN THE ASIA-PACIFIC REGION

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Environmental Protection Administration Taiwan (EPAT), National Central University (NCU), U.S. Environmental Protection Agency (USEPA) and National Atmospheric Deposition Program (NADP) have worked together since 2012 to establish the Asia-Pacific Mercury Monitoring Network (APMMN). The goals of the APMMN are 1) to systematically monitor wet deposition and atmospheric concentrations of Hg in a network of stations throughout the Asia-Pacific region, and 2) to assist these countries in capacity building for mercury monitoring abilities. EPAT and NCU are committed to this effort and network development. EPAT has provided wet deposition samplers (MIC-B type) to support rainwater sampling at sites in partner countries. Several regional atmospheric Hg workshops and APMMN training workshops were held in Taipei, Taiwan (2012), Washington D.C. United States (2013), Hanoi, Vietnam (2014), Minamata, Japan (2015), Bangkok Thailand (2016), Taiyuan, Taiwan (2017) and Manilla, Philippines (2018). EPAT has funded the Center for Environment Monitoring and Technology at NCU to support environmental monitoring in general, and APMMN operations and training in particular. Further, NCU operates the APMMN network laboratory, which provides for network sample analysis, quality assurance, network operation, and data storage for APMMN. Network operation began in 2014 for total Hg wet deposition. Currently, 6 sites are now making weekly measurements of Hg wet deposition in 6 countries. Establishment of additional sites are underway and measurements of Hg wet deposition will be added over time. A side-by-side intercomparison between the samplers (MIC-B and N-CON samplers) is ongoing on the NCU campus to assure comparable data quality between APMMN and NADP/MDN. Available results from the network will be produced showing the concentrations and depositions measured in Asia to date, and other quality assurance measurements for the network will also be provided. APMMN may expand to include other media (e.g. water, biota) in the future. EPAT, USEPA, NADP and NCU are committed to continued support of APMMN and its operation into the future.

PRELIMINARY STUDY AND PILOT PROJECT FOR THE COMPREHENSIVE MERCURY MONITORING NETWORK IN SOUTH KOREA

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The Republic of Korea had signed the Minamata Convention on Mercury in September 2014, and is under the ratification as of 2019. The Ministry of Environment has performed a preliminary study since 2016 under Articles 19 and 22 of the Convention for the purpose of reporting the circulation, movement and behavior in the aquatic system. Field sampling was conducted on 10 sites including 1 background, 5 artificial lakes and 4 rivers where fish species and environmental samples such as water, sediment were collected. They were divided into background level monitoring and environmental change assessment points. Water sampling was collected during spring and fall, sediments and fishes were conducted during spring season. All samples were analyzed total mercury, methyl mercury, and general items such as temperature, TOC, chlorophyll-a, electro-conductivity etc in water column. Fish species were top-level predator such as bass, piscivorous chub, steel barbel, blue gl etc. These fish were analyzed for T-Hg, MeHg, C/N isotope and these were attempted considering ecological and environmental factors by calculating the biological concentration factor (BSAF) and the nutritional step biological expansion factor (TMF). Additionally conservative elements (Li) were measured to interpret of the results in the sediments. Statistical techniques such as PCA, Pearson correlation analysis, and multi-linear regression were used to determine the correlation between the biogeochemical properties of environmental media and the mercury concentration. The major mercury sources were identified by estimating the contribution rate of mercury into water body. Total mercury in the river was higher than the lakes, and spring is higher than autumn. T-Hg in the lake shows the higher than that of the river and T-Hg is more correlated with conservative elements (Li) in the sediments. Fish mercury which is corrected with the fish length normalization is correlated with the concentration of methyl water in sediment. It was also found that the higher correlation with the primary production than T-Hg in the water body. These various results will be studied to categorize the characteristics of mercury behavior in the reservoirs and rivers in Korea, and is to be used as a scientific tool for monitoring mercury in fish and identifying potential sources of mercury in water body. Based on the results of this pilot project, national integrated mercury monitoring network will be launched from 2021, which is planning to link with existing national environmental measuring network or as a network for mercury monitoring and fate in environment.

Acknowledgements

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M.P.4.17

APPLICATION OF MINAMATA CONVENTION ON MANAGEMENT OF MERCURY CONTAMINATED SITES AFTER CINNABAR MINING

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In the past centuries, cinnabar was mined at two places, in Slovakia. There were Růžňany (Spisská Nová Ves; GPS: 48.8786333,20.6848306) and Malachov (district Banská Bystrica; GPS: 48.7098421,19.0841059). Both localities are recorded in Register of contaminated sites and belong to potentially contaminated sites. These areas represent an environmental burden because naturally occurred cinnabar in the geological subsoil still represents a source of gradually releasing mercury into soil, groundwater or air. Moreover, mining activity has left extensive mine waste heaps, mining excavations or uncover and exposed rocks although any mining activity stopped several centuries ago. Currently, mine waste heaps are cover by managed forests and there are educational trails for tourists along mining excavations. Both localities are populated by the rural population in spite of environmental and human health risk. Total mercury can enter into food chain by growing vegetables and fruits, harvesting berries and mushrooms, keeping cattle and sheep. Thus may present a health risk to permanent inhabitants over the years of eating local agricultural products. Our paper describes the current situation at one of the mentioned localities, Malachov, with regard to the total mercury content in the environmental compartments and the possible health risk to the inhabitants. We also evaluate strategies for human health protection provided by local and state government. Slovak republic as one of the 107 states that have ratified the Minamata Convention and so committed itself to protect human health and the environment form anthropogenic emissions and releases of mercury and mercury compounds.

In the paper we evaluate especially the fulfillment of Article 12, which obliges states to adopt guidelines on managing of polluted sites by mercury, including assessment of the risks to human health as well as engaging the public into finding strategies for management of such sites.

Acknowledgements

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MOVING TOWARDS MERCURY-FREE FUTURE: THE TRANSITION TO MERCURY-FREE DENTISTRY IN EUROPE

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Dental amalgam, a compound of mercury (43- 54%) combined with other metals including silver, copper, and tin, is currently the largest use of mercury in the European Union and a significant source of environmental pollution. Of the total amount of mercury used by dentists in the EU (75 tonnes per year on average) approximately 56 t/y ends up in patients’ teeth.

In modern dentistry, restorations are increasingly made with mercury-free, tooth-coloured materials – they comprise ca. 66% of tooth restorations in the EU. Not only do these materials look better, but they require the dentist to remove less tooth material and they bear a lower risk for health and environment.

Since new cost-effective and clinically-effective filling materials are already established in several European countries, the only consistent measure for a transition to mercury-free dentistry would be to start integrating these new materials into the national reimbursement schemes. The public health care system merely should adjust the reimbursement fees to the slightly higher material-costs of the alternative filing materials, always keeping in mind that the additional environmental costs for the use of dental amalgam will be significantly reduced.

The EU Mercury Regulation 2017/852 confirms the decision towards phasing down and eventually phasing out the use of mercury added dental amalgam in the EU. The regulation, beyond banning its use to children under the age of 15 and pregnant or breastfeeding women, further requests that Member states should set out a national plan concerning the measures it intends to implement to phase down the use of dental amalgam.

This presentation will review the status of the implementation of the EU Regulation on Mercury with regards to dental amalgam, and in particular the development of National Action Plans from European member states with regard to the transition to mercury-free alternatives.

MERCURY SPREAD TO SOIL: URBAN AND INDUSTRIAL CONTAMINATION

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Mercury is a chemical of global concern. It is characterized by long-range atmospheric transport, persistence in the environment once anthropogenically introduced, ability to bioaccumulate in ecosystems and significant negative effects towards human health and the environment.

Study was performed on mercury releases per source categories. In Armenia the main sources of mercury releases (kg Hg/year) to land were Waste deposition + waste water treatment; Crematoria and cemeteries; Consumer products (whole lifecycle); Other product/ process use. The inventory of mercury releases was done with the use of UNEP "Toolkit for identification and quantification of mercury releases (January 2013)."

Summary data on estimated mercury releases to land revealed the following:

- Consumer products (whole lifecycle): 4.4 Kg (2.3%)
- Other product/ process use: 0.2 Kg (0.2%)
- Waste deposition + waste water treatment: 184.8 Kg (97.2%)
- Crematoria and cemeteries: 0.4 Kg (0.3%)

The Center for Ecological-Noosphere Studies (National Academy of Science of the Republic of Armenia) performed analyses of soil samples taken near the Former Chemical Plant in Vanadzor City. In 4.16km2 Hg contents were 1.2-2.15 times higher than local background (LB). Intensive LB excesses were spatially located in industrial area-close to the Chemical plant and in the residential part. The geo-accumulation (Igeo) index showed that uncontaminated or moderately contaminated levels were detected in 2 samples located in industrial and 5 samples- in residential areas. The remaining samples were classified as uncontaminated (Igeo<0) suggesting the possible natural origin of Hg. The potential ecological risk index method (PERI) revealed low level in 22.15 km2 of city area. Moderate level was observed in 3.85 km2 of residential and industrial areas and characterized by mosaic distribution. High level was observed only in one sampling site located in a residential area close to private homes.

METHYLMercury POISONING (SO-CALLED MINAMATA DISEASE) PATIENTS ARE NOT RECOGNIZED AS MINAMATA DISEASE IN JAPAN.

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(1)Meeting to support The third Niigata Minamata Disease Lawsuit (2)Kido Hospital

In Japan, methylmercury by-produced in the acetaldehyde production process was released to the sea and river for a long period of 29 to 35 years. Methylmercury poisoning (so-called Minamata disease) occurred in residents who continuously ate fishes accumulated methylmercury. Such poisoning that has been exposed to methylmercury over a long period of time is rare in the world.

The Japanese government will not accept Minamata disease unless it matches the combination of the specified symptoms. It is 63 years since the incident was announced, but there are only 2,997 patients that the Japanese government has recognized Minamata disease so far. In addition to this, there are 32,891 patients who ate fishes accumulated methylmercury daily and have the distal dominant sensory disturbance of the extremities. However, the Japanese government insists that they are not Minamata disease because they do not have the combinations of symptoms.

The combination of symptoms designated by the Japanese government necessarily include the distal dominant sensory disturbance of the extremities. And it is reported that the distal dominant sensory disturbance of the extremities seen in Minamata disease is characterized by being the most frequent and difficult to lighthearted.

Dr. Harada examined whether those who received methylmercury exposure could have distal dominant sensory disturbance of the extremities. As a result, the distal dominant sensory disturbance was confirmed in 47 out of 89 people. On the other hand, Dr. Kumamoto examined a group not exposed to methylmercury and confirmed a patient with the distal dominant sensory disturbance of the extremities. As a result, the distal dominant sensory disturbance of the extremities was confirmed in only 3 out of 1270 people.

To investigate the health effects of exposure to methylmercury, we compared the incidence of sensory disturbance in groups exposed to methylmercury and those not exposed to methylmercury. As a result, there was a clear difference between the odds ratio of 473 times. And, owing to exposure to methylmercury, the probability that distal dominant sensory disturbance of the extremities was caused (exposed group contribution risk ratio) was 99.8%. If we can confirm the distal dominant sensory disturbance of the extremities, we should recognize it as Minamata disease.

This time we report on the influence of the distal dominant sensory disturbance of the extremities caused by methylmercury exposure use the population and the number of patients about the village of the Agano River basin in Niigata.
SUMMARY DATA OF ESTIMATED MERCURY RELEAS-ES PER SOURCE CATEGORY: 2015

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In the frames of Minamata Initial Assessment in the Republic of Armenia, data estimation was done on mercury releases per source categories according to UNEP “Toolkit for identification and quantification of mercury releases (January 2013)”. Main finding included the following categories and releases. Mercury releases to air (Kg Hg/y):

- Extraction and use of fuel/energy sources: 2.5 Kg (0.5%)
- Zinc, copper concentrates and black copper: 45.1 Kg (9.7%)
- Production of other minerals and materials: 36.8 Kg (7.9%)
- Consumer products (whole lifecycle): 4.4 Kg (0.9%)
- Waste incineration and burning: 357 Kg (76.1%)
- Mercury manometers: total amount of mercury contained in measuring and non-measuring devices with mercury content throughout the territory of the Republic of Belarus. Data on the amount of mercury in one device of any kind and purpose vary in different sources. Therefore, averaged values were taken to calculate the approximate amount of mercury.

According to the results of the valuation inventory in health care institutions of the Republic of Belarus, as of December 31, 2017, there are about 190 thousand units of medical mercury thermometers in circulation, which is approximately 355 kg of mercury; about 14.5 thousand special-purpose thermometers, which is approximately equal to 360 kg of mercury; 1.3 thousand units of mercury manometers (4 kg of mercury); 2.7 thousand units of mercury sphygmomanometers, which is about 220 kg of mercury; 110 units of mercury barometers, which is approximately 134 kg of mercury; 20 thousand units of hygrometers with mercury filling, which is approximately 40 kg; 90 units of psychrometers, which is about 180 g of mercury; about 1 million 750 thousand fluorescent lamps, in terms of about 175 kg of mercury. The total amount of mercury contained in measuring and non-measuring devices of health care institutions of the Republic of Belarus was approximately 1.2 tons.

THE RESULTS OF THE ESTIMATED INVENTORY OF MERCURY-CONTAINING INSTRUMENTS IN THE HEALTH CARE SYSTEM OF THE REPUBLIC OF BELARUS

SYCHVK, Siarhei: ILYUKOVA, Iryna; PRATASEVICH, Ulyana

In order to track the distribution of mercury-containing devices on the territory of the Republic of Belarus, in the first quarter of 2018, the Republican unitary enterprise "Scientific Practical Centre of Hygiene" conducted an assessment inventory of mercury-containing devices in health care institutions of the Republic of Belarus. Information was requested in accordance with Part I of Annex A of the Minamata Convention on mercury. The data obtained relate to the years 2016-2017. In the Republic of Belarus, more than two thousand health care institutions provide medical care to the population. For the assessment inventory of mercury-containing devices selected 29 medical institutions, which are identified as typical. Among the selected institutions are higher and secondary specialized educational institutions, sanatoriums, city and district hospitals and clinics, regional hospitals, patho-anatomical bureaus, hygiene and epidemiology centers at various levels, dispensaries, republican scientific and practical centers.

It is assumed that institutions of the same profile are equipped equally. Information obtained from one or two single-profile typical institutions were taken as the average among organizations of the same profile. Knowledge of the number of medical institutions of each profile and the average number of mercury-containing devices within each of them made it possible to calculate the approximate total number of devices with mercury content throughout the territory of the Republic of Belarus.

TRADE-INDUCED ATMOSPHERIC MERCURY DEP-O-SITION AND OUTFLOW OVER CHINA

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4) University of Cambridge
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Mercury (Hg) is characterized by the ability to migrate between continents and adverse effects on human health, arousing great concerns around the world. In addition to long-range atmospheric transport, Hg emissions can be geographically relocated through economic trade. Moreover, the transboundary transport of large anthropogenic Hg emissions from China has attracted particular attention, especially from neighboring countries. Here, we investigate the effect of China’s interregional trade on atmospheric Hg deposition over China, using an atmospheric transport model and multiregional input-output analysis. We also simulate the atmospheric Hg outflow from China and investigate the impacts of Chinese interprovincial trade on the outflow. In general, total atmospheric Hg deposition over China is 408.8 Mg yr-1, and 32% of this is embodied in China’s interregional trade, with the hotspots occurring over Gansu, Henan, Hebei, and Yunnan provinces. Interprovincial trade considerably redistributes atmospheric Hg deposition over China, with a range in deposition flux from ~104% to +28%. Developed regions, such as the Yangtze River Delta (Shanghai, Jiangsu, and Zhejiang) and Guangdong, avoid Hg deposition over their geographical boundaries, instead causing additional Hg deposition over developed provinces. Transferring advanced technology from developed regions to their developing trade partners would be an effective measure to mitigate China’s Hg pollution. The results also show outflows of 423.0 Mg of anthropogenic Hg, consisting of 65.9% of the total Chinese anthropogenic emissions, from China to other countries. Chinese interprovincial trade promotes a net decrease in the atmospheric outflow from China, reducing the chance of risks to foreign countries derived from transboundary Hg pollution from China. Our findings are relevant to interprovincial efforts to reduce trans-boundary Hg pollution in China.
STATE-OF-ART OF ENVIRONMENTAL INDICATORS AND METRICS ON MERCURY AMBIENT AIR MONITORING AND POTENTIAL TOOLS TO TRACK PROGRESS OF AIR MERCURY LEVELS WITHIN THE MINAMATA CONVENTION

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The environment is a complex system and assessing environmental trends is not an easy task. Environmental indicators and metrics help track changes in the environment by selecting key measures, which may be chemical, physical, chemical, biological or socio-economic, based on the best scientific understanding of the whole environment. Key selected measures provide useful information about the whole system and, if they capture the complexity of the system, can lead to accurate interpretations.

Mercury is one of the most relevant environmental issue of global concern due to its persistence into the environment, its long-range atmospheric transportation, its ability to bio-accumulate in ecosystems and its significant negative effects on human health and the environment. Mercury for these special features is therefore recognized as a toxic, persistent, and mobile contaminant that requires immediate global action to address the problem of global mercury pollution in the world, accounts for about 40% of total gold production in Latin America. In the last decade, Peru, the largest gold producer in Latin America, has experienced an explosion in illegal ASGM in the regions of Madre de Dios and Puno. These miners use varying rudimentary methods to extract and process gold, including the mixture of ore with mercury to form an amalgam, which is then burned to recover the gold. Because this is often conducted in residential areas, miners, their families and their communities directly inhale significant amounts of mercury vapor, which can lead to miscarriages, respiratory failure, psychiatric reactions, cardiovascular diseases and death. Furthermore, ASGM in Madre de Dios causes significant environmental degradation, as it requires rainforest deforestation.

This study presents the methodology and efficacy of a four-and-a-half-year intervention, conducted by the environmental health non-profit organization Pure Earth and funded by the United States Department of State, to reduce mercury contamination and use in ASGM communities in Peru. In both regions, Pure Earth raised local awareness regarding the dangers of mercury pollution through community workshops and also educated miners in alternative mercury-free techniques. Although some miners, primarily women, adopted the Filipino mercury-free method, others were reluctant to change deeply ingrained practices. Responding to this development, Pure Earth introduced alternative mercury-reducing techniques more suited to the miners’ local conditions, such as shaking tables.

The third component of intervention involved site cleanup. In the mining community of Ollachea, Puno, Pure Earth remediated eight tons of contaminated soil and constructed eleven tailing ponds to store large amounts of mining waste and reduce downstream impacts. In Madre de Dios, the project implemented a reforestation plantation in 3.5 hectares of degraded land in two mining concessions, in order to reduce ASGM’s environmental impact and provide miners with a model for proper mine closure.

To our knowledge, this is the first project in Peru to combine technical trainings with remediation efforts. Along with scientific information on mercury contamination in an ASGM site, the project gained experience working directly with miners, an essential step in reducing mercury pollution in the ASGM sector. The results and challenges of this intervention will therefore provide valuable information that could be incorporated into similar initiatives.

MERCURY CO-BENEFITS OF CLIMATE POLICIES ON RICE MERCURY CONCENTRATION AND EXPOSURE IN CHINA

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In China, both climate mitigation policies under the Paris Agreement and mercury controls under the Minamata Convention affect atmospheric mercury emissions, which may result in health benefits for those who consume rice. Rice consumption is known to be an important mercury exposure pathway to humans in China. Here, we combine mercury and climate policies that mitigate atmospheric mercury emissions from various anthropogenic sectors to quantify changes in Chinese rice methylmercury concentrations, exposure, and health impacts through an integrate model assessment. China Regional Economic Model (CREM) is used to construct mercury and climate policy relevant future mercury emission scenarios. A global scale atmospheric chemistry transport model (GEOS-Chem) and a rice paddy biogeochemical
cycle model for mercury are used to simulate mercury emissions and deposition to Chinese rice paddies, and to simulate the resulting rice methymercury concentrations, respectively. Our results suggest that mercury policy is more effective in mitigating Chinese rice methymercury levels compared to climate policy at a national scale. Under our future scenarios, the Chinese rice methymercury concentration decreases by 3.7% under mercury policy alone, while it decreases by 1.3% under strict climate policy, relative to Year 2030 under no policy. Mercury policies combined with climate policies resulted in 4.3% reduction in rice methymercury level, suggesting that mercury policies that implement mercury-specific capture technologies in combustion and energy intensive sectors as well as abatement of mercury-added products and mining are important for rice methymercury reduction. Provincial-level spatial variations of potential influences and mercury co-benefits of climate policies in mitigating human methymercury exposure via rice ingestion in China are also examined. Central China, which demonstrates the highest rice production, consumption, and elevated baseline rice mercury concentrations exceeding the China National Standard Limit of 20ng THg/g, is subject to the largest mercury policy-relevant health benefits. This suggests potentially significant health benefits to those who depend heavily on rice and are exposed to large amount of methymercury via rice consumption in China. Overall, potential co-benefits of climate policies on rice methymercury reduction are expected to be relatively little compared to the implementation of mercury policy alone in China. Thus, China’s commitment on the Minamata Convention on Mercury is critical for reducing rice methymercury levels in China.

M.P.4.30

MERCURY POLLUTION IN CHILE: CURRENT STATUS AND FUTURE PROSPECTS

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Chile has great geological wealth, with its main economic activity being the extraction and smelting of different metals including gold. It has a long coastline, thus marine resources are not only important for local consumption but also for international use. In addition, a large mountain range with over 2,000 volcanoes runs along the country from north to south, and is a natural source of mercury and it is well known that the global transport of mercury reaches cold areas (high mountains and glaciers). In addition, 40% of energy in Chile in 2018 was provided by coal combustion, another important mercury source. A review in 2004 showed the historical use of mercury in Chile since pre-Columbian times, but revealed a scarcity of information on mercury in Chile. Fifteen years later we strongly believe that an update in this area is necessary to evaluate the progress of the implementation of the Minamata Convention. Here, we review scientific literature on different mercury issues in Chile by gathering bibliographic data from Scopus, Springer, Web of Science and Science Direct. We classify research into two categories: environmental pollution and human contamination. In the environmental studies, most information is on mercury in abiotic matrices and there is not good spatial representation in the country. In the human studies, mercury analysis in hair was done in the 90’s, there was an evaluation of mercury and neuromotor function in children and artisan gold miners in one location, and was one study of dietary mercury two locations in Chile. There is an urgent need for more studies to evaluate the exposure and effects of mercury, both in the environment and in humans, to generate a solid baseline. Our conclusions are that we need: (1) to distinguish what percentage of mercury corresponds to natural sources versus anthropogenic emissions; (2) to generate plans that diminish industrial emissions and provide substitutions for products that contain mercury; (3) to standardize the analytical methodology; and (4) to promote the generation of advanced human capital and the acquisition of equipment to with this research.

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THE DRAGONFLY MERCURY PROJECT: TEMPORAL TRENDS IN MERCURY CONCENTRATIONS OF DRAGONFLY BIOSENTINELS FROM ACADIA NATIONAL PARK, MAINE, USA

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DELIBERATION ON PUBLIC HEALTH STRATEGIES FOR THE ASGM SECTOR THAT AIM TO MEET THE GOALS OF THE MINAMATA CONVENTION

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Artisanal and Small-scale Gold Mining (ASGM) is the largest source of mercury pollution in the world. Though the sector provides an important livelihood for more than 10 million miners worldwide, severe health and environmental hazards for miners and surrounding communities often result from ASGM activity. The Minamata Convention obliges countries with ASGM to develop a National Action Plan (NAP) for ASGM that includes a public health strategy. Central elements of this strategy include the gathering of information on mercury exposure and other ASGM-related diseases and injuries, the adoption of science-based guidelines on mercury exposure, training for health-care workers and awareness-training for mining and other affected communities. Initial information from countries that are developing public health strategies for their ASGM sectors show severe shortcomings in terms of accessibility of adequate health care, knowledge in the health care sector about diagnostic protocols and prevention guidelines, as well as availability of diagnostic tools, especially in remote ASGM communities. These represent a major barrier for obtaining the goals of the Minamata Convention. Furthermore, the capacity of many national health information systems is not equipped yet to adequately capture relevant data. In view of the limited budgets allocated to the public health sector in many countries, financing the necessary steps will be a challenge. A successful public health strategy will require innovative and concerted efforts of government organizations, research institutions, CBOs and NGOs, and should build on existing public health programs and structures. For example, a routine surveillance system, based on a standardized electronic medical record system, could capture and report cases of mercury exposure and potentially mercury related health problems. The interface developed for the ASGM communities could also report on other diseases and help to improve screening for early intervention in ASGM communities. The presentation will discuss possible strategies for a successful public health response to some existing health hazards in the ASGM sector.
METHYL MERCURY CYCLING AT THE SURFACE OF THE SEA: INTERACTION OF RAIN AND SEAWATER

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Methylated mercury is an environmental toxicant that has the capability to bioaccumulate in marine organisms even if seawater concentrations are low (pg/L). Therefore, gaining a better understanding of the factors that affect methylmercury (MeHg) in the ocean is crucial. In the surface oceans, photodegradation has been viewed as the primary pathway to demethylate MeHg (DiMento and Mason 2017). However, results from our series of microcosm experiments suggest that other pathways may need to be considered. The experimental design consists of bulk and filtered seawater mixed with rain at various proportions (e.g. 0.00, 0.04, 0.09, and 0.14) with a final volume of 125 mL, all in triplicate. The rain water was collected during 4 different storm event types i.e. squall line, hurricane remnants, extratropical cyclone, and isolated convection. Upon mixing rain with seawater the solution was immediately acidified to a final concentration of 0.5% (vol./vol.) with trace metal grade hydrochloric acid. These water samples were analyzed using Tekran 2700 following the methods described by Munson et al. (2014). The detection limit for MeHg was 0.011 ng/L. In support of novel pathway for MeHg demethylation we have found that mixing of rain and bulk seawater resulted in a decline of MeHg concentration (maximum = 81%) proportionally to increasing fraction of rain. MeHg concentration remained unchanged when the experiment was repeated using filtered seawater.
**T.P.1.1**

**MIGRATORY SEABIRDS AS BIOVECTORS OF MERCURY TO THE ARCTIC**

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Investigating the spatial dynamics of mercury (Hg) in polar environments is essential to better understand the vulnerability of these regions and of their ecosystems to this toxicant. Previous studies modelled Hg fluxes to/from the Arctic and highlighted the role played by oceanic and atmospheric currents and by river runoff in the transport of midlatitude Hg to the Arctic. However, the role of biovectors has been hardly considered. Seabirds were showed to act as biovectors of Hg at local scale, transporting important quantities of Hg from their at-sea feeding grounds to their nearby terrestrial nesting site. In addition, seabirds are highly mobile species, migrating over hundreds to thousands of kilometers every year between their Arctic breeding site and their non-Arctic wintering areas. At these latter places, they could accumulate large amounts of Hg which they could then transport to the Arctic when migrating back to reproduce. However, this potential role of seabirds as large scale biovectors of Hg to the Arctic has never been explored.

We tested the hypothesis that migratory seabirds transfer large amounts of Hg from their wintering to their breeding sites through feather molt. The molt of feathers in indeed a major Hg excretion route, where >80% of Hg accumulated since the last molting sequence is excreted to newly synthesized feathers. These feathers, which hold Hg accumulated in a specific region (e.g. wintering site) will then be replaced and thus released in other regions (e.g. breeding sites) where they will be degraded, releasing their Hg.

To this end, we measured Hg concentrations in feathers of five alcid species from 35 breeding sites located all around the Arctic (>3000 samples). Alcids have two molts per year (one pre-nuptial molt where only head feathers are replaced and one post-nuptial molts with a complete plumage replacement) so feathers indicate Hg accumulated by birds specifically during the non-Arctic winter period (Head Feathers) and during the Arctic breeding period (Body Feathers). Concurrently, carcasses of these five species were dissected to measure the total mass of feathers that molt during each period. A combination of these two information allowed to determine for each species and population the quantity of mercury excreted to feathers and specifically transferred to the Arctic. These information were then combined to data on population abundance and wintering areas to estimate the role of these species in the transportation of Hg to the Arctic according to their breeding and non-breeding distributions.

**T.P.1.2**

**MERCURY LEVELS IN ANTARCTIC ECOSYSTEM (BARTON PENINSULA, KING GEORGE ISLAND)**

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This study aimed at examining levels of total mercury (THg) and methylmercury (MeHg) in Antarctic ecosystem of the Barton Peninsula on King George Island in the South Shetland Islands, where one of South Korea's scientific bases, King Sejong Station, is located. King George Island is one of the most heavily human-impacted areas from tourism, scientific and fishing activities. While a number of studies have reported total mercury concentrations in Antarctic organisms, there is very little information on methylmercury. In this study, a range of tissues from benthic invertebrates, fish, and birds as well as snow, water, and vegetation were collected in austral summer from 2016-2017 and 2017-2018. For vegetation, THg in lichen (Usnea sp.) were overall higher than moss (Sanionia sp.), ranging from 59.9 to 461 ng/g and from 28.0 to 153 ng/g, respectively. Average THg and MeHg (%MeHg) in unfiltered seawater were 0.41±0.17 and 0.017±0.004 ng/L (3.92±1.44%), respectively. For snow, THg and MeHg (%MeHg) averaged 2.54±2.45 and 0.46±0.79 ng/L (11.3±10.0%), respectively. For biota, from benthic invertebrates to birds (penguins and skua), THg concentrations ranged from 0.015 to 18.9 mg/kg, indicating biomagnification. Overall, our results fell within a comparable range with previous studies. Further analysis of MeHg in biota is currently underway, nonetheless our study suggest the necessity of continuing ecosystem monitoring in order to assess impacts caused by anthropogenic activities in Antarctica.

**T.P.1.3**

**MERCURY ISOTOPE AS A TOOL TO INVESTIGATE THE SPATIAL ORIGIN OF ARCTIC SEABIRD CONTAMINATION**

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As a consequence of their high position in marine trophic webs, seabirds are considered as effective bioindicators of marine contamination since they integrate biomagnifying pollutants, such as mercury (Hg), via food intake. Despite no direct Hg inputs in the Arctic region, Arctic top predators are among the most exposed organisms to Hg, which is bioaccumulated as highly toxic organometallic methylmercury (MeHg). Specific foraging habitats and migratory movements of Arctic seabirds determine their exposure to distinct environmental MeHg sources in marine ecosystems. Here, we focused on little auks (Alle alle), a zooplanktivorous seabird species, which are particularly interesting for Hg isotopic studies in the Arctic Ocean since they reflect MeHg accumulation in a short food web that is strongly dependent on sea ice abundance and seawater temperature. Besides, this migratory seabird species presents two feather moult during their annual cycle: a first "nuptial" moult when they only replace head feathers, and a second body feather moult at the end of their breeding period. Due to different Hg integration times between types of feather, we can study Hg contamination during both non-breeding and breeding seasons in a same individual. The measurement of Hg isotopic mass dependent (MDF, δ202Hg) and independent (MIF, Δ199Hg) fractionation has become an essential tool for identifying Hg sources and quantifying its reactivity within the different marine compartments. Here, we investigated Hg isotopes in head and body feathers of four distant colonies of little auks from the Arctic Ocean presenting specific wintering areas. Hg isotopic signatures obtained in both types of feather clearly separated little auk populations geographically, permitting the identification of distinct ecosystems corresponding to both the breeding and the migration areas. Although slight differences on δ202Hg values were observed between the two types of feather at the individual level, Δ199Hg values were significantly higher for body feathers than for head feathers in all the individuals independently of the colony (0.36% on average). Since Hg MIF is mainly affected by Hg photochemistry and is preserved up to the food web, differences in Δ199Hg values between feathers may be the result of a different Hg photochemical extent related to seasonal variability (summer vs winter) and/or geographical biogeochemical characteristics (Arctic Ocean vs wintery areas). This study highlights the utility of Hg isotopes to help elucidating the Hg exposure of migratory seabirds during their whole annual cycle and open a new horizon for exploring Hg dynamics in large zones of the ocean.
MERCURY IN SOILS OF RUSSIAN ARCTIC

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Human activity has significantly altered the natural global geochemical cycle of Hg due to man-made anthropogenic emissions. The Arctic is particularly concerned regarding environmental risks for Hg, because this region is especially vulnerable to global Hg pollution. The datasets on atmospheric Hg flux for the Arctic, environmental archives (profiles of soil, peat, lake sediments) are particularly important sources of data for understanding the flux history. These data also provide the basis for understanding the political steps to be taken in the future (like the recently adopted Minamata Convention).

Mercury was determined in soil profiles in different parts of the Russian Arctic: delta of Lena River, Taimyr peninsula (Noril’sk), and Kola peninsula (Nikel, Monchegorsk). The soils from background areas as well as the soils from industrial areas (near smelters) were studied.

Mercury was determined by pyrolysis of solid samples with pre-concentration of mercury on gold collector and subsequent registration on AA spectrometer.

Mercury concentrations in the background areas (ng/g): in the lower horizons of cores 10–30 (Kola peninsula), 10–30 (Taimyr peninsula), 30 (Lena River) and in topsoils 70–150 (Kola peninsula), 90 (Lena River).

The results show that Hg in most samples is enriched in the surface soils layer and associated with organic matter. Hg levels in mineral soils were substantially lower than in the corresponding surface soils.

The difference of Hg distribution in depth with other (crust) elements shows that mercury is predominantly derived from atmospheric deposition. The obtained concentrations of Hg for soils in the Russian Arctic are similar to results of other researchers for various sectors of Arctic.

Some differences can be explained by proximity of industrial centres and various contents of organic matter in the surface layer. This work was supported by RFBR (project Arctica No 18-05-60012) and scientific program UB RAS (project № 18-5-5-43).
Air-sea gas flux is an important pathway for mercury cycling in polar regions. Mercury evasion, usually in the form of elemental mercury, is a major sink for cryospheric and oceanic mercury. This is due to the high mobility of elemental mercury, which is readily redistributed between the atmosphere and seawater. However, it is influenced by the presence of a sea ice cover, which is hypothesised to act as a physical barrier. Previous studies focused on total mercury and methylmercury distributions in sea ice, while the distribution of elemental mercury was much less studied.

When ice starts growing, dissolved gaseous mercury (DGM) may accumulate in intermediate water underneath the sea ice cover or be trapped within the ice layer; in either case, air-sea gas exchange will be limited. As sea ice grows thicker and decreases its permeability, the distribution of elemental mercury will change accordingly when the DGM concentration in the sea ice cover decreases at the same time. Meanwhile, due to the weakening of air-sea gas exchange, DGM in intermediate water and gaseous elemental mercury (GEM) in the atmosphere above the ice can also change during the growth of sea ice. To study elemental mercury dynamics under natural cryospheric conditions, here we report a controlled mesocosm study carried out over a sea ice grow-melt cycle at the Sea-ice Environmental Research Facility (SERF), University of Manitoba, Winnipeg, Canada. A system (12 ft. in length; 5 ft. in width) consisting of twelve mesocosms was planted in an outdoor seawater pool and froze into ice during sea ice growth. Individual mesocosm was covered with clear/dark poly sheeting to create a constrained headspace of at least 25 L above ice surface for atmospheric GEM sampling. DGM in ice intermediate seawater and ice core samples were measured discretely over the sea ice grow-melt cycle, as well as the diurnal variation of GEM in the mesocosm air.

Preliminary results show that DGM in intermediate water decreases gradually when the sea ice cover is present; within the ice core, DGM is found to be enriched in granular sea ice compared to columnar sea ice. Our results indicate the redistribution of elemental mercury over a sea ice grow-melt cycle is controlled by both physical and chemical processes in the simulated cryospheric environment.

COASTAL DARKENING: IMPLICATIONS FOR THE TRANSPORT, BIOAVAILABILITY AND TROPHIC TRANSFER OF CONTAMINANTS IN NORTHERN COASTAL WATERS

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Increased loading of terrestrial material to coastal ecosystems is driving changes in the transport, bioavailability, uptake and trophic transfer of contaminants such as mercury (Hg) and persistent organic pollutants (POPs) at the land-ocean interface. Despite increasing evidence that increased terrestrial inputs are changing the biogeochemical and ecological regimes of Northern freshwater systems with implications for contaminant transport and food-web accumulation, there has been little focus on this topic in nearby and economically important coastal waters. The nutrient, carbon and sediment loads that are associated with terrestrial inputs can have significant ecological implications, causing changes in primary carbon sources, trophic interactions and prey quality. How these indirect effects of darkening relate to contaminant dynamics is complex and often contradictory in nature. We present here a conceptual model that identifies and integrates direct and indirect consequences of increased terrestrial run-off and subsequent darkening on the transport, bioavailability, and trophic transfer of contaminants in coastal ecosystems.

SEASONALITY OF METHYLMERCURY HOTSPOTS AT THE AQUATIC-TERRESTRIAL INTERFACE IN A HIGH ARCTIC FRESHWATER CATCHMENT

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Methylmercury (MeHg) is a toxin which bioaccumulates and biomagnifies through food webs. In the Arctic, elevated concentrations of MeHg in freshwater fish are a potential health concern for Indigenous peoples. Understanding seasonal, and spatial, variation in sources of MeHg at the terrestrial-aquatic interface is increasingly important to predict how climate change will alter cycling of MeHg in Arctic freshwater systems. This research, carried out in a High Arctic freshwater sub-catchment (Eillesmere Island, Nunavut, Canada) aims to determine where MeHg production and degradation hotspots occur along a continuum that includes permafrost seeps, a lake, a series of ponds, a wetland and a stream, and to examine how MeHg cycling differs between the ice-on and ice-free seasons. To address these objectives, field-based experiments were used to quantify Hg methylation and MeHg demethylation and were combined with spatiotemporal surveys of MeHg and total Hg concentrations. Preliminary data indicates MeHg is produced in the lake and pond sites, but wetland soils act as a sink for MeHg reducing its export to downstream ecosystems. Interestingly, during the ice-on period, lake waters had MeHg concentrations over eight times higher than during the previous summer, suggesting that timing of peak methylation in Arctic lakes may differ from temperate lakes as a consequence of prolonged ice cover. This research will allow us to understand how predicted reductions in ice cover and increased permafrost thaw, for example, will impact MeHg exposure in Arctic ecosystems.
MERCURY BEHAVIOUR AND DISTRIBUTION IN SOILS WITHIN ICE-FREE AREAS OF THE NORTHERN ANTARCTIC PENINSULA REGION

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Antarctica is considered one of the few areas that remain pristine due to scarce human activity and its isolation from large industrial centres. Even so, there is evidence that different pollutants are found in Antarctic ecosystems. This is especially important within ice-free areas and one of these pollutants is mercury (Hg), of which the Polar regions are important sinks. Hg, which may have a natural or anthropogenic origin, has a high atmospheric residence time (up to 1 year) and can be transported from remote places until it oxidizes to gaseous divalent compounds that are deposited on the land surface. Oceanic currents or bioaccumulation of this element through the food chain are other transport means. In the latter case, animal excrements and remains deposit Hg within the ice-free areas where penguin, sea bird and seal colonies have their breeding grounds. Human activities at the bases and tourism are a further source that may also contribute to mercury deposition. However, Hg may be present naturally due to the abundance of volcanic materials in certain areas of the Antarctic Peninsula and the South Shetland Islands. There are few studies on Hg in soils for Antarctica and, therefore, there is a need to better understand the Hg behaviour and distribution in soil profiles from site specific areas and conditions. The objective of this work is to study the distribution of Hg in the horizons of different soil profiles sampled on Deception Island, Fildes Peninsula (King George Island) and Punta Cierva (Antarctic Peninsula). These soils have developed on different parent materials, geomorphological features and biological influence, resulting in poorly developed shallow soils, consistent with the Antarctic climatic conditions. In all the established soil horizons, a physical-chemical characterization was carried out and total Hg was measured. Overall results indicate significant differences between the Hg concentrations for the different locations. Furthermore, differences were also observed for the distribution of Hg with depth which was related to abiotic and biotic factors influenced by periglacial processes. As expected, there is a strong relationship between Hg distribution and available free iron oxides and organic matter content that prevents the movement of Hg in the soil profile. The subsequent analysis of the distribution of Hg within the different horizons associated to the geographical locations provides valuable information on the origin and dynamics of the corresponding pollutant.

MERCURY DYNAMICS IN FISH MUSCLE DURING WINTER AND SUMMER IN SUBARCTIC LAKES

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Subarctic regions are characterised by major seasonal shifts in both light and temperature, varying from the warm, well-illuminated summer through to cold ice-covered winter conditions that extend for half of the year. We know that these contrasting conditions have major impacts on lake productivity and activity of fish, but we know far less about how seasonality affects mercury concentrations and accumulation in a key storage tissue, dorsal muscle. Here, we assessed how muscle mercury concentrations and accumulation varied in autumn and spring spawning species in a large and a small subarctic lake both supporting a multispecies fish communities including polymorphic whitefish (Coregonus lavaretus). Both lakes and different fish species are targeted by local fishers during summer and winter. We measured total mercury, stable isotopes of carbon and nitrogen and the elemental ratio of carbon and nitrogen from muscle tissue as well as size, condition, age and growth of abundant fish species in each lake. We hypothesized that autumn spawning species and whitefish morphs would show proportionally higher mercury concentrations than spring spawning species during winter due their long period of decreasing body condition after reproduction in late autumn. Our results showed that fish were less active and had reduced body condition in winter compared to summer. We found elevated mercury concentrations in winter than summer in most autumn and spring spawning fish species indicating importance of winter in overall mercury dynamics. The lowered fish condition in winter resulted in the concentration of mercury in dorsal muscle tissue and, while summer growth diluted concentration. Our results suggest that fish captured in winter represent a greater risk of mercury exposure than summer fish, with obvious potential human health implications. Furthermore, the differences we observed in summer and winter mercury concentrations have implications for optimising timing in future studies and monitoring programmes.

LONG TERM VARIATION IN ARCTIC FRONTAL POSITIONS AND ITS IMPACT ON DIRECT ANTHROPOGENIC EMISSIONS IN POLAR REGIONS

WANG, Danhan; MAO, Huiting

Identified between Arctic and Polar air mass, the Arctic front is a discontinuous front within the boundary layer. In winter, the Arctic front sets a transport barrier in the lower atmosphere, together with isentropic surfaces to form domes over the Arctic, known as the Arctic dome. Air pollution in the Arctic is attributed to local sources and long-range transport from lower latitudes. Emissions from North America could hardly penetrate the Arctic dome in winter. Over the Eurasian continent, the Arctic fronts can reach lower latitude, which can enclose significant amounts of direct anthropogenic emissions within the Arctic dome. Conceivably the positions of Arctic fronts can affect the total amount of anthropogenic emissions directly injected into the Arctic atmosphere. As the Arctic has been warming at a rate twice faster than the rest of the globe, it is important to find out whether there are interannual to long-term variations in the positions of Arctic fronts, which would have an immediate impact on Arctic pollution. In the future, the rapid loss of sea ice is likely to accelerate urbanization and increase local air pollution sources. In this study we will focus on emission sources of mercury as mercury pollution is an important environmental problem in the Arctic region. We apply different methods to identify the positions of Arctic fronts and examine the impact of their temporal variations on direct mercury emissions within the Arctic dome.

TOTAL MERCURY IN SEDIMENTS AND ORGANISMS FROM ISFJORD, SVALBARD

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Polar regions are important in the mercury cycle, because in this regions it is readily deposited to the lands and seas surface during a springtime Atmospheric Mercury Depletion Event (AMDE). The Svalbard is the sys-
term in transition – this is a region where climate change is most visible in the world. This area is also interesting because of possible mercury sources such as a complex pattern of surface currents carrying both warm and cold water masses into the region, varying geological bedrock, and recent glaciers melting. The benthic organisms, especially starfish can be valuable bioindicators for contamination with heavy metals. For that reason, in July 2018, selected benthic organisms were collected form three stations in Spitsbergen fjord. The first location was reference station, and the second and third stations were located in Isfjord. The algae, brittle stars, sea urchins, sea snails and star fish were collected. In addition, bottom sediment was collected. Obtained results showed that the most contaminated in Hg organisms were starfish (average 379 ng/g d.w.). Starfish are highly positioned carnivores in the benthic food web: they feed on clams, oysters, snails, other shell molluscs, brachiopods, hermit crabs, and inactive or dying fish. The lowest concentrations were measured in algae samples (average 5 ng/g d.w.). Differences in mercury concentrations in the obtained results did not occur only between organisms, but also between stations. The most contaminated area was station located close to the birds nests and residue of the mine, which certainly had the influence on the results.

**PENGUINS DETOXIFY MEH IN LIVER AS EVIDENCED BY Δ202HG AND %MEH**

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The main exposure route of methylmercury (MeHg) in marine birds is via ingestion of fish and invertebrates. The primary diet of the Adelie (Pygoscelis adeliae), Chinstrap (Pygoscelis antarcticus) and Gentoo (Pygoscelis papua) penguins is krill (Euphausiacea) whereas other species such as Emperor penguins consume krill but are also avid piscivores. Moreover, Adelie penguin chicks are often preyed upon by Skuas (Stercorarius maccormicki). The continuous exposure to MeHg from ingested diet leads to steady incline in MeHg concentrations in these birds, particularly Emperor penguins and skua which are feeding at a higher trophic level. As in other vertebrates this MeHg build up is exacerbated by higher rate of assimilation in relation to its elimination. The hypothesis stating that MeHg is detoxified in seabird livers has been put forth, however no study further investigated this process. Here we used Hg stable isotopes as a tool to determine whether MeHg could be detoxified in penguin and skua livers. Our study relied on the overall hypothesis that the processes of MeHg degradation in liver cells would alter the isotopic signature of total Hg. Specifically the mass dependent fractionation (MDF) of 202Hg. Furthermore, we hypothesized that such altered signature of THg would persist in bird kidneys due to this organs role in regulation of metabolic waste products. Measurements of THg, MeHg and stable isotopic composition of THg were performed on skeletal muscles, heart tissues, livers, kidneys, and stomachs. We have determined that average concentrations of THg and MeHg varied across penguin species, and skua showed highest concentrations reflecting its predatory status in the Antarctic food web. In support of our hypothesis, we have found that δ202Hg was isotopically depleted in livers and kidneys in comparison to the muscle, heart and stomach tissues by 0.6 to 1 ‰, in emperor penguins and skua. Furthermore, liver and kidney tissues displaying depleted isotopic compositions also display lower % MeHg in comparison to other tissues.

**TOTAL MERCURY IN CHLOROCERYLE AMERICANA (GMELIN, 1788) IN THE BRAZILIAN AMAZON**

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Mercury is a highly toxic global contaminant naturally found in the Amazon, with biomagnification capability in the aquatic trophic chain. The use of piscivorous birds for biomonitoring of mercurial contamination is increasing, mainly due to the non-mobility of the bird in the feathers. The concentrations of total mercury in different tissue of Chloroceryle americana from the Teles Pires River (n = 21, weight 30 g) and Juruna River (n = 24; weight 28 g) samples in the southern Brazilian Amazon during the periods of September 2016 and January 2017. The results obtained evidenced high concentrations of total mercury, on average two times higher in the green kingfisher of the Teles Pires River than all the sampled tissues. The increasing behavior of mercury concentrations between tissues was muscle < liver < feather. High THg concentrations in liver were found in C. americana in the Juruna River (0.589 μg.g-1 ± 0.196) and Teles Pires River (1.499 μg.g-1 ± 0.792). A total of 58% of feather samples (5.514 ± 2.351 μg.g-1) and 90% of the Teles Pires River (11.570 ± 5.226 μg.g-1) were higher than the mercury levels associated with reproductive-related adverse effects of 5 μg.g-1. The THg concentrations suggest special attention for the areas sampled due to the installation projects of dams in the region, as well as the advance of soy monoculture in the southern end of the Amazon, potentiating the bioaccumulation of mercury.

**TOTAL MERCURY AND METHYLMERCURY CONCENTRATION IN POTENTIALLY CONSUMED FISH CAPTURED IN TRACKS OF THE TELES PIRES AND JURUE-NA RIVERS, SOUTH AMAZONIA**

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In addition to the natural emanations of mercury, we can observe through several studies that the Amazon have been the target of anthropogenic activities such as: mining, burning, conversion of land for agricultural purposes, livestock and dam construction. Such activities contribute to increasing environmental contamination and consequently potential intoxication to biota and human health. We analyzed concentrations of total mercury and methylmercury in nine species of potentially consumed fish caught in the Teles Pires and Juruna rivers, southern Amazonia. The detection of THg and MeHg was performed using Atomic Absorption Spectrometer. Concentrations of THg in the muscle were higher in the fish species captured in the Juruna River when compared to the concentrations obtained for the same species from the Teles Pires River. For the Teles Pires River, the concentration of MeHg in the muscle of the nine species of fish was superior to 83% of the THg. While for the Juruna River, the MeHg concentration was higher than 69%. Considering the impacts of MeHg intoxication and knowing that fish represents the main source of protein in the traditional population, we suggest that the population of the study sites should be oriented towards fish intake and that the consumption of non-predatory species, in order to avoid further exposures to the metal.
TOTAL MERCURY IN SOIL AND LEACHATE FROM MUNICIPAL SOLID WASTE LANDFILL IN INDIA

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Total mercury (THg) levels were investigated in the top soil layer and leachate collected from periphery of Deonar Dumping Ground in Mumbai, India. Deonar Dumping Ground, established in 1927 is one of the oldest and largest dumping ground for municipal solid waste in India. It is located in eastern suburbs of Mumbai city, adjacent to Thane Creek and surrounded by residential areas. It covers an area of 1.32 square kilometres and receives around 2000 tonnes per year of solid waste from Mumbai. The samples were collected and analysed for THg with Milestone make DMA-1. THg levels in top soil layer ranged from 64.6 to 1942.08 μg kg⁻¹ with a mean of 485.24 μg kg⁻¹ and a 95% confidence interval for the mean of 322.68 to 647.81 μg kg⁻¹. Leachate THg ranged from 0.5 to 14.21 μg kg⁻¹ with a mean of 2.28 μg kg⁻¹ and a 95% confidence interval for the mean of 0.99 to 3.58 μg kg⁻¹. THg concentration in leachate corresponded with the values reported in literature but THg in soil was found to be twofold of the values reported in literature. High temporal and spatial variation were observed with five samples showing THg concentration in soil above 1000 μg kg⁻¹. Statistical relationship between THg concentration and physicochemical parameters such as pH, chemical oxygen demand (COD), turbidity, total solids (TS), total dissolved solids (TDS) and total suspended solids (TSS) were determined. Pearson correlation coefficient analysis showed strong correlation between COD, TSS, turbidity with THg in leachate. However, for TS and TDS very weak correlation was observed. THg in soil and leachate also showed weak correlation. Due to frequent fires and since the dumping ground is not scientifically managed, the groundwater and surrounding areas face hazard of mercury pollution.

TOTAL MERCURY CONTENT OF NATURAL SPRINGS AND OTHER DRINKING WATER SOURCES IN SOUTHEASTERN NIGERIA

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This study investigated the total mercury (THg) content of ground and surface water sources used for domestic purposes in some districts within the shale bedrock terrain of two two states (Abia and Imo States) in Southeastern Nigeria located within latitudes 4°15’N and 6°58’N and longitude 6°50’E and 7°59’E. There are two principal geological formations in the states namely Bende-Ameiki and the coastal plain sands otherwise known as Benin Formation. The Bende-Ameiki formation overlies the impervious Imo shale group of Paleocene age, which is characterized by lateral and vertical variations in lithology. Water sampling and preservation were performed in accordance with the procedure prescribed by American Public Health Association. A total of 124 water samples from 13 natural springs, 24 streams, 80 boreholes and 7 hand-dug wells were collected from rural and urban areas. Measurement of Hg was done using PE-1000 Nippon mercury analyzer (CV-AFS) equipped with auto sample changer (HT-300A). Sample (200 μL) was auto injected into the sample heating section and decomposed using appropriate settings. Mercury was atomized in the catalytic section, then collected and concentrated in the form of gold amalgam in the Hg collection section. The Hg was then released and atomized again through the Hg collection section being heated and detected using the AFS at a wavelength of 253.7 nm. Results of recovery studies varied from 101 to 107 %. The results varied widely within and between the sampled water sources. The THg (μg/L) varied from 0.010±0.011 (max 0.060) for Imo State to 0.022±0.048 (max 0.250) for Abia State for borehole; 0.010±0.009 (max 0.025) for Imo State to 0.003±0.005 (max 0.010) for Abia State for streams; and, 0.006±0.008 (max 0.020) for Imo State to 0.001±0.002 (max 0.005) for Abia State for springs. For hand dug well water sources the THg was 0.012±0.007 (max 0.020) for Imo State while the only sampled source in Abia State has a THg content of 0.015. The data obtained were compared with national and international guidelines for drinking water and were found to below stipulated limits. The estimated HQingestion were generally very low, indicating no adverse health effects on human and potential non-carcinogenic risk arising from using the water from the various sources for drinking and other domestic applications.

INVENTORY OF MERCURY RELEASES IN INDONESIA 2017

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The inventory of mercury (Hg) releases in Indonesia had been conducted by the use of the toolkit for identification and quantification of mercury releases Level-1 and partly Level-2, made available by the UNEP. The toolkit calculates Hg release based on mass balances for each mercury release source type. The inventory Level-1 works with activity rate which quantifies the mercury inputs from the amount of mercury-containing material fed into the system, and pre-determined factors used in the calculation of mercury inputs to society and releases, the so-called the default input factors and default output distribution factor. These factors were derived from data on mercury inputs and releases from such mercury source types from available literature and other relevant data sources. All the mercury fed into the system with materials and fuels will come out again, either as releases to the environment or in some kind of product stream. The inventory Level-2 works with the same activity rates, but different input factors and output distribution factors, which were developed from site specific data sampling. The results of Hg inventory Level-1 shows that total mercury released in 2017 was estimated approximately 406 ton Hg/year. The individual mercury release which contribute the highest mercury inputs were: gold extraction with mercury amalgamation in Artisanal Small-scale Gold Mining (60% of total release, or about 244 ton Hg/year), primary metal production excluding gold production by amalgamation (17.2%), use and disposal of products with mercury content (4%), coal combustion and other coal use (3.4%). Results of Hg Inventory Level-2 from ASGM were estimated to release approximately 1,850 ton Hg/year to the environment or more than 7.5 times higher than Level-1, while the coal combustion and other coal use were estimated to release approximately 133 ton Hg/year or almost 10 times higher than Level-1. This is actually not surprising results, since there are more than 850 hotspots of ASGM all over Indonesia with the average use of 46.54 Kg Hg/gold produced, and coal fired power plants are the main source of electricity supply with more than 29,880 MW installed in 2017 combusting more than 78 million ton of coal/year. Most of the Hg are released to the atmosphere, i.e. 48% of the total Hg emission to all pathways, make Indonesian most likely are breathing the Hg-containing air every day.
MERCURY AND SELENIUM IN FISHES OF LAGO YOJOA, HONDURAS

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Lago Yojoa is a large, eutrophic lake located in northern Honduras. It is monomictic with a pronounced warm, anoxic hypolimnion. The lake and its watershed have an extensive recent history of human-mediated manipulation including hydrologic alteration, non-ferrous mining and the introduction of exotic species to support both aquaculture and a sport fishery. Previous work has documented elevated levels of heavy metals (copper, zinc, cadmium, and lead) in both sediments and fish tissue from the lake but no data on other heavy metals has been previously reported. Here we present data on mercury (Hg) and selenium (Se) concentrations in sediments and four species of fish from Lago Yojoa. The mean Hg concentration in sediments (n=78) was 0.50 ± 0.02 micrograms/gram, dry weight (μg/g, dw) with a range from 0.06 – 1.06 μg/g, dw. Selenium concentrations in sediments were 2.91 ± 0.11 μg/g, dw, with a range from 0.7 – 5.37 μg/g, dw. Largemouth bass (Micropterus salmoides) had Hg concentrations of 0.863 ± 0.095 parts per million, wet weight (ppm, ww) (n=37) with an Se:Hg molar ratio of 1.15. The jaguar cichlid (Parachromis managuensis) had a mean Hg concentration of 0.492 ± 0.140 ppm, ww (n=21) with an Se:Hg molar ratio of 1.67. The benthic bigmouth sleeper (Gobiomorus dormitor) had similar Hg concentrations (0.415 ± 0.084 ppm, ww; n=10) with a higher Se:Hg molar ratio f 2.74. Nile tilapia (Oreochromis niloticus) are present in Lago Yojoa as a result of aquaculture practices in the lake and have Hg concentrations of 0.098 ± 0.017 ppm, ww (n=4) and an Se:Hg molar ratio of 9.90. Length – Hg and stable nitrogen isotope – Hg relationships illustrate the importance of bioaccumulation and biomagnification of Hg in the fishes of Lago Yojoa. The elevated Hg concentrations in fishes represent a human and ecosystem health risk, particularly to the human populations that utilize this fishery as a primary source of protein. There is very little variation in Se concentrations in fishes (mean = 0.379 ± 0.016 ppm, ww; range = 0.234 – 0.542 ppm, ww) and changes in the Se:Hg molar ratio is driven by variations in Hg concentrations. Data on Se in fishes from Lago Yojoa contributes to the growing, but still slim, body of data on Se concentrations in freshwater fishes in the tropics.

SMALL MAMMALS AS BIOMONITORS OF MERCURY CONTAMINATION IN TWO MOUNTAINOUS NATIONAL PARKS OF THE SOUTH EAST BRAZIL

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Atmospheric deposition of pollutants in mountain regions is a target of growing concerns by the scientific community. Among them we can highlight mercury (Hg), for presenting a wide dispersion on the environment and for the processes of bioaccumulation and biomagnification. However, the ecotoxicological effects of Hg in pristine and legally protected areas are still globally scarce. Therefore, the main goal of this study was to determine the presence of Hg in small mammals community of two National Parks (Itatiaia and Serra dos Órgãos, SE Brasil), evaluating the influence of parameters such as: spatial variations, trophic relations, morphometric characteristics and gender of the studied species. To do so, sampling campaigns (2013-2016) were carried on at the parks in distinct altitudinal ranges: 900-1200m and 1900-2200m in two different phyto physiognomies: Ombrophile mountain forest and altitude fields, respectively. A total of 111 animals were sampled comprising 12 species. After the euthanasia of the animals, the liver samples were freeze dried and then Hg was quantified by cold vapor atomic absorption spectrometry. As a result, a broad range in the total Hg concentrations (10 – 5500 μg/kg dry weight) were observed for all species. Part of this variations seems to be intimately related to each genus/species food habits. The greatest concentrations were observed in marsupials and rodents with preferential insectivorous food habits. No significant differences were detected between males and females, neither in morphometric parameters. Higher concentrations in male and female small mammals were observed in the ombrophile mountain forest.
SEASONAL PATTERNS OF ATMOSPHERIC MERCURY IN TROPICAL SOUTH AMERICA AS INFERRED BY A TGM CONTINUOUS RECORD AT THE CHACALTAYA STATION (5240 M) IN BOLIVIA

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We performed high resolution continuous measurements of TGM at mount Chacaltaya in Bolivia during 07.2014 – 02.2016. The GAW station, located on the Cordillera mountains at 5240 mslm, spends part of its time above the planetary boundary layer of the surrounding Altiplano and is influenced by a very diverse mix of altiplanic, amazonic and sometimes pacific air masses.

In spite of the closeness to the nearby urban agglomeration of La Paz-El Alto, local contamination seemed to have no significant effect on measured TGM for most of the year, with the notable exception of “San Juan” on the eve of June 24 when bonfires occur along the metropolitan area.

In good agreement with the sparse amount of TGM data available on the continent, we obtained a mean concentration of 0.90 + 0.23 ng/m3 for the first year of measurement.

We observed strong seasonal patterns, with highest concentrations just at the onset of auroral summer (wet season) and lower concentrations during auroral winter (dry season), including the remarkably low mean concentration of 0.71+0.15 ng/m3 in July 2014.

During August - October a strong increase of TGM was registered. With the help of CO and CO2 concentrations as auxiliary data, we could link this observation to large-scale biomass burning events occurring at that time of the year all over the Bolivian and part of the Peruvian lowlands. Using HYSPIT back-trajectories and clustering techniques, we determined that among the highest TGM (0.95 + 0.22 ng/m3) were associated with northern - amazonic air masses arriving at CHC after passing over the “Madre de Dios” river - a region of extensive small-scale miner (ASM) gold mining activities both in Bolivia and Peru. These air masses also showed increased TGM concentrations during the biomass burning season. Low mean concentrations (0.82 + 0.19 ng/m3) were registered for air masses originating in the south-eastern Bolivian lowlands. North-western altiplanic air masses showed lowest TGM concentrations (0.79 + 0.19 ng/m3), much lower than southern altiplanic air masses (0.97 + 0.26 ng/m3). We tentatively explain this difference with the latter’s passage over outgassing volcanoes in the central volcanic zone. We discuss other possible factors influencing the seasonal TGM cycle, namely changes in ocean-air flux rates due to heating of the Pacific Ocean in summer and shifts in vegetation cover during growing phases. We address these factors with the help of the Oceanic Niño Index and MODIS EVI-index satellite data.

T.P.1.25

MERCURY LEVELS IN ANTHROPOGENIC AQUATIC ECOSYSTEMS CREATED BY ARTISANAL GOLD MINING IN THE PERUVIAN AMAZON

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The Madre de Dios region of southeastern Peru has been recognized as one of the global biodiversity hotspots. This is also a region that has experienced a boom of artisanal and small-scale gold mining (ASGM) over the last 18 years resulting in an estimated annual release of 185 tons of mercury into the environment. As of December 2018, ASGM has deforested 115,550 ha of rainforest, and converted 15.6% of deforested areas into water-filled mining pits, creating ~ 18,000 hectares of a novel anthropogenic aquatic ecosystem. Concentrations and dynamics of mercury in these mining pits and resulting impacts on wildlife and fish-consuming human populations have been poorly studied.

This study reports the results of a cross-sectional study of mercury concentrations in sediments and fish of water bodies created by ASGM (mining ponds) and non-impacted natural oxbow lakes in Madre de Dios. We collected 1,257 specimens of 40 fish species, and 155 benthic sediment samples from 15 mining ponds and 11 natural lakes located at varying distances from mining activities. Total mercury concentrations were measured by direct mercury analysis (EPA Method 7473) using a Milestone DMA-80 mercury analyzer. Results indicate that fish mercury concentrations were higher in mining ponds vs natural lakes. Fish mercury concentrations increased with trophic level in both mining pits and natural lakes indicating that mercury biomagnification was occurring regardless of water body origin.

Mercury concentrations of low trophic level fish in both waterbody types were mainly lower than WHO reference levels for human consumption (0.5 mg/g), however mercury levels in high trophic level fish were generally above WHO reference levels.

No significant difference was found between mercury concentrations of benthic sediments in mining ponds and natural lakes. These results suggest that there are significant impacts of ASGM on the biogeochemical characteristics of mining ponds, which in Madre de Dios represent ~ 20,000 ha of new water bodies. Ongoing studies describing the aquatic and riparian biodiversity in mining ponds, and mercury concentration of several taxa will help further illuminate the mobility of bioavailable mercury resulting from these anthropogenic hydrosapes and contribute to risk assessments for wildlife and human mercury exposure.

T.P.1.26

MERCURY CONCENTRATION IN OUNCE JAGUAR (PANTHERA ONCA), TAIAMÁ ECOLOGICAL STATION, PANTANAL OF MATO GROSSO, BRAZIL

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Mercury is one of the pollutants most resistant to degradation and its bioaccumulation can be highly harmful to aquatic biota, transposing trophic chain levels and reaching top food chain predatory mammals. The Taimá Ecological Station is a Federal / ICMBIO reserve. The jaguars of Taimá have as preferential diet the fish and alligator, already evaluated in other studies as biomarkers of mercurial contamination in the Pantanal of Mato Grosso, Brazil. The objective of this study was to evaluate the concentrations of total mercury in jaguar (Panthera onca), using a non – invasive method of barbed wire and adhesive tape traps
and collection of hairs samples obtained in collar / ICMBIO / CENAP. To obtain the composite samples, seven sample points were monitored for six months with Trap camera, with the objective of individualizing the animals and groups. A total of 15 samples were collected, of which 13 were individual and 02 were composites (03 and 04 individuals per sample). For the quantification of the concentrations of total mercury was used atomic absorption spectrophotometer, Perkin Elmer (FIMS - system). The average concentration of mercury (µg/Kg) was 4,265,448 (2,130,531 min and 7,259,444 max.). There was no significant difference in the concentrations of total mercury between the sexes (T test = 1,571, df = 10,8, p = 0.143), although the females presented the highest concentrations, which can certainly cause over the years, biodiversity. Age also did not explain the variations in concentrations (R2 = 0.1603; p = 0.1753). However, there was a significant negative difference between the concentrations of total mercury and the weight of the animals (R2 = 0.3516, p = 0.03269). Thus, lighter animals had the highest concentrations of mercury in the body, suggesting that a mechanism of mercury demethylation may be occurring throughout the life of these animals or individual factors of metal absorption in the body. The results are unprecedented and demonstrate bioaccumulation through trophic chain levels, reaching the largest predatory cat in the Pantanal, Mato Grosso, Brazil through its diet almost exclusively of fish and alligators.

T.P.1.27

BIOMAGNIFICATION OF CONTAMINANTS IN A MARINE FOOD WEB (NW MEDITERRANEAN SEA): SPE- CIFICATION OF ARSENIC AND MERCURY TOXIC FORMS

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Contamination of marine environments is a major problem worldwide, owing to its effects on biodiversity, marine resource exploitation and human health. Arsenic (As) and mercury (Hg) tend to bioaccumulate in organisms and their inorganic (As III, DMA, MMA and As VI) and organic (MMHg) forms respectively are highly toxic (carcinogenic and neurotoxic). The speciation of As and Hg was studied in a pelagic food web in the Gulf of Lions (NW Mediterranean Sea), where trophic relationships have been previously determined. The aim of this study was to better understand the patterns of biomagnification and bioaccumulation of these elements. Analytical methods used to quantify the toxic forms of As and Hg are described in Labat et al. (2007, https://doi.org/10.1051/ata:2007004) and Heimbürger et al. (2010, https://doi.org/10.1016/j.gca.2010.06.036). Stable isotope analyses were used to identify the carbon sources (δ13C) and to estimate the trophic levels of the species (δ15N). Sixteen compartments were analyzed: Rhone River particulate organic matter, phytoplankton (80-200 µm), three size classes of zooplankton ([200-300 µm], [300-500 µm], [500-1000 µm]), two groups of large macrozooplankton (Meganymphides norvegica, Diacmesoda lobata), three zooplanktivorous teleosts (Sardina pilchardus, Engraulis encrasiculus, Sprattus sprattus), three mesopelagic teleosts (Trachurus trachurus, Scomber scombrus, Micromesistius poutassou) and three cephalopods (Ilexx coindetii, Todarodes ebalanea, Todarodes sagittatus). Biomagnification (increase with trophic level) was evidenced for tAs, tMMA, tMMA and tHg, whereas MMA and AsV were bioreduced. The highest mean values of tAs and tHg were measured in Todarodes ebalanea (68595 ng/g DW) and Micromesistius poutassou (1,303 mg DW) respectively, while their lowest values were measured in marine phytoplankton (80-200 µm) (495 µg DW and 0.001 ng/mg DW respectively). For tMMA and tHg the highest mean values were measured in Micromesistius poutassou (1.059 mg DW) and tMMA Sprattus sprattus (368.2 ng/g DW) respectively, while the highest tMMA values were measured in Micromesistius poutassou (tMMA 1.059 mg DW). Strong interspecific variations were observed, even between species positioned at similar trophic level, which highlighted the importance of their bi-
of 1 L/min, creating an opposite flow. The outgoing air containing the equilibrium concentration of DGM was analyzed using a Tekran 2537A CVAFS instrument. GEM in air was measured at a height of 7 m and 29 m using a similar instrument. The bulk method, or the two-layer thin-film model, was used to determine Hg0 evasion. Acquired results showed average concentrations of DGM, GEM and Hg0-fluxes as 13.5 ± 3.5 (5.9-31) ng/m3, 1.3 ± 0.2 (0.8-3.2) ng/m3 and 0.5 ± 0.5 (-0.3-3.1) ng/m2 h, respectively. A clear diurnal variation of DGM concentrations and Hg0 flux was observed, presuming that temperature and light induced production of DGM was of significance in shallower waters.

T.P.1.30

HG ACCUMULATION AND HG STABLE ISOTOPE SIGNATURES IN DEEP SEA SEDIMENTS FROM THE SOUTH CHINA SEA

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Deep sea sediments are a terminal sink in the global Hg cycle. Hg burial rates and long-term patterns in accumulation are poorly constrained, yet necessary for understanding the global Hg budget and variations in Hg deposition throughout Earth history. In the modern Hg cycle, atmospheric inputs are the main source of Hg to pelagic ocean regions while rivers are a dominant source in coastal regions. Here we present Hg concentrations and isotopic composition for two deep sea sediment cores (Sites U1431 and U1433) retrieved 4300 m below sea level in the South China Sea during the International Ocean Discovery Program (IODP) expedition. The two profiles integrate the last 12 and 8 million years of sediment accumulation (including Pleistocene, Pliocene and part of the Miocene eras). Supporting data also include organic carbon accumulation and carbon isotope ratios (Δ13C). One core (site U1431) shows a shift in organic carbon origin (terrestrial/marine environments), as indicated by carbon isotope ratios. Terrestrial carbon inputs are generally associated with extremely low sediment Hg concentrations (median 3.3 ng g-1, n = 71, 12 to 8 Ma), while periods dominated by marine organic carbon burial show substantially higher Hg concentration (median 50 ng g-1, n = 37, since 8 Ma). Marine organic matter was the primary carbon source since 8 Ma at Site U1433 yet no clear trend in sediment Hg concentration was observed, despite variations from 17 to 100 ng g-1. In the contemporary era, terrestrial Hg inputs with negative δ202Hg and Δ199Hg and insignificant Δ200Hg are dominant in the estuarine environment, resulting in distinct Hg isotope signatures compared to offshore sediments integrating Hg from atmospheric Hg(lll) deposition with positive Δ199Hg and Δ200Hg. Additional Hg isotope analyses in the two deep sea sediment cores will be used to provide new information on past dynamics.

T.P.1.31

INVESTIGATING HG SPECIES BIOAVAILABILITY IN THE MINE-IMPACTED GULF OF TRIESTE (NORTHERN ADRIATIC)

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Bioaccumulation of sea-borne mercury species results in their biomagnification in marine food webs, often with detrimental effects to local ecosystems and increased exposure to humans. Gulf of Trieste has been under continuous 500 year-long Hg stress due to Hg mining in Idrija, Slovenia. 1.5 tons of Hg are annually still transported into the Gulf, deposited onto the sediment or distributed further towards Adriatic. Hg is prone to microbial methylation to monomethyl mercury (MeHg) in anoxic marine sediments during sulphate and metal reduction processes. The existence of its bioavailable species is a result of a complex biogeochemical transformations, as well as specifics of sources and sinks. To assess the lability and therefore bioavailability of Hg species, we applied for the first time Diffusive Gradients in Thin-films (DGT) technique in the water column and sediment in the Gulf of Trieste. Ratios of MeHg/THg in the water column and sediment porewaters ranged 10-75% and were much higher than previously observed values. Comparing our results with previously published labile Hg assessments (filtration and SnCl2 reduction) revealed that labile THg values coincided more for water column and less for sediment porewater. On the contrary, labile MeHg values assessed with these techniques were more similar in porewater than seawater.

In sediment porewater, labile THg and MeHg concentrations varied with depth (1-7 ng/L and 0.3-2.2 ng/L for THg and MeHg, respectively). MeHg concentrations were higher at previously determined depths of sulphate reduction. Variability in THg concentration were probably due to fractionation between solid and dissolved phase. Sediments appear to be a source of labile Hg species (1.13 ng/L and 0.78 ng/L for THg and MeHg, respectively) to the water column, facilitating complication and transport with organic matter and/or uptake into the lower food web. These species are only a small fraction of their total environmental amount yet may play one of the most important roles in the interaction with biota.

This work also shows that DGTs can provide valuable data on spatial and temporal variation in Hg bioavailability caused by global change-driven transitions of coastal areas. Such information will be key to support successful mitigation strategies to Hg toxicity in the future.

T.P.1.32

IMPACT OF METEOROLOGICAL CONDITIONS ON THE VARIABILITY OF LABILE PARTICULATE MERCURY IN RIVERS AND ITS INFLOW INTO THE SOUTHERN BALTIIC SEA

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The combustion of fossil fuel is a main source of mercury in the Baltic Sea coastal area. Despite the restrictions introduced to limit emissions, the decrease in mercury concentration in the environment is not proportional to the decrease in its emissions from anthropogenic sources. One of the reasons is the remobilization of Hg deposited on land. Mercury undergoes retention in the surface layers of the soil, rich in organic matter. The samples were taken seasonally and after intense precipitation in the years 2015-2017 from four rivers of the southern Baltic Sea (Puck Bay) catchment area: Reda, Zagórska Struga, Gidepka, Płutnica. The aim of the present study was to determine the impact of meteorological and hydrological phenomena on the riverine transport of bioavailable particulate mercury into the southern Baltic. The thermo-desorption method was used to determine the labile and stable mercury forms in suspended particulate matter (SPM). Due to conducted analysis, six periods were designated: heating, non-heating, drought, precipitation, downpours, thaws, during which the river suspended particulate matter was enriched with various forms of mercury. In a heating season, the river SPM adsorbed Hg (mainly bound with halogenides) was a dominant form. In addition, downpours and thaws intensified surface runoff, causing an increase in the share of this mercury form in SPM. In the non-heating season, the main form was the mercury absorbed inside organic matter. Whereas, droughts contributed to the formation of HgS in a large river and to the inflow of adsorbed Hg in smaller rivers. An increase of share of individual forms of Hg in river SPM in untypical periods caused an increase of labile mercury load introduced into the southern Baltic Sea.
T.P.1.33

REVIEW OF RECENT ADVANCES IN MERCURY RESEARCH: NEW INSIGHT INTO FACTORS CONTROLLING OCEAN MERCURY CYCLING

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From the first measurements of mercury in the ocean to high-resolution data produced by the international GEOTRACES program, this review discusses new insights from 30 years of oceanic mercury data. Analytical advancements and improvements in trace-metal clean sampling techniques have improved the quantity and quality of marine mercury data that now includes the Arctic, Atlantic, Pacific, and Southern Oceans. In seawater, mercury is found as gaseous elemental- or dimethyl-mercury, bound to ligands and particles, and as monomethyl-mercury, the neurotoxic compound that bioaccumulates in marine fish.

Cycling between these various chemical forms is mediated by abiotic and biotic reactions. Most mercury deposited to the ocean is reduced and a re-emitted to the atmosphere. Remaining mercury can be methylated in oxic seawater and low-oxygen regions of the water column where heterotrophic microorganisms are most active. Methylmercury correlates with proxies for heterotrophic activity in some studies, however, this trend is not consistent across multiple ocean basins. Genes homologous to hgcA (responsible for Hg methylation) have been found ever, this trend is not consistent across multiple ocean basins. Genes homologous to hgcA (responsible for Hg methylation) have been found.

Methylmercury is the most bioavailable form of mercury (Hg) in the environment. Uptake of MeHg into the marine food web is directly related to MeHg concentrations in the water column, which change spatially and temporally due to diverse number of sources and sinks. While there have been many studies in freshwater environments, there is still limited data on MeHg concentrations in the water column of the ocean. Recently, studies have been completed in the North Atlantic Ocean, South Atlantic Ocean, North Pacific Ocean and the South Pacific Ocean. These studies have showed a strong spatial variation of elevated MeHg in open ocean environments, and especially with depth. However, many of the recent studies have only focused on the surface waters, or water depths above 1500 m. The MeHg concentrations for deep water column is more rarely determined. In this study, which collected samples throughout the water column during the US GEOTRACEs GP15 cruise in the North and equatorial Pacific Ocean, which is from Seattle to Tahiti from Sept 18 to Nov 24, 2018. We measured total methylated Hg (i.e. the sum of MeHg and dimethylmercury, determined from acidified samples analyzed post-cruise). The data was used to further develop our understanding of the connections between the deep ocean and the surface ocean in terms of MeHg cycling, in both dissolved phase and particulate phase, based on our cruise GP15 and the results of others. The presentation will detail the results of the cruise and provide insights into the primary factors controlling the concentration of methylated Hg in the Pacific Ocean, and how that impacts human exposure.

T.P.1.35

DISTRIBUTION OF TOTAL DISSOLVED METHYLMERCURY ON PACIFIC: EVIDENCE FROM GP15

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Monomethylmercury (MeHg) is the most bioavailable form of mercury (Hg) in the environment. Uptake of MeHg into the marine food web is directly related to MeHg concentrations in the water column, which change spatially and temporally due to diverse number of sources and sinks. While there have been many studies in freshwater environments, there is still limited data on MeHg concentrations in the water column of the ocean. Recently, studies have been completed in the North Atlantic Ocean, South Atlantic Ocean, North Pacific Ocean and the South Pacific Ocean. These studies have showed a strong spatial variation of elevated MeHg in open ocean environments, and especially with depth. However, many of the recent studies have only focused on the surface waters, or water depths above 1500 m. The MeHg concentrations for deep water column is more rarely determined. In this study, which collected samples throughout the water column during the US GEOTRACEs GP15 cruise in the North and equatorial Pacific Ocean, which is from Seattle to Tahiti from Sept 18 to Nov 24, 2018. We measured total methylated Hg (i.e. the sum of MeHg and dimethylmercury, determined from acidified samples analyzed post-cruise). The data was used to further develop our understanding of the connections between the deep ocean and the surface ocean in terms of MeHg cycling, in both dissolved phase and particulate phase, based on our cruise GP15 and the results of others. The presentation will detail the results of the cruise and provide insights into the primary factors controlling the concentration of methylated Hg in the Pacific Ocean, and how that impacts human exposure.

T.P.1.34

SPATIAL DIFFERENCES AND FORAGING PATTERNS INFLUENCE MERCURY EXPOSURE IN A DECLINING SEABIRD IN ATLANTIC CANADA: LEACH’S STORM-PETREL

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Leach’s storm-petrel (Oceanodroma leucorhoa = Hydrobates leucorhoa) is a small seabird species that was listed as globally vulnerable on the IUCN’s Red List of Threatened Species in 2016. Breeding populations have declined more than 30% over the last three generations in Atlantic Canada. Elevated mercury exposure may be contributing to this species’ decline. To assess this possibility, we measured mercury concentrations and stable carbon, nitrogen and sulphur isotope ratios in the eggs and blood of adult Leach’s storm-petrels at five breeding colonies across Atlantic Canada. Eggs were collected soon after laying in 2016, 2017 and 2018. Blood was collected from incubating adults (in different nesting burrows from the egg collections) about a month later. We also collected blood from incubating adults whose foraging movements during incubation were tracked using GPS tags. We measured total mercury and stable carbon (δ13C), nitrogen (δ15N) and sulphur (δ34S) isotope ratios in egg contents and whole blood. Geometric mean mercury concentrations in the blood of adult Leach’s storm-petrels were significantly greater at two colonies around Newfoundland (Baccalieu & Gull Islands, NL) than at three colonies in the Bay of Fundy and Scotian Shelf (Country Island & Bon Portage Islands, NS and Kent Island, NB). A slightly different spatial pattern emerged from the storm-petrel eggs, where the geometric mean mercury concentrations were significantly greater at three colonies (Baccalieu, Gull & Bon Portage Islands) than at Kent Island in the Bay of Fundy. Nevertheless, the geometric mean blood and egg mercury concentrations at each colony were highly correlated.

T.P.1.36

VERTICAL PROFILES OF DISSOLVED HG SPECIES IN THE WESTERN PART OF SUB-ARCTIC NORTH PACIFIC

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It is well known that methylmercury (MeHg) intake into humans and wild animals are mainly caused by fish consumption. In addition, sea
surface is one of the main contributors for atmospheric mercury (Hg). Understanding on chemical reactions of Hg including the methylation and transformation project in marine environment is extremely important for evaluating the air-sea exchange of Hg and bio-accumulation of MeHg in fishes. However, mercury speciation and distribution in the global ocean is poorly understood. In this study, we determined total, methyl- and gaseous Hg concentrations in the dissolved phase of seawater samples from 2014-2020, project #R013 DAIMON, and supported with co-financed project W81/INTERREG BSR/2016.

The research work was fund by the Ministry of Science and Higher Education from the 2016-2020, project #R013 DAIMON, and supported with co-financed project W81/INTERREG BSR/2016.

The research work was fund by the Institute of Oceanology of the Polish Academy of Sciences (statutory task no. II. 2).

T.P.1.38
CLIMATE AS A MASTER DRIVER OF UNUSUAL HIGH Hg ACCUMULATION IN ANTARCTIC AQUATIC SEDIMENTS

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The importance of natural processes on the accumulation of mercury (Hg) through time has been recently demonstrated by two different sedimentary records (lake and marine diatom ooze sediments) from maritime Antarctica. The Hg accumulation records of the two systems reveal unexpected similarities during the past 1000 years. Due to the different nature of the sediments and the distance between the locations (ca. 5500 km), we postulate that a regional climatic systems and their changes across time may be the main driver. Lake Limnopol is a small, ultra-oligotrophic lake located on Livingston Island (South Shetland Islands) near the tip of the Antarctic Peninsula. Here a combination of different processes (volcanic activity and lake ice freezing-thawing) explains uniquely high Hg accumulations in the sediments (up to 4900 μg m⁻² yr⁻¹). On the other hand, the Adélie Basin core (continental shelf off the coast of Wilkes Land) was collected in an oceanic environment that exhibits high primary productivity primarily driven by diatoms. In this area, diatom blooms and related biomass sedimentation appear to act as a vector for rapid Hg transport and deposition to sediments sequestration, assumingly through water phase Hg scavenging of atmospheric Hg taken up by the ocean. Thus, the diatom ooze (biogenic pelagic sediments which contain more than 30% diatom remains) record obtained from Adélie Basin exhibits the highest Hg accumulation rates ever reported for marine sediments (up to 1800 μg m⁻² yr⁻¹). Despite the obvious differences between the records, both share common trends over time; Hg accumulation rates fluctuate simultaneously in both systems. It is not clear what mechanism is behind the similarities between both sedimentary records, but climate shifts seem to be the most likely cause. The melting of the lake and an increase in productivity under warmer conditions and higher irradiance in the water column could have occurred. Similarly, the sensitivity of the Adélie Basin site to the sea ice extent means the effect of climate on this record can also not be ruled out. Understanding the role of the Hg dissolution equilibrium between the atmosphere and the water columns, algae scavenging, and how climate affects these processes might be key to better understanding these unique sedimentation rates as well as improving our knowledge of Hg cycling in aquatic systems in general.

T.P.1.40
LABILE AND STABLE MERCURY IN A NON-NATIVE HARRIS MUD CRAB (RHITHROPOANEUS HARRISII) FROM THE SOUTHERN BALTIC SEA

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Within the past few decades a new species of crab has appeared in the food web of the southern Baltic Sea region; Rhithropanopeus harrisi. The aim of the present study was to estimate the level of total, labile and stable mercury concentrations in this species collected from the southern Baltic Sea (Puck Bay, Poland) in July 2015. Analyses of the concentrations of total mercury and its forms were performed using the thermodesorption method where the risk of contamination is reduced. The concentrations of both total mercury and its particular forms did not differ statistically significant between males and females. The concentration of total mercury in the tested crab was at a low level (median 25 ng g⁻¹ sm), organic mercury accounted for 67% of this. The share of this mercury fraction, as well as the Hgtot, increased with the size class of the crabs. An increase in the concentration of mercury bound mainly with halides along with the width of the carapace was
observed only up to size class 6 (12.4-14.4 mm). That was probably due to the intense consumption of microalgae which supply mineral substances needed to build the carapace during growth and molting. Older (larger) crabs become more predatory and this resulted in an increase in their share of organic mercury. In larger individuals, the share of stable forms of mercury increased, and the fraction of labile mercury bound with halides decreased, which may indicate an increase in the mechanism that purifies the body from toxic Hg. Due to the increasing-ly common occurrence of R. harrisi in the Gulf of Gdańsk region and the low HgTOT concentration in its body, and assuming that it is bound to become a more and more common component of the diet of fish, it can be supposed that the load of toxic mercury entering the trophic network in the studied area is likely to decrease.

T.P.1.41

METHYLMERCURY: A NEW TRACER FOR THE REMINERALIZATION OF ORGANIC MATTER?

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Grasping how the carbon cycle works is a fundamental step in understanding climate change we are facing. One of the key processes of the carbon cycle is the microbial remineralization of organic matter in the ocean. Surface ocean primary production takes up nutrients while generating oxygen. In counterpart, microbes feeding on sinking organic matter consume oxygen and release nutrients back into the water column, a process called remineralization. The importance of this process in the drawdown of atmospheric carbon is well known, but remains ill-constrained. To quantify this process, excess Barium (Baxs) is typically used as a tracer, even though the usefulness of barium in biological activities is not yet well understood. We use data from the 2017 PEACETIME and 2014 GEOVIDE GEOTRACES cruises to explore how methy mercury (MeHg) produced along the water column could be used as a complementary remineralization tracer. The application of the Baxs tracer requires the measurements of other elements like aluminium and oxygen values. That is why we try to develop MeHg as a complementary tracer to better understand the remineralization processes. For this presentation both barium and MeHg were studied and compared as tracers of remineralization. The results are complemented by preliminary campaigns of the MERTOX project in the northwestern Mediterranean. The objective of this project is to understand mercury methylation phenomena in marine ecosystems based on the OMZ study in Peru. Future campaigns may provide additional information to the GEOTRACES data.

T.P.1.43

PRELIMINARY RESULTS FROM THE MERMEX/HIPPOCAMPE CRUISE TO THE WESTERN MEDITERRANEAN SEA: DISTRIBUTION OF MERCURY CHEMICAL SPECIES IN THEIR DISSOLVED AND PARTICULATE FORMS.

KNOERY, Joel1; THOMAS, Bastien2; BANARU, Daniela2; HEIMBURGER-EROBAVIDA, Lars-Eric2; CHIFFLET, Sandrine2; THE HIPPOCAMPE, Scientific Party

Within the framework of the French Mermex programme, the Hippecampe cruise will have sailed between northern and southern banks of the Mediterranean Sea in April/May 2019. The R/V Antéa and her companions will have occupied twenty or so stations will have been occupied. Mercury levels and speciation will be investigated in the water column, suspended matter, and in its planktonic compartments. Preliminary data aiming at describing the mercury transfer pathways will be presented. The different marine ecosystems traversed in 2019 will be compared and contrasted, as well as contrasted with homologous, earlier data produced during the GMOS project.

The presentation will thus focus on the scientific framework of the project, the mercury shipboard data, and initial laboratory data from the Hippecampe cruise.

T.P.1.42

BEACH WRACK AS THE VECTOR FOR MERCURY CONTAMINATION IN COASTAL ENVIRONMENT.

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Coastal and estuarine ecosystems have been, and still are, heavily influenced by the human species through pollution and habitat loss throughout the world. Substantial amount of pollution in the coastal zone comes from the remobilization from sediments, contaminated by uncontrolled discharges in second half of XX century. Therefore not only coastal but also basin fluxes can transport contamination, but also marine to terrestrial fluxes can be observed. One example is the beach wrack – decaying plant and algae material deposited on the coast due to currents and storms. Algae accumulate mercury form the seawater, while marine plants in addition accumulate this metal also from sediments via root systems.

The urbanisation of the coastal zone has contributed to a rise in Hg concentration in macroalgae. Surface run-off entering bays together with the Mediterranean rainwater from sources such as storm drains, has led to higher mercury concentrations in Cladophora sp. in such areas in comparison with areas located further away. Among macroalgae, those which accumulated Hg the most effectively in the Southern Baltic were brown and red algae, a finding related to the chemical composition and construction of the cell wall of the thallus. The inflow of pollutants from river drainage areas also contributed to an increase in the concentrations of this metal in vascular plants, notably Zostera marina. Suspended particulate matter introduced to the sea via rivers, particularly in bays, was deposited close to the shore and became a source of Hg entering pore water and, in turn, vascular plants. Additionally, the capacity of vascular plants to accumulate chemical substances from pore water led to the accumulation of historical mercury deposits in the sediments. As a result, Potamogeton pectinatus demonstrated a biaccumulation factor 60 % higher than that of Furcellaria lumbricalis. After deposition on the beach, plant material decomposes, and mercury contained in it is released to the coastal zone. This may lead to the enhanced mercury bioavailability, elevated concentration in life abundant coastal waters, and also transfer of this metal to organisms living on the beach. Analysis of beach sediments collected bi monthly in 2019 show elevated mercury concentration in areas where beach wrack is present in comparison to exposed sand, which indicates potential impact of decaying macrophyto benthos on the coastal ecosystem.
LOCAL AND STABLE FORMS OF MERCURY IN THE SUSPENDED PARTICULATE MATTER AND SURFACE SEDIMENTS OF THE BALTIC SEA

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Mercury (Hg) is one of the most dangerous environmental global pollutants. It is especially related to its toxicity which is dependent on the chemical form. Labile mercury fractions can be easily adsorbed or absorbed by an organism, while stable fractions are biologically unavailable. Even low labile mercury concentrations in the organism can lead to irreversible damage to the brain and nervous system, as well as to the disruption of hormonal and enzymatic reactions.

The Baltic Sea is a semi-enclosed, inland sea with a limited water exchange with the North Sea. Due to that fact the river inflow is the main source of mercury in this region (with dominant share of particulate mercury). The pollutants, including Hg, which enter the Baltic Sea basin are deposited in the surface sediments. It is estimated that over 50% of Hg in the sediments can be reintroduced into the water column due to the resuspension and diffusion processes. What is more, the sediments are inhabited by benthic flora and fauna which can accumulate Hg in their tissues and transfer it to the higher trophic levels. Owing to that fact it is crucial to investigate the labile and stable forms of mercury in the surface sediments.

Study was conducted in years 2016-2017 in different regions of the Baltic Sea (i.e. Baltic Proper, Bothnian Bay and Bornholm Basin). Surface sediments (top 5 cm) were collected using van Veen grab sampler. Samples of suspended particulate matter were obtained by filtering collected water through 0.7 μm Whatman GF/F microfiber filters. Total mercury concentration and mercury fractions in surface sediments and suspended particulate matter were analyzed using the 5-steppermodesorption method on DMA-80 analyzer.

Both total mercury concentrations and percentage share of distinguished labile and stable fractions in suspended particulate matter and bottom sediments differed geographically and depended on ecological-dynamic conditions of the near-bottom zone. Additionally, in the case of suspended particulate matter, mercury level and the percentage share of its forms varied also in the water column. In the case of surface sediments it also depended on the type of sea bottom (including grain size and organic matter content). What is important, over a half of total mercury in the sediments was in the labile, bioavailable form, that can easily enter the marine trophic chain.

POSSIBILITY OF MERCURY TRANSLOCATION FROM CONTAMINATED SEDIMENT RESUSPENSION DURING DECOMMISSIONING

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Mercury is a common contaminant which can be found naturally in subsea reservoir of the Gulf of Thailand. During the petroleum drilling, the drilling fluid will convey mercury from the petroleum reservoir to the surface with drill cuttings. Then the cuttings contaminated with mercury will be returned to the sea and deposited in the vicinity of wells. Mercury can be strongly adsorbed by organic matter and onto particulate matters during deposition. During diagenesis, the formation of mercury-sulfur complexes in sediment makes mercury become less mobile. One of the most concerns during decommissioning execution of the platform, i.e. lifting jacket structure, is transformation of mercury to be more toxic species. Here, we studied sediment re-deposition rate and recovery period after resuspension of contaminated sediment. The results revealed that the stirring up sediment decreased rapidly in the first 30 minutes, and the level of suspended solids was reduced to the same as background level within 10 hours. Dissolved organic carbon (DOC) in seawater was increased to 3.9 – 6.7 mg/L, and remaining constantly throughout the study. Dissolved total mercury (T-Hg) in seawater declined dramatically within 5 minutes after resuspension, from 330 ± 30 to 25 ± 7.5 ng/L (same level as control set), whereas reactive mercury was less than 0.5 ng/L at all times. For particulate mercury, it was found similar to the suspended solid. The concentration of particulate mercury decreased from 2642 ± 291 µg/L to 177 ± 33, 102 ± 12, 52 ± 2.4, 27 ± 0.4 and 25 ± 2.4 µg/L at 5, 10, 20, 45 and 60 minutes, respectively. The level of dissolved T-Hg was higher than ambient level (<0.5 ng/L) is probably due to the increasing of DOC from resuspension event. From the results, after lifting jacket we would suggest “to leave sediment in situ without further disturbance” as one of contaminated sediment management options for decommissioning.

METHYLMERCURY BIOAVAILABILITY AND PELAGIC FOOD WEB STRUCTURE AFFECT ITS BIOACCUMULATION IN COASTAL SEAS – A BALTIC SEA CASE STUDY

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Mercury is a common contaminant which can be found naturally in subsea reservoir of the Gulf of Thailand. During the petroleum drilling, the drilling fluid will convey mercury from the petroleum reservoir to the surface with drill cuttings. Then the cuttings contaminated with mercury will be returned to the sea and deposited in the vicinity of wells. Mercury can be strongly adsorbed by organic matter and onto particulate matters during deposition. During diagenesis, the formation of mercury-sulfur complexes in sediment makes mercury become less mobile. One of the most concerns during decommissioning execution of the platform, i.e. lifting jacket structure, is transformation of mercury to be more toxic species. Here, we studied sediment re-deposition rate and recovery period after resuspension of contaminated sediment. The results revealed that the stirring up sediment decreased rapidly in the first 30 minutes, and the level of suspended solids was reduced to the same as background level within 10 hours. Dissolved organic carbon (DOC) in seawater was increased to 3.9 – 6.7 mg/L, and remaining constantly throughout the study. Dissolved total mercury (T-Hg) in seawater declined dramatically within 5 minutes after resuspension, from 330 ± 30 to 25 ± 7.5 ng/L (same level as control set), whereas reactive mercury was less than 0.5 ng/L at all times. For particulate mercury, it was found similar to the suspended solid. The concentration of particulate mercury decreased from 2642 ± 291 µg/L to 177 ± 33, 102 ± 12, 52 ± 2.4, 27 ± 0.4 and 25 ± 2.4 µg/L at 5, 10, 20, 45 and 60 minutes, respectively. The level of dissolved T-Hg was higher than ambient level (<0.5 ng/L) is probably due to the increasing of DOC from resuspension event. From the results, after lifting jacket we would suggest “to leave sediment in situ without further disturbance” as one of contaminated sediment management options for decommissioning.
THE BIOGEOCHEMISTRY OF MERCURY IN THE BAR- ENTS SEA

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In the Arctic region, the bioaccumulation of toxic methylmercury (MeHg) in marine biota remains a major problem for both human and ecosystem health. Studies on biogeochemical cycling of mercury in the Arctic Ocean suggest biological methylation and uptake of mercury in the shallow mixed layer, but important regional and seasonal knowl- edge of marine mercury cycling remains limited and incomplete. While MeHg bioaccumulation in Barents Sea (BS) aquatic organisms has been documented, no knowledge about in situ concentrations of mercury speciation nor its transformation in this climate vulnerable region has been published. Affected by climate change, shifts in the BS water mass mixing, variable ice cover, and seasonal primary productivity suggest changes to mercury biogeochemical cycling and dynamics. Therefore, determining seasonal levels and water column methylation of mercury in the BS is crucial for understanding both MeHg bioaccumulation and for evaluating climate change’s impact on mercury in the Arctic. In association with the Nansen Legacy project, unfiltered samples for total mercury (THg) and MeHg were taken from two stations with a trace-metal clean GO FLO bottle sampling system during the August 2018 cruise. Unpreserved THg samples were analyzed by CVAFS on a custom gold trap setup at the Mediterranean Institute of Oceanography. Preserved MeHg samples were organically extracted after propagation and will be analyzed by GC-ID-ICP-MS. THg surface levels (10-40m depth) of 0.97±0.17pM and 0.94±0.11pM were measured in the Nansen Basin (NB) (83.33°N, 31.53°E) and the Northern Bar- ents Sea (NBS) (79.75°N, 33.99°E), respectively. At the pycnocline (90-200m depth), THg concentrations decreased to 0.62±0.09pM and 0.55±0.10pM in the NB and NBS, respectively. For the future, mercury speciation measurements will be taken from the Barents Sea water column in all seasons and sediment samples will be collected. Measurements will be analyzed primarily by CVAFS or by GC-ID-ICP-MS. In addition, enriched mercury isotope incubations will be used to determine rates of methylation and demethylation in the Barents Sea water column in the shallow mixed layer and pycnocline. The samples collected at the water column depths will be compared to previous studies in the Central Arctic Ocean and the Canadian Arctic Archipelago to evaluate at which depths biological methylation primarily takes place in the Barents Sea. Water and sediment samples will be combined with physical oceanography knowledge to create a clearer picture of Hg biogeochemistry in the BS.

T.P.1.47

DOES THE MATERNAL TRANSFER OF MERCURY POS- ES A THREAT TO A GREY SEAL PUP?

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Maternal transfer of toxic substances (through the placenta during gestation or with milk during lactation) may lead to variety of adverse effects and is considered as particularly dangerous as it affects mammalian offspring in the early stages of life when their immune system is not fully developed.

In the Baltic grey seal (Halichoreres grypus grypus; Fabricius, 1791) population, the highest mortality is observed among grey seal pups. Therefore, it can be assumed that juvenile individuals are extremely sensitive to changes occurring in the environment. As a consequence, their condition and health in the first period of life may have a key impact on their future fate. The aim of the study was to investigate whether the mercury obtained through the maternal transfer poses a threat to a grey seal pup or if the natural development of a newborn grey seal during the first few months may introduce mechanisms for decreasing its mercury body burden.

The research was conducted in cooperation with Professor Krzysztof Skóra’s Hel Marine Station (Institute of Oceanography, University of Gdańsk), the facility which deals with reintroduction of the grey seal into the southern Baltic Sea. Presented poster summarizes four-year-long experiment during which 12 grey seal pups were born at the Station. Approximately three-month stay at the station runs in accordance with natural processes which newborn seals undergo in the wild. Pups were first fed by mothers then they went through the postweaning fast to start finally independent life eating fish. The material for chemical analyses included pups’ blood, fur (neonatal fur and new pelage) and excrements. Additionally, samples of food (milk as well as fish) were collected. Concentration of total mercury (HgTOT) was measured using an AMA 254 atomic absorption spectrometer. Methyl mercury (MeHg) was analyzed using atomic fluorescence spectroscopy after prior separation on a chromatographic column using MERX-M analyzer.

The study examined the changes in mercury concentration during first three months of grey seal’s life and showed how juvenile seals can deal with mercury that is transferred to their bodies during foetal development and nursing. In conclusion it can be said that natural development provides mechanisms which can effectively protect pups against mercury toxicity.

T.P.1.48

TOTAL MERCURY IN SEAWATER AND SEDIMENTS OF SARONIKOS GULF, GREECE

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Saronikos gulf is the marine area adjacent to the city of Athens. To the north on the coastline of the relatively enclosed Elefsis bay various types of industries began operation in the early 1900’s and industrial activity peaked from 1960 to 1990. Currently the industrial activities include shipyards, oil refineries, cement production plants and various smaller units (chemicals, oil products storage etc.). Apart from the industrial zone other activities also add to the Hg load. The population of urban centres around Saronikos (Athens, Piraeus, suburbs) is estimated to be around 3 million. There are two waste water treatment plants, Psitalia and Thirasio, discharging treated effluents in Saronikos and Elefsis bay respectively; there is increased atmospheric pollution due to vehicle traffic and household heating and finally increased ship traffic since Piraeus is the largest port of Greece. As part of on-going monitoring representative seawater and sediments samples from Saronikos were collected in 2017. The measurements for total Hg in seawater and sediments will be presented in comparison to data from previous studies and quality guidelines. Total Hg in seawater was examined in two periods of 2017 (March, September / October), in Elefsis Bay and Inner - Outer Saronikos. Sea- water samples were collected and analysed according to EPA method 1631 using a Tekran 2500 CVFAS Detector. The sediment samples were frozen after collection, then freeze-dried and sieved for the separation of the silt-clay and sand fractions. The total metal contents Hg were extracted via digestion with concentrated nitric acid in closed
Teflon cups. Hg concentrations were measured by Cold Vapour Atomic Adsorption Spectrometry (VGA 77 generator - Varian SpectraA 200). All total Hg concentrations in seawater samples were lower than 70ng/L (maximum allowable concentration in coastal waters under EU 2013/39). We have observed a slight decrease of Hg concentrations in Saronikos Gulf compared to previous data. The total Hg levels of sediments decrease from the more polluted Elefsis bay and Inner Saronikos to the Outer gulf. In the two most affected stations Hg exceeded both the ERL and ERM sediment guidelines and in a few other stations the ERL limit therefore toxic effects to biota are plausible.

The Hg pollution status of Saronikos Gulf is not very alarming but due to the multitude of polluting activities and in line with the implementation of EU Water Framework Directive and Marine Strategy Framework Directive monitoring efforts in Saronikos gulf and Elefsis bay are continuing.

T.P.1.50

FACTORS AFFECTING THE TRANSFORMATION OF HG IN THE COASTAL ZONE IN THE VICINITY OF RIVER MOUTH (SOUTHERN BALTIC SEA)

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In coastal areas, rivers are the main source of mercury. Hg of riverine origin only in a small part reaches the open water of the sea, most of it accumulates in the coastal zone and estuaries near the river mouth. Therefore, the coastal areas are particularly vulnerable to mercury contamination, where this metal accumulates and biomagnifies in the trophic chain, creating a real threat to human health. The aim of this research was to determine the main factors that affect the Hg transformation in the coastal zone and its transport to the open sea and sediments. The research was conducted in 2016 at the mouth of two rivers: Vistula and Reda (southern Baltic Sea). The Hg concentration were measured in water, SPM and sediment taken from stations at different distances from the river mouths. The obtained results show that river mouths are a specific environment in which the mixing of waters with different chemical composition, density and temperature occurs. The mixing of water masses results in a decrease in concentration of total and particulate mercury in seawater along with the distance from the river mouth. This is because the ‘dilution’ of the Hg-rich material washed off from land by the particulate matter of marine origin. In the river mouth, the concentration of mercury is also dependent on the distribution of the suspended particulate matter. It has been observed that with the increase in salinity, the concentration of dissolved mercury decreases and the concentration of particulate mercury increases. This could be a consequence of the decrease in the concentration of mercury complexing ligands, resulting in adsorption of dissolved metal on the particles and flocculation of organic colloids with the possible transformation of dissolved forms into larger aggregates. Also primary production was important factor affecting the transformation of mercury in the coastal zone.

T.P.1.51

MERCURY FORMS IN THE BENTHIC FOOD WEB OF A TEMPERATE COASTAL LAGOON (SOUTHERN BALTIC SEA)

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Mercury (Hg) is one of the most toxic elements - it leads to irreversible damage of the brain and the nervous system. Hg is introduced into the human body mainly via the consumption of fish and seafood - hence, it is particularly important to determine the processes that condition the trophodynamic of Hg in the marine environment. The study was carried out in the coastal zone of the Puck Lagoon (southern Baltic Sea). The research material, collected in the summer of 2017, consisted of macrozoobenthic organisms and elements of their diet - suspended matter, surface sediments and macrophytobenthos. The samples were analysed for total Hg concentration (HgTOT) and for Hg fractions, using the five-step thermodesorption method. The results showed that the level of HgTOT in zoobenthic organisms was associated with dietary preferences of individual species and the share of bioavailable Hg in their food. The Hg fractionation in the macrofauna was conditioned by biological features (morphological structure) and environmental parameters (oxygenation, pH) which shape the mobility and assimilation of Hg. Larger body surface of organisms was conducive to the adsorption of the most labile Hg compounds. The absorption of the most dangerous organic Hg forms in macrofauna was more effective in aerobic conditions, at low primary production and with limited inflow of organic matter. The above factors also influenced the increase of Hg bioavailability in sediments. The trophic transfer of Hg in the Puck Lagoon in the summer season was about twice as large as the global average - the Hg concentration increased up to four times on each subsequent trophic level. The increase in Hg transfer in the food chain was favoured by the limited biomass of primary producers, and consequently of zoobenthos. An important factor influencing the biomagnification process was also the share of labile Hg in macrozoobenthos.

T.P.1.52

THE NEW WORKPLACE HAZARD – MERCURY VAPOUR AND AEROSOLS AS A RESULT OF THERMAL-GENERATING MECHANICS, APPLICATIONS & MAINTENANCE WORKS

HUNTER, Lee

Even though it is just a ‘metal’, in industries where Mercury is a naturally occurring contaminant or even a required process component its dynamic and phenomenal cyclic characteristics are still not widely known or fully understood.

Global industry continues to drive forward with production, research, development, adaptation, mitigation, treatment and disposal of mercury, mercury compounds and mercury-contaminated products, but there are still large areas of the industrial process that have yet to be fully or properly addressed, although it could be argued that is mainly due to it being directly related to end-of-life on the process and containment infrastructure. The issue... is carbon steel.

Carbon steel acts as a scavenger, capturing any mercury and mercury compounds from within process streams and retaining it, in various conditions, along the surface of the steel, within layers of corrosion, areas of deposition and within the surface matrix of the steel substrate. In particular, Mercury contamination can cause problems to offshore processing platforms and other downstream hydrocarbon production facilities, as well as the intermediate infrastructure. The Oil & Gas industry is aware of the cycle phenomenon whereby Mercury is absorbed into the surface matrix of carbon steel pipelines during the process and transportation of contaminated hydrocarbon mediums and its subsequent ability to desorb back out from the steel surface and return to those same, or new uncontaminated, streams. However, the fate of the carbon steel pipelines, vessels and equipment falls under further limitations with lengthy, costly and typically unverifiable results... until now!

As a growing concern among operators and companies around the world the decommissioning, disassembly and disposal of contaminated assets, subsea pipelines, platforms and refineries has always had its limits with current legislation, and most commercial applications, only dealing with the decontamination of free (adsorbed) Mercury from system internals prior to its decommissioning.

It is now possible to fully remove mercury from the surface matrix of carbon steel, in a repeatable manner, which ensures that the decontaminated carbon steel sections meet the strict acceptance criteria for recycling purposes using a licensed steel smelter.
Understanding the contaminant and how it behaves under certain conditions has been key to developing a selection of decontamination methods and applications that can now be applied quickly and methodically in remote locations as well as sensitive and dynamic environments while also providing flexibility and certainty to meet limited, but licensed, final waste disposal routes and best practices.

T.P.1.53

HG Δ202 ANALYSIS CAN REVEAL HG ACCUMULATION WITH CHANGES IN FOOD SOURCES AND HG METABOLISM BY ISOTOPE ANALYSIS IN A POD OF LONG-FINNED PILOT WHALES

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Mercury (Hg) is a toxic heavy metal which is globally distributed through the atmosphere, in which Hg has a residence time of up to 1 year. Atmospheric Hg is predominantly deposited in oceans, one of the major reservoirs of Hg on Earth. In aquatic environments, inorganic Hg species are converted into the more toxic compound methylmercury (MeHg). This conversion proceeds via biotic or abiotic methylation, occurring in sediment and/or in the water column. MeHg exposure of aquatic biota occurs mainly via the diet, resulting in the bioaccumulation and biomagnification of MeHg across food web, leading to high Hg levels in predatory animals.

Whales accumulate mercury (Hg), but do not seem to show evidence of toxic effects. Analysis of different tissues (liver, kidney, muscle) and biofluids (blood, milk) from a pod of stranded long-finned pilot whales (Globicephala melas) showed accumulation of Hg as a function of age, with significant decrease in the MeHg fractions. Isotopic analysis revealed differences between juvenile and adult whales. During the first period of life, Hg in liver became isotopically lighter (Δ202Hg decreased) with strongly decreasing methylmercury (MeHg) fraction. We suggest this is due to preferential demethylation of the lighter Hg isotopes and transport of Hg to less sensitive organs, such as muscles. Also changes in diet, with high MeHg intake in utero and during lactation, followed by increasing consumption of solid food contributes to this behavior. Interestingly, this trend in Δ202Hg is reversed for livers of adult whales (increasing Δ202Hg value), which is accompanied by a progressive decrease of Δ202Hg in muscle at older ages. These total Hg (THg) isotopic trends suggest changes in the Hg metabolism of the whales and development of (a) detoxification mechanisms (e.g., formation of HgSe particles), and a Hg redistribution within the different organs of long-finned pilot whales.

Literature:

T.P.1.54

CONCENTRATION OF TOTAL MERCURY AND SELENIUM IN BROWN BOOBIE (SULA LEUCOGASTER) FEATHERS FROM THE BRAZILIAN COAST

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The marine environment is the final destination of anthropic pollutants, which can accumulate in the biota. Among these pollutants, trace elements generate concern for their persistence and toxicity. In this way, we highlight mercury because its biomagnification potential and selenium, which although essential, can be toxic at high concentrations. Therefore, the use of long-lived and high trophic position sentinels, such as seabirds, is important for monitoring marine areas around the world. Therefore, this pioneer study aims to evaluate the exposure of brown boobie (Sula leucogaster) to total mercury and selenium in different islands of the Brazilian coast. Wing feathers were collected in 2015 in the archipelagos of São Pedro and São Paulo (SPSP; 987 km of the coast, nMale=10, nFemale=3), Abrolhos (AB; 65 km, nMale=5, nFemale=6) and Cagarras (IC; 4 km, nMale=5, nFemale=4). The determination of Hg was made by cold vapor generation atomic absorption spectrometry (FIMS-400) and Se by graphite furnace atomic absorption spectrometry (GFAAS). Concentrations (μg·kg⁻¹, dry weight, mean±SD) of total Hg in AB (6368.2±2912.7) were significantly higher (p=0.02) than in SPSP (4210.9±1405.8), and Hg values in IC (2753±1206) were significantly lower than AB and SPSP. Regarding Se concentrations, a significant difference (p<0.001) was observed between males (3570.7±942.3) and females (8681.2±144.5) nesting in AB. Regarding Se, concentrations in IC (1700±565.6) were significantly lower. Females (3096±391.7) in SPSP had significantly higher concentrations of Se (p=0.003) than males (2320±305.7). The molar ratio of Se and Hg in SPSP was 1.66±0.58, 1.09±0.76 for AB and 2.66±1.80 for IC. Selenium is recognized for being involved in detoxification processes of Hg, however, the observed results suggest that this process does not occur in the specie in question. The differences between the genders can be correlated with the fact that the female is bigger than the male, and may be diving deeper than the males, having access to prey items that the males does not have. Despite being closer to the coast, Hg concentrations in IC were lower, which could be explained by the presence of more suspended solids in Guanabara Bay, decreasing the availability of Hg to the biota. The concentrations of Hg in the present study are high when compared to birds from other parts of the globe. However, Se concentrations of the present study appear to pose no risk to birds. Understanding the sources of Hg and Se along the Brazilian coast is necessary to better interpret our results.

T.P.1.55

SOUTH POLAR SKUA AS A MONITOR OF MERCURY IN ANTARCTIC ENVIRONMENT

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Antarctica is one of the last remote regions of the planet but the growth of tourism and scientific activities in the region, besides contamination on a global scale can increase the contaminants levels even in these pristine areas. Thus, understanding the role of migratory birds such as the south polar skua (Stercorarius maccormicki) in the transport of contaminants is important for studies of environmental contamination in remote areas. Among the global contaminants, we highlight mercury (Hg) due to its toxicity and biomagnification potential. Skuas are in the top of food chain and long-lived, thus they are susceptible to the accumulation of this metal. This study aimed to measure Hg concentration in total blood, a non-lethal sampling method, of the south polar skua from Admiralty Bay, southeast coast of King George Island, Antarctica. Whole blood (n=19; 9 female and 10 males) was collected in the Antarctic summer of 2013-2014, with a disposable syringe and stored in the 1.0 ml eppendorf. Mercury was quantified by cold vapor generation atomic absorption spectrometry (FIMS-400, Perking-Elmer). All analyses were performed at the Radioisotope Laboratory Eduardo Penna Franca at Federal University of Rio de Janeiro. The concentrations (μg·kg⁻¹, dry weight, mean±SD) of total Hg were 2962±891 and 3245±1463 in females and males respectively. Besides being usually reported lower levels of mercury in females, due to egg laying, in this study concentrations of Hg in blood were not signific
icantly different between males and females. Blood is a metabolically active matrix, which represents recent exposure and/or remobilization of contaminants from internal tissues. The levels observed probably reflect the diet of the past days/weeks prior to sampling, what makes difficult to see potential differences, given the similarity of the diet between the genders. Comparing to other studies, lower levels were observed for blood cells in Antarctic skua chicks (511± 100 μg.kg-1, dry weight, mean ± SD; Carravieri et al. 2017, Environ Pollut. 228, 464-473), which could indicate a bioaccumulative potential of mercury for this specie. Studies integrating other matrices such as feathers and faeces are important for a better understanding of the toxicokinetics in Antarctic birds and its interactions of the environment.

T.P.1.56

MERCURY IN AQUATIC SYSTEMS OF NAHUEL HUA-PI NATIONAL PARK: A NATURAL BIOGEOCHEMICAL HOTSPOT IN NORTHERN PATAGONIA

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Nahuel Huapi National Park (NHPN) includes many freshwater oligotrophic ecosystems born in the Andes that are the main water source for the vast arid stretch of Northeastern Patagonia which holds most human settlements and activities of the region. In headwater catchments several investigations have reported moderate to high Hg levels in lake sediments, aquatic biota and terrestrial bioindicators, attributing them to long and short range atmospheric transport, volcanic activity in the Andes and biomass burning. The sharp W-E orographic precipita-

T.P.1.57

MARINE SPONGES AS BIOMONITORS OF HG POLLUTION: NEW INSIGHT ON HG CYCLE IN THE MARINE ENVIRONMENT

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Mercury (Hg) is non-essential and highly toxic element. It naturally occurs in the environment although it is considered rather rare calcophile element. Hg releases to the marine environment have increased in the recent years due to natural and anthropogenic processes. The ocean plays an important role in the global mercury cycle, acting both as a dis-

T.P.1.58

MERCURY CONTAMINATION IN WATER AND ITS BIOCHEMICAL- PHYSIOLOGICAL RESPONSES IN FISHES

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The fish have been found to be a useful model in bioclinical research on toxicology. Effects of Hg on different fish species have been intensively studied by various workers. Two factors need immediate attention are the metal bioavailability which plays a paramount role in heavy metal accumulation in body tissue and their physiological effects. Mercury ac-

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to retain maximum Hg residue in gills than in liver, muscles and brain (Panigrahi and Misra, 1979). The identification of tissue and species-specific physiological measurements in fish can be applicable in determining aquatic health both in the formulation of water quality criteria and as a biological sensor for detecting any sudden change in water quality. Some recent reviews (Jain and Mukta, 2003; Jain and Mittal, 2004) have consolidated the effects of heavy metals in fishes. Measuring of events like aberrant behaviour, histological lesions or biochemical alterations such as elevation in blood sugars (hyperglycemia), proteolysis and lipolysis as mediated by rise in adrenaline are typically generalized stress responses. In ventilation and heart beat frequency etc are nonspecific, where as changes in cellular enzyme activity and the stress protein induction are specific. The enzymatic functions like changes in SDH and ALAD are categorized as specific responses which may be more suitable for bio-monitoring fish health and water pollution in fields. Lactate, pyruvate and succinic dehydrogenase enzymes are all key control points in the flow of carbon through glycolysis and the citric acid cycle (Sastri and Rao, 1982). Mercury is apparently a strong inhibitor of these enzymes in the freshwater teleost, commonly called the murrel. Stress proteins commonly termed as heat shock proteins (hsp) constitute another important feature of chemical toxicity. The stress proteins are a group of cellular proteins whose synthesis increases when the cell is subjected to any sort of stress. Part of the process of acclimation to a toxicant may involve stress proteins. This study thus focus on tissue specific changes in certain digestive and metabolic enzymes and tissue protein profile as an index of Hg toxicity in a most commonly culturable teleost Cyprinus carpio in North Indian conditions. These studies were conducted with respect to body muscles, liver, gills, kidney, and blood.

**TOTAL MERCURY CONCENTRATIONS IN KOREAN MUSSELS (MYTILUS CORCUSUS) FOR MARINE ENVIRONMENTAL MONITORING FROM 2017 TO 2018, KOREA**

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Marine ecosystems are frequently exposed to a variety of chronic and acute pollutants derived from anthropogenic production and consumption activities. Mussels are sessile (can provide location-specific information), medium-sized (have enough tissue matrix for chemical analysis), filter-feeders (show accumulation of pollutant chemicals in the gut), and biologically active exchange with the atmosphere and by serving as a vast reservoir of Hg with lifetimes that can span tens of thousands of years. Re-emission of Hg from soils also prolongs the effective lifetime of Hg in the biosphere. Dry deposition is thought to be the primary source of mercury to surface soils. However, North American data on total atmospheric deposition fluxes only weakly correlate with spatial patterns of soil mercury concentrations. These observations highlight the importance of internal cycling and retention dynamics in the context of soil Hg storage. Here we present results from an updated version of the Global Terrestrial Mercury Model (GTMM) and compare results for the United States to more than 4,800 soil measurements. Main science updates include: (1) a revised parameterization for dry deposition of Hg in the GEOS-Chem atmospheric model, (2) variable partitioning of deposited Hg in soil depending on the abundance and lability of sulfur pools in the organic carbon matrix, (3) adjusted fractions of Hg0 released following organic carbon decomposition based on a synthesis of recent measurements. We present an updated budget for the magnitude and spatial distribution of global Hg soil reservoirs, anthropogenic contributions to different soil pools, and implications for changes in the global atmospheric reservoir over time.

**ASSESSMENT OF ATMOSPHERIC POLLUTION WITH MERCURY FROM NUCLEAR FUEL CYCLE ENTERPRISES VIA THE POPULAR LEAVES AND TREE RINGS**

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The aim of the research was to estimate concentrations and speciation of mercury in leaves, leaf litter and tree rings of poplar in the influence
zone of anthropogenic source. The field and laboratory experiments were conducted in 2014-2018 years. Mercury content was measured by atomic absorption (ppb) using a GA-915+ mercury analyzer with a pyrolysis device PYRO-915.

The average gross content of mercury in poplar leaves (dry matter) in the urbanized area is 56 ppb. The highest concentration was found in the influence zone of the nuclear fuel cycle enterprise. The average concentration of mercury in the poplar leaves in the vicinity of the industrial zone was 198 ppb, which is almost 8 times higher than the regional background (25 ppb) of the cities of Siberia and Far East (Russia). Investigation of mercury speciation in the poplar leaves showed that the free form presented with Hg2Cl2 is predominant (4-100%). In several samples from different experiments, we found physically bound form - HgCl2 (7-80%). These mercury compounds are the most mobile, capable of migration and transformation, and therefore the most dangerous in terms of environmental pollution.

The results of the experiment, devoted to observe changes in the mercury content depending on the season, showed a clear trend of increased concentrations in poplar leaves at the end of the growing season. The speciation of mercury accumulated in the leaf plate also change as the physiological characteristics of the poplar leaf change during the growing season. In the beginning of the growing season, the physically bound mercury is prevalent in poplar leaves (67%), the free form takes 32%, the chemically bound and sulfide forms are found in trace amounts (less than 1%). At the end of the growing season, the first two forms exchange with each other.

The research of dynamics in the mercury concentration according to tree rings showed high concentrations of mercury (157 ppb) in 1967-1985 years, that indicates the maximum anthropogenic impact of the plant on the environment. The period of 2000-2017 years is characterized by lower concentrations (63 ppb) due to enterprise investment in conversion to new technologies, introduction of environmental management, quality management, etc.

**T.P.1.63**

ASSESSMENT OF THE VEGETATION UPTAKE OF ATMOSPHERIC MERCURY ACROSS EUROPE

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The direction and quantity of mercury (Hg) exchange between the atmosphere and terrestrial surfaces remains poorly constrained. The purpose of this study was to assess the uptake of gaseous elemental mercury (GEM) by trees across Europe. We investigated the temporal evolution of the foliar Hg pool in trees from 10 European sites along a latitudinal transect from Northern Finland to Switzerland during the 2018 growing season. We took monthly foliage samples of four abundant European tree species at a forest research station in Switzerland. At every other European site we took respective foliage samples two to three times during the 2018 growing season. Our results show that Hg concentrations in foliage increased linearly over the growing season at all European sites. This is true for broadleaves and for needles of different needle age classes. The average Hg uptake rate in leaves of beech canopies at the Swiss forest research station was 5 ± 0.6 ng Hg per g d.w. and month. The average uptake rate in current season and one-year old needles from two spruce trees at the Swiss forest research station was 1.3 ± 0.4 ng Hg per g d.w. and month. These quantities reveal that foliar uptake of GEM represents a massive sink for atmospheric Hg. We will also discuss the potential effect of foliar GEM uptake on atmospheric GEM concentrations measured simultaneously at 5 of the sites. Our determined mercury uptake rates by European foliage will help to improve the dry deposition parametrization in mercury cycling models.

**T.P.1.64**

ABSORPTION AND ADSORPTION OF ATMOSPHERIC MERCURY BY URBAN GREENLAND PLANTS

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Mercury is an important pollutant that can be transported globally in atmosphere. Urban area as the main source of anthropogenic mercury emission, its mercury air pollution cannot be ignored. Plants have been indicated to show a great role in mercury biogeochemistry. Common species in urban forest were studied to understand the process of mercury uptake & absorption, storage and returning to soil. Six typical sites in Shanghai were selected from different urbanized area to investigate plant, atmosphere, and soil mercury contamination. Measurements were taken to study the ecological indicators such as DBH, surface area, and leaf thickness in plant samples. The results indicate that plants have the ability to transport mercury from the atmosphere. Through the process of absorption and adsorption, the mercury in the atmosphere is stored in the plants, and then return to the soil through littering. This study provides a scientific basis for the role of urban plants on atmospheric mercury purification, as well as a reference for further study to reveal the role of plants in mercury recycle in urban air-soil ecosystem.

**T.P.1.65**

A REVISIT OF GLOBAL VOLCANIC MERCURY EMISSION FLUX: INSIGHTS FROM MEASUREMENTS AT POÁS VOLCANO OVER ACTIVE AND INACTIVE STAGES OF VOLCANIC ACTIVITY

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Volcanic systems are a poorly-constrained, natural contributor to the global mercury (Hg) cycle. Despite several estimates toward the global amount of Hg emitted by volcanoes, only a small handful of these features have sufficient data to extrapolate a Hg flux estimation. The lack of measurements from these sources has led to uncertainty over the emission of Hg over multiple phases of activity. Additional confusion surrounds the range of measured emissions, with orders of magnitude difference between the Hg/SO2 ratio of the highest and lowest volcanoes. Poás Volcano, Costa Rica, has the lowest measured Hg/SO2 ratio in reported literature. During April, 2017, a new phase of activity was demarcated by a phreatomagmatic eruption in the main crater, removing a crater lake and an adjacent magma dome. Activity during this phase was characterized by a high frequency of smaller eruptions and an up to five times increase in the SO2 flux. This provided a rare opportunity to collect comprehensive Hg data from an active phase of Poás and compare with data collected earlier during an inactive phase by two different research groups. Atmospheric, ash, and water samples were collected from Poás over two sampling seasons: during the inactive period over 2015–2016 and during an eruptive period of 2017–2018. During the active period both passive and active samplers were used to collect atmospheric Hg in a transect from the main plume; ash was collected from the top of passive samplers; and water was collected from a hydrothermal field within the crater. During the inactive stage real-time atmospheric Hg speciation measurements...
LONGTIME MONITORING OF MERCURY IN TREE FOULAGE IN AUSTRIA FROM 1986 TILL 2016

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In Austria, the impact of mercury has been assessed since 1986 on 709 sample plots of the Austrian Bio-Indicator Grid with Picea abies (639 plots), Pinus silvestris & nigra (70 plots). On each plot samples of the current shoot of two trees were analyzed. The samples were collected in the upper part of the crown each October. These annual sampling allows a precise evaluation of the temporal and regional development of the mercury impact. With the quick and easy analytical method (Altec-AMA 254) and the stored retain samples it was possible for the first time to evaluate the mercury impact before 2000. The analytical method is contamination-free and sensitive enough to determine naturally occurring mercury concentrations in tree foliage. Especially noticeable are the areas with pig-iron and steel production in the region around Linz, but also in Leoben/Donawitz. Surprisingly the impact is detectable from Linz over 120 km downstream the Danube until St. Pölten. According to the VOEST-Alpine company, 720 kg mercury were emitted by the sintering plant in Linz in the year 2000. At the moment, the processing of mercury-containing Austrian iron ore is one of the important mercury sources in Austria. But due to reducing measures a clear decrease of the mercury impact in these regions can be observed. In the south of Austria elevated mercury levels could be found in Brückl/Carinthia. Here amalgam electrodes were used in chlor alkali process of the chlorine plant until the end of the nineties. This source of mercury pollution was eliminated by a technological change. But polluted chalk was stored here in a special waste disposal site and was used in a nearby cement plant. Both sources and the historical mercury contamination are the reasons for the elevated mercury levels in the surrounding of Brückl. The second Austrian chlor alkali electrolysis in Hallein was closed down and rehabilitated at the end of the nineties. Consequently, its effects on Hg-contents are only visible on the compiled maps from 1986 and 1996. In the Inn Valley/Tyrol elevated mercury levels were detected in the areas around Schwaz (former silver mining) and Brixlegg (copper recycling). In Brixlegg the highest mercury concentration in tree foliage in Austrian could be found in October 2015 (0.68 mg Hg/kg). A mercury contamination of the copper scrap was the reason for this high pollution of the Inn Valley.

HOW DOES LITTERFALL INFLUENCES HG CONTENT OF A DECIDUOUS FOREST SOIL?

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Soils are the main Hg receptor in terrestrial ecosystems and play a key role in the global Hg cycling. Atmospheric Hg can reach the soil surface via wet and dry deposition, but litterfall constitutes an additional pathway for Hg transference to forest soils. Whatever the mechanism depositing Hg in uppermost soil layers, organic matter is one of the main actors involved in the potential Hg accumulation in forest soils. The aim of this work was to assess how litterfall contributes to Hg deposition in a deciduous forest soil. To achieve this, organic horizons (n=8) and mineral soil layers from two profiles (A and B; n=19) were sampled in a deciduous forest plot until a depth of 50-60 cm. Moreover, litterfall samples were collected on a monthly basis in the same plot during 2015 and 2016.

Forest management as a driver for mehg formation and mobilization from soils to surface waters

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In a study spanning over eight catchments in boreal Sweden, we collected 200 soil samples to evaluated whether forest management create soil environments of high MeHg net formation. Furthermore, we tested if these environments were associated with distinct microbial communities. The percentage of MeHg out of total Hg (%MeHg) in soils, as an indication of net MeHg formation, was significantly higher in one of the two catchments subjected to stem and stump harvest compared to catchment subjected to stem only harvest (n=3) or undisturbed forests (n=3). Removal of stumps, as a way to meet future demand for biofuels from forests, can cause more severe soil compaction and soil disturbance compared to traditional stem only harvest. High %MeHg in soils coincided with a high bacterial diversity and a high relative abundance of bacterial families known to include Hg methylators. Environments of high MeHg formation, so called Hg methylation hotspots, were often observed in water-filled cavities created by stump removal or water-logged and disturbed soil environments associated with driving damages. Although stump harvest created environments of high MeHg formation, MeHg in runoff from the same catchment did not increase after stump harvest. We suggest the combination of MeHg formation in soils and the hydrological connectivity between Hg methylation hotspots and surface waters determine the risk that forestry operations will increase MeHg in runoff. In a parallel study we are thereby evaluating how hydrological connected potential Hg methylation hotspots are to surface waters in areas subjected to forest management, by a hydrological modeling approach informed by high resolution topographic mapping. Results indicate that forest machinery driving, especially in the near-stream zone, will greatly influence the hydrological connectivity between potential Hg methylation hotspots and streams, highlighting the importance of minimizing the risk of surface flows on compacted soils, e.g. by applying soil cover during forwarder traffic or the use of sufficient riparian buffers along streams.
deposition through litterfall onto these soils, during 2015 and 2016, was 26 and 21 µg m⁻², respectively. Mercury enrichment factor, calculated using Al as conservative element, were 55 and 51 for Oi and Oe+Oa layers, respectively and 19, on average, for mineral layers of both soil profiles. This suggests that atmospheric sources, rather than lithological ones, was responsible for the Hg accumulated (HgTres) in the studied forest plot. Stored Hg (HgTres) was higher in the mineral layers of both soil profiles (mean profile A: 2.2 ± 0.9 mg m⁻²; mean profile B: 2.2 ± 0.5 mg m⁻²) than in organic horizons (Oi: 0.010 ± 0.002 mg m⁻²; Oe+Oa: 0.096 ± 0.049 mg m⁻²). The Hg/C ratio, a better approach to assess the vertical variability of Hg in a soil profile, was averaged as 0.11 and 0.24 µg Hg g⁻¹ C in Oi and Oe+Oa layers, and about 3 µg Hg g⁻¹ C in mineral soil layers. As a conclusion, litterfall seems to contribute to Hg accumulation in forest soils away from a significant point source, although the intensity of this process is strongly dependent of the soil C dynamics.

**T.P.1.69**

**CONTRASTED HG CONTAMINATION IN SOILS AND SEDIMENTS IN THE AREA OF THE DOBCZYCE RESERVOIR**

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The majority of present total mercury (Hg) releases to the environment are through atmosphere emissions from human activities, such as coal burning and smelting of metal ores. Mercury returns to the Earth’s surfaces by both wet and dry fallouts and accumulates on soils. Therefore, can have a long-term impact on freshwater ecosystems with transfer via soil erosion being an important process. The main aim of our study was to compare the Hg contamination in soils from four land use types (forest, arable land, meadows and pastures, and residential areas), bottom sediments, and suspended matter in two tributaries (the Raba River and Wolinka Stream watersheds) of the main drinking water reservoir of Cracow City. The Raba River watershed is more populated and shows 13 % of its total area covered by built surfaces, while urbanized areas cover only 3 % in the Wolinka Stream watershed. Mercury concentrations presented here were measured by CVAAS and these results will complement greatly the existing database for metallic elements for the environment. Overall, higher Hg concentrations were measured in the Raba River watershed than in the Wolinka Stream watershed, especially in the bottom sediments (median values 0.305 mg/kg and 0.034 mg/kg, respectively). Elevated Hg concentrations were also detected in arable land (median value 0.200 mg/kg and 0.050 mg/kg, respectively), and meadows and pastures (median value 0.117 mg/kg and 0.046 mg/kg, respectively). Compared to the upper crust geochemical background value (0.04 kg/kg), the Wolinka Stream watershed does not present significant contamination, whereas in the Raba River watershed, arable land showed a 4-fold factor, and meadows and pastures a 2-fold factor. The contrasted Hg concentrations are interpreted as differences in local land use management, including anthropogenic activities such as coal burning, direct inputs from municipal pollution, sludge wastewater management.

**T.P.1.70**

**FOREST AS AN IMPORTANT ENVIRONMENT FOR ATMOSPHERIC MERCURY MONITORING IN KOREA**

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In Korea, there are many natural (coastal evaporation, volcanic emissions) and anthropogenic (coal-fired power plants, waste incineration, cement production) mercury emission sources and forests are thought to be an important sink for atmospheric mercury. Here, we conducted a preliminary study to determine if forest litter and soil can be used as monitoring media for assessing spatially variable atmospheric mercury concentrations and sinks. We selected two sites – Bihak Mountain known to be influenced by mercury evaded from nearby coastal regions, and Halla Mountain widely characterized as a background site with little anthropogenic mercury influence. We sampled organic soil, coniferous, and deciduous litter, and measured them for total mercury concentration (THg) using the AAS. Our results showed on average 2 times lower THg concentrations in the litter and soil from Bihak Mountain (81.74±25.58 ng/g (n=3), 128.42±28.49 ng/g (n=3), respectively) compared to Halla Mountain (204.33±2.52 ng/g (n=1), 234.30±11.02 ng/g (n=1), respectively), which is widely characterized as an important background site for atmospheric mercury monitoring in Korea. The higher THg concentrations observed in the Halla Mountain soil and leaf litter can be attributed to a higher annual average precipitation and a lower soil temperature, which can lead to a higher atmospheric mercury deposition and a lower soil mercury evasion, respectively. We also observed an overall increasing trend in THg concentrations in the leaf litter and soil with increasing elevation (litter (n=4): 50.91±2.34, 109.29±5.25, 85.02±1.92, and 204.33±2.52 ng/g, at an elevation of 625m, 727m, 739m, and 975m, respectively, soil (n=4): 116.57±5.51, 165.24±3.98, 103.47±4.80, and 234.30±11.02 ng/g, at 625m, 727m, 739m, and 975m, respectively), suggesting that climatic factors can govern the magnitude of mercury input and output from the forest. Among the samples collected in Bihak Mountain, significantly higher THg concentrations were observed in deciduous litter (109.29±5.25 ng/g (n=1)) and soil (165.24±3.98 ng/g (n=1)) compared to coniferous litter (50.91±2.34 ng/g (n=1)) and soil (116.57±5.51 ng/g (n=1)). Mercury bound to deciduous leaves are more likely to be degraded and be sequestered into organic soil, consistent with results from many previous studies. Our results suggest that comprehensive monitoring of THg concentrations in forest media is necessary for selecting an appropriate background site and for understanding climatic and biogeochemical factors governing spatially variable differences in atmospheric mercury. We plan to expand the site characterization to locations of distinct mercury sources (natural, anthropogenic, and transboundary influences from China), tree species (deciduous, coniferous, and mix), and elevation.

**T.P.1.71**

**DYNAMIC CHANGE CHARACTERISTICS OF MERCURY IN LITTER OF TYPICAL SUBTROPICAL FOREST SYSTEM IN SOUTHWEST CHINA**

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As a special heavy metal, mercury can migrate through the middle and long distances of the atmosphere and spread around the world. For this wide-ranging global mercury pollution problem, terrestrial ecosystems have complex biological systems and large biomes, and are important research areas. Forest ecosystems on land are considered to be the largest and most The most abundant area. The forest ecosystem absorbs mercury from the atmosphere and releases mercury through the release and rainfall evaporation. Hence, it is also considered to be the active pool of mercury. The litter layer is an important part of the energy and material circulation of forest ecosystems. Its research will help people to master the kinetics and related mechanisms and laws of mercury migration and transformation in forest systems. Through one year of monitoring research, this experiment found: In evergreen broad-leaved forests and coniferous forests, the leaves continuously absorb mercury from the developmental to the deciduous stage, and the segmentation regression model analysis shows that the accumulation of mercury has seasonal differences. During the whole lifetime of forest species, the methylation and demethylation change were much larger than the total mercury. As the litter decomposed, the mass and unit concentration of mercury increased, and
A HIGH-RESOLUTION ANNUAL NET FLOW OF MERCURY FROM THE ATMOSPHERE TO BIOMASS OF MAJOR CROPS IN CHINA

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Terrestrial ecosystems serve as sinks and re-emission sources for atmospheric mercury (Hg). Quantitative estimation of air-surface mercury flux is necessary in setting up a regional mercury budget. In this study, we firstly conducted the open top chambers (OTCs) and soil mercury enriched experiments for setting up the correlation of gaseous elemental mercury (GEM) in air to biomass mercury in crops tissues. Linear responses of Hg accumulation in foliage and stem to GEM level in air was founded in maize (Zea mays L.), wheat (Triticum aestivum L.) and Rice (Oryza sativa L.), and yet the Hg accumulation in foliage/ stem is not correlated to soil Hg concentrations. And then combining the soil enriched mercury isotope tracer experiment in our study and literature reports, we quantified crop tissues assimilation coefficients of atmospheric GEM. A bottom-up approach was used to develop the annual net Hg flux from the atmosphere to biomass of major crops in China. Mercury concentrations in the tissues (root, stem, foliage, hull, and grain) of maize, wheat and rice were sampled and measured in 31 provinces covering main grain producing areas in China. Combining the crop assimilation coefficients of atmospheric GEM derived from OTCs and stable isotope tracer technique with biomass mass from official statistics data (1978-2016) at the provincial level, Hg annual uptake flux from the atmosphere to superficial water bodies by runoff, erosion or lost to the atmosphere by volatilization. Moreover, subsuperficial horizons behave as a geochemical barrier preventing the Hg percolation to groundwater, where it could be easily transformed to the most toxic form of Hg, methylmercury. All of this can contribute to the role of podzolic soils as a Hg sink rather than a source.

MERCURY CONTENT AND DISTRIBUTION IN PODZOLIC FOREST SOILS FROM AN ATLANTIC SW EUROPE AREA: ROLE OF SOIL COMPONENTS AND PEDOGENESIS

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Forest soils constitute one of the main mercury reservoirs in terrestrial ecosystems, accounting up to 75 % of the Hg present in the biosphere. In soils characterized by a background Hg content, Hg is predominantly deposited from the atmosphere and it is accumulated in surface horizons associated to organic matter. However, there are soils where Hg can be stored in deeper layers as podzolic soils, what are widely spread worldwide. Soil processes and soil components involved in such a particular Hg behaviour are still under discussion, and they deserve to be investigated. This work assess the distribution of total Hg (HgT) with soil depth in fifteen podzolic forest soils from an Atlantic area of SW Europe (Galicia, NW Spain) in order to elucidate what is involved in the vertical mobilization of Hg. A total of 127 samples of different soil horizons were characterized in this study. The highest HgT concentration was found in O horizons (144 ± 41 µg kg⁻¹), diminishing downwards the soil profile from 73 ± 47 µg kg⁻¹ in A horizons to a minimum value of 12 ± 9 µg kg⁻¹ in the E horizons. Afterwards, a subsuperficial peak of HgT concentration corresponding to illuvial horizons (Bh and Bs) was found, showing values of 66 ± 28 µg kg⁻¹ and 105 ± 64 µg kg⁻¹, respectively. However, HgT diminished again in C horizon (36 ± 25 µg kg⁻¹). Vertical HgT distribution in podzolic soils could be explained by the downward mobilization of organic matter and Al and Fe compounds, as part of the podsolization process, which are accompanied by Hg which shows a close geochemical affinity by these soil components. This is consistent with significant and positive correlations found between Hg and C (r=0.492; p<0.000), Hg and sodium pyrophosphate extracted Al (r=0.607; p<0.000), and Hg and sodium pyrophosphate extracted Fe (r=0.505; p<0.000). The pedogenetic process that take place in podzolic soils contributes to retain Hg in subsuperficial soil layers avoiding its possible mobilization to superficial water bodies by runoff, erosion or lost to the atmosphere by volatilization. Moreover, subsuperficial horizons behave as a geochemical barrier preventing the Hg percolation to groundwater, where it could be easily transformed to the most toxic form of Hg, methylmercury. All of this can contribute to the role of podzolic soils as a Hg sink rather than a source.

MERCURY EMISSIONS HISTORY OF THE RUDNANY ORE DISTRICT AS RECORDED BY EUROPEAN LARCH TREE RINGS

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We recently showed that tree rings of European larch (Larix decidua) are a promising new archive of changes in atmospheric Hg levels in central Europe. After pioneer research in the Czech Republic, we focused on a highly contaminated site in Slovakia, the Rudnany ore mining district. Little is known about the history of pollution in this region, however lumped historic Rudnany Hg emissions were reported to be over 25000 tons prior to 1895. In the period 1895-1957, after application of Hg separation from effluent thermal ore processing gasses, estimated lumped Hg emissions decreased to 308 tons. In 1992, just before the plant closed, annual Hg emissions from thermal processing of Cu and Fe ores at Rudnany were estimated at approximately 4 t/yr. This amount is comparable to the annual anthropogenic Hg emissions to atmosphere for the entire Czech Republic. Five larch trees were cored at distances of 0.5-5 km from the old processing plant. The cores were sectioned to 5-year segments and analyzed for total Hg concentrations by CV-AAS method. The larch trees were 50 to 85 years old and mean Hg concentrations in the oldest tree ring segments covering the period 1933-1952 were >1000 µg/kg. Since 1953, mean tree ring Hg concentrations declined with a minor local peak of 237 µg/kg in the period 1978-1982, when ore mining peaked. In the segment 1969-1992, covering the period of ore mining cessation in 1992, mean tree ring Hg decreased to 98 µg/kg. A further decrease of the tree ring mean Hg concentration to 15 µg/kg occurred in the most
The methylmethylation of mercury (Hg) is well studied in the marine environment due to the high toxicity of monomethylmercury (MMHg). However, there is still a lack of knowledge concerning MMHg formation in soils. Our main aims with this study were i) to assess the small high-throughput MMHg extraction and analysis method using HPLC-ICP-MS, which we will present, as well as results from an inter-laboratory comparison. This substantial dataset allowed us to show that in the contaminated Swiss sites, MMHg concentrations increased linearly with Hgtot concentrations while MMHg/Hgtot decreased with increasing Hg concentrations. In top soils of Swiss background sites, we found that Hg correlated with OC concentrations, which is consistent with the property of natural organic matter (NOM) to efficiently adsorb airborne Hg.

The soils were sampled along rectangular grids in 5-meter intervals. The resulting 380 individual soil samples were analysed for Hg, MMHg, other relevant metals and standard soil parameters such as pH, N, S and organic carbon (OC). To make this possible, we developed a high-throughput MMHg extraction and analysis method using HPLC-ICP-MS, which will present, as well as results from an inter-laboratory comparison. This substantial dataset allowed us to show that in the contaminated Swiss sites, MMHg concentrations increased linearly with Hgtot concentrations while MMHg/Hgtot decreased with increasing Hg concentrations. In top soils of Swiss background sites, we found that Hg correlated with OC concentrations, which is consistent with the property of natural organic matter (NOM) to efficiently adsorb airborne Hg. Further, MMHg/Hgtot was significantly higher in top soils than in the mineral soils of the same Swiss background sites. We further suggest that MMHg/Hgtot varies with land-use types (crops vs. pasture).

The results from the Chinese sites will also be presented and compared to those of the Swiss sites in order to draw general conclusions about MMHg formation and distribution in soils.

**METHYL MERCURY DISTRIBUTION AND FORMATION IN POLLUTED AGRICULTURAL SOILS.**

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**THE ROLE OF NON-NATIVE EARTHWORMS IN THE TERRESTRIAL BIOACCUMULATION AND CYCLING OF MERCURY IN NORTHERN CALIFORNIA, USA.**

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California’s geology, mining history and atmospheric deposition have led to extensive accumulation of mercury in the Bay Area, with troubling implications for local human, wildlife and environmental health. Although mercury is well studied in aquatic ecosystems, little work has focused on the terrestrial biota. However, we know that soil organisms, such as earthworms, are quite important because they make mercury more bioavailable to other organisms through bioturbation and decomposition, and because they are a primary food item for many other belowground larvae. Because emergent aquatic insects can have high concentrations of methyl mercury (MeHg) in their tissues, it has been hypothesized that nestlings whose diets consist of a high proportion of odonates would be contaminated with levels of MeHg that are hazardous to their health. There have been no studies of the relationship between MeHg contamination of nestling Red-winged Blackbirds and their diet. The objective of our study was to measure the concentration of MeHg in the blood of nestling Red-winged Blackbirds and to estimate the proportion of emergent aquatic insects and terrestrial insects in their diet using stable isotopes of nitrogen. We conducted our study at an atmospherically-contaminated site, the Eagle Mountain Fish Hatchery, Fort Worth, Texas, USA. Previous studies at the Hatchery demonstrated that emergent aquatic insects have high concentrations of MeHg, while terrestrial insects on the pond shorelines have low concentrations of MeHg. Red-winged Blackbirds nested in cattails in 20 ponds from April 9 to July 30 2017. We collected 424 blood samples from 243 nestlings from 88 nests (1-2 samples from 1-4 nestlings per nest). MeHg was detected in nestling blood, suggesting that Red-winged Blackbird nestlings were fed emergent aquatic insects. However, concentrations of MeHg in nestling blood were low (mean = 0.020 µg/g ww) and below established risk thresholds. Concentrations of MeHg and nitrogen stable isotope ratios of nestling blood indicate that terrestrial insects composed a high proportion of their diets. Our results suggest that nestling Red-winged Blackbirds may not be at risk of MeHg contamination when terrestrial organisms dominate their diet.

**METHYL MERCURY CONTAMINATION AND DIET OF NESTLING RED-WINGED BLACKBIRDS.**

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Red-winged Blackbirds (Agelaius phoeniceus) are found throughout North America, often nesting in cattails in ponds and wetlands. Diet studies have revealed that adults feed their nestlings both emergent aquatic insects, like odonates, and terrestrial insects, like lepidopteran larvae. Because emergent aquatic insects can have high concentrations of methyl mercury (MeHg) in their tissues, it has been hypothesized that nestlings whose diets consist of a high proportion of odonates would be contaminated with levels of MeHg that are hazardous to their health. There have been no studies of the relationship between MeHg contamination of nestling Red-winged Blackbirds and their diet. The objective of our study was to measure the concentration of MeHg in the blood of nestling Red-winged Blackbirds and to estimate the proportion of emergent aquatic insects and terrestrial insects in their diet using stable isotopes of nitrogen. We conducted our study at an atmospherically-contaminated site, the Eagle Mountain Fish Hatchery, Fort Worth, Texas, USA. Previous studies at the Hatchery demonstrated that emergent aquatic insects have high concentrations of MeHg, while terrestrial insects on the pond shorelines have low concentrations of MeHg. Red-winged Blackbirds nested in cattails in 20 ponds from April 9 to July 30 2017. We collected 424 blood samples from 243 nestlings from 88 nests (1-2 samples from 1-4 nestlings per nest). MeHg was detected in nestling blood, suggesting that Red-winged Blackbird nestlings were fed emergent aquatic insects. However, concentrations of MeHg in nestling blood were low (mean = 0.020 µg/g ww) and below established risk thresholds. Concentrations of MeHg and nitrogen stable isotope ratios of nestling blood indicate that terrestrial insects composed a high proportion of their diets. Our results suggest that nestling Red-winged Blackbirds may not be at risk of MeHg contamination when terrestrial organisms dominate their diet.
spatially model the earthworm contribution of mercury within a local system using differences in disturbance history and ecological variables, and 4) will contribute information appropriate to regulation standards and potential remediation strategies. Preliminary data demonstrate high variability of mercury values among taxa and across our soil gradient. Our work has broad implications for evaluating mercury bioavailability across terrestrial ecosystems with invasive earthworm communities and for predicting the uptake of this toxicant by higher trophic levels (e.g. earthworm-feeding birds and mammals).

T.P.1.79

OCCURRENCE, RETENTION AND METHYLATION IN SOILS OF A HISTORIC CINNABAR MINED SITE, GRAVELOTTE, SOUTH AFRICA

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Historic cinnabar mine workings denotes environmental concerns by releasing mercury (Hg) of little known release and transport mechanisms. In South Africa, the deposits of cinnabar are anomalous occurrence discovered within three Provinces and its was only in the Murchison Range to a group of Archean greenstone belts in the Limpopo Province that cinnabar mining operation took place in 1940. The Hg deposit played a major role of Hg methylation over time. In this site the Hg ore was mined, milled, roasted and stored for six years, discerning a new pattern of Hg pollution from a geological setting of native Hg in the Ga-Selati River catchment.

Hg distribution pathways, concentrations and speciation were studied to evaluate the extend of contamination and potential Hg mobility in the old workings. Environmental variables such as pH, SO4, dissolved organic carbon and % soil moisture content were measured and correlated to the Hg concentration to determine the influence they have to Hg methylation and mobility.

Maximum concentration of total Hg (TotHg) 11118 ng/g and methyl-mercury (MeHg) 15.43 ng/g (0.14% of TotHg) were found in the soils located close to the excavation area (open pit) used to access the cinnabar ore. Within 350 meters away from the excavation area, Hg concentration decreased to TotHg 2010 ng/g and MeHg 3.08 ng/g (0.15% of the TotHg). Off the site (1.3 km from the boundary) the TotHg and MeHg concentrations were: 283ng/g and 0.53 ng/g (0.19% of the TotHg) respectively. Thermal-desorption method revealed <1% of TotHg was present in the toxic MeHg form in the studied soils representing potential long-term environmental risks.

Our study indicated that Hg contamination is high within the vicinity of the mined area and reduces downhill away from the site. The maximum concentration of 11118 ng/g exceeds the allowable Hg levels of protection of ecosystem health and water resources of 4100 ng/g and 1000 ng/g respectively of the National Norms and Standards for remediation of contaminated land and soil quality in South Africa, Notice 467 of 2013.

T.P.1.81

THE INTERACTION OF MICROBIAL DIVERSITY AND FOREST MANAGEMENT WITH BIOACCUMULATION OF METHYL MERCURY IN ORGANIC SOILS

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Methylmercury (MeHg) in surface waters poses risks to aquatic biotic communities, and to wildlife and humans consuming fish or other aquatic food resources. In Latvia the data on Hg and MeHg levels in fish are limited, but recent studies suggest that fish Hg concentrations have increased in large parts of the northern hemisphere are far above the European Union standards (0.02 mg Hg kg−1) for good ecological status. Furthermore, the Hg concentrations are often above the the limit safe consumption of fish as a food source set by the World Health Organization (0.5 mg Hg kg-1). Results of Interreg Baltic Sea Region Programme project Water management in Baltic forests (WAMBAF) have revealed increased concentrations of Hg in sediments and biota downstream of a beaver dam, located on drainage ditch in drained peatland. As the percentage of organic soils in Latvia is high, the questions related to the processes influencing water quality are of high interest.

Forest management, e.g. forest harvest and drainage network maintenance, may increase leaching of Hg and MeHg from soils to surface waters and enhance MeHg formation in water-saturated soils. As there is a high variation in the response to forestry between sites, knowledge about processes causing elevated MeHg formation in managed forest areas is of great value. Mercury methylation is a microbial process which occurs in anaerobic conditions, and is generally carried out by dissimilatory sulfate-reducing bacteria (DSRB) and dissimilatory iron-reducing bacteria (DIRB), as well as by methanogens and Firmicutes. A two gene cluster hgca (encoding a putative corrinoid protein) and hgcB (encoding a 2[4Fe-4S] ferredoxin) is required for Hg methylation. As methanogens play an important role methylating Hg in both terrestrial and aquatic environments, an interplay between MeHg formation and methane (CH4) emissions may be expected. However, this interplay has not been well studied.

This paper presents the first results on interactions of soil microbial communities with MeHg formation processes, obtained by correlating microbial profiles and functional analyses with soil and water properties and Hg and MeHg levels in samples collected in eight sampling sites in water environment undergoing different management impact levels such as ditch cleaning and beaver dam removal/retention. The study is being implemented in close cooperation with the above-mentioned Interreg project team, ensuring synergy between already obtained knowledge on MeHg outputs into freshwater ecosystems and adding new data on microbial diversity and functionality.

T.P.1.82

UNDERSTANDING MERCURY CYCLING IN TIBETAN GLACIATED ENVIRONMENT: RECENT PROGRESS AND REMAINING GAPS

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Glacierized mountain environments can preserve and release mercury (Hg) and play an important role in regional Hg cycling. In the Tibetan Plateau (TP), most glaciers have been retreating at unprecedented rate in recent decades, acting as one of the most active factors in regional hydrological cycling. We summarized recent studies on Hg distribution, transport, and accumulation in Tibetan glacierized environments. We highlight that melting glacier may represent a stimulator that exports Hg to glacier-fed ecosystems. We identified major knowledge gaps and proposed future research needs with several emphases, including quantifying Hg in glacier ablation zone, depicting Hg transport and transformation in glacial rivers during spring melt season, and better constraining glacier-export Hg and its environmental risks to the downstream. Besides, Hg isotopic technical, passive sampling and hydrological transport model should be utilized to improve the understanding of Hg cycling in high mountain regions in the TP.
PRESENCE OF MERCURY IN BIOFERTILIZERS MANUFACTURED FROM AGRICULTURAL WASTES.

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One of the most important objectives of sustainable agriculture is to maximize the reusability of wastes in the manufacturing of fertilizers, by means of using agricultural wastes in this process. Thus, new techniques, aimed to reuse those agricultural residues, minimizing both losses of nutrients and pollution dissemination, are being developed nowadays.

In Castilla-La Mancha region (South-Central Spain), wine industry produces important volumes of wastes. Composting of biodegradable components, under controlled conditions, can drive to the production of soils conditioners and/or organic fertilizers.

Both the Spanish and the European normative limit the presence of heavy metals (Hg, Cd, Cr) in this type of products, which should not overcome concentrations of 0.4, 0.7 and 70 mg·kg-1, respectively.

In the study presented here, 12 different blends of vine shoots with different agronomic wastes (pomace, wet-pomace, sheep manure and bovine manure) were composted and analysed for Hg, in order to assess their possible toxicity linked to this metal. Concentrations resulted in values between 0.109 and 0.138 mg·kg-1, with an average of 0.123 mg·kg-1. These values are below the legal limit for these products, and therefore can be used as an organic fertilizer.

Mercury concentrations were higher when pomace was used in the blend (0.133 mg·kg-1) that when using sheep or bovine manure (0.113 mg·kg-1 and 115 mg·kg-1 respectively). No statistically significant correlations have been found between Hg and any other elements, probably meaning that the provenance of this pollutant could not be related with the original components of the composts, but with incorporation of this element from atmospheric presence.

As most important conclusion, the products obtained in these composting processes of vine shoots are well below legal limits, being, then, suitable for their incorporation to the soil.

MUD DAUBER NESTS AS SOURCES OF SPIDERS IN MERCURY MONITORING STUDIES

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Shoreline spiders that feed on mercury (Hg)-contaminated insects emerging from water bodies can serve as biosentinels of Hg contamination of aquatic ecosystems. Most investigations that utilize shoreline spiders as biosentinels of Hg contamination have involved long-jawed orb weavers (Tetragnatha spp.). Long-jawed orb weavers construct webs to capture emergent insects along shorelines of waterbodies. In this study, we collected long-jawed orb weavers along the shoreline of the Clear Fork of the Trinity River, Fort Worth, Texas, USA on May 17, June 8, July 9 and 11, 2016 to determine if the river was contaminated with Hg. The long-jawed orb weavers were contaminated with high concentrations of Hg (361 ng/g dry weight), indicating that the river is contaminated with Hg. We then examined whether spider taxa in the nests of mud dauber wasps (Sceliphron caementarium) collected from bridges and a building along the Clear Fork of the Trinity River could be used as a source of spiders in Hg monitoring studies. Adult mud daubers build mud nests on human-made structures near rivers and lakes. In each cell of the nest, a female mud dauber lays a single egg which the provisions with up to 25 live, paralyzed spiders. Each mud dauber nest is composed of one to 26 cells containing hundreds of spiders. On February 1, July 17 and 27, 2016, we collected a total of 350 mud dauber nests that contained 2,015 spiders. Five families of spiders were abundant in the mud dauber nests: orb weavers (Araneidae, 13%), jumping spiders (Salticidae, 25%), crab spiders (Thomisidae, 13%), lynx spiders (Oxyopidae, 20%), and cobweb spiders (Theridiidae, 29%). All families were found to be contaminated with Hg; orb weavers (439 ng/g), jumping spiders (196 ng/g), crab spiders (151 ng/g), lynx spiders (190 ng/g), and cobweb spiders (257 ng/g). Our study suggests that shoreline spiders found in nests of mud dauber wasps have potential as biosentinels of Hg contamination of rivers.

TRANSPORTATION AND MOBILITY OF MERCURY IN TYPICAL KARST CATCHMENT OF GUIZHOU, CHINA

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Mercury (Hg) has unique geochemical behavioural characteristics in karst areas, but in-depth systematic research on Hg in karst areas is lacking. Guizhou province is located in the heart of karst, south western China. Therefore, research on transportation and mobility of Hg in typical karst catchment can provide scientific basis for prevention
SPATIAL TRENDS IN ACCUMULATION OF MERCURY IN WILD PINE MARTENS OF NORTH-WESTERN RUSSIA (VOLOGDA REGION)

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The Vologda region lies in the area of 145.7 thousand square kilometers. The territory of the region is heterogeneous in its climatic parameters, including hydrography. The pine martens (Martes martes L) is a widespread, numerous, eurybiotic consumer of the highest order of terrestrial ecosystems of the North-Western Russia. The purpose of this study was to study the accumulation and distribution of mercury in the tissues of M. martes living in the territory of the Vologda region (North-Western Russia) in areas with different climatic parameters.

The study was carried out from 2008 to 2018 on the territory of the Vologda region (North-Western Russia). The amount of mercury was measured in the liver, kidney, muscle, brain, spleen, wall of the intestine, chyme and the hair from 163 M. martes. The metal concentration was determined by the atomic absorption of pyrolysis method, done with the help of the mercury analyzer RA-915M. The measurement accuracy was controlled by using certified biological material DOLT-5. Correlation between the amount of the metal in different pairs of animal organs and the dependence of the amount of metal in animal tissues on the climatic parameters of their habitat areas were determined using nonparametric Spearman coefficient (rs, ps<0.05).

The mercury concentration in the tissues of the M. martes varies widely – from 0.001 mg/kg of wet mass in the brain to 5.66 mg/kg of wet mass in the hair. The average concentration (AM±SD) of the metal for the studied species (mg/kg wet mass) decreases in the row: hair (1.80±1.34) > kidneys (0.50±0.34) > liver (0.30±0.21) > muscles (0.27±0.20) >chyme (0.17±0.16) > spleen (0.16±0.13) > intestinal wall (0.14±0.14) > brain (0.10±0.08). The percentage of moisture in the marten's tissues decreases in the following order: intestinal wall (79%) >chyme (78%) > brain (77%) > spleen (76%) > kidney (73%) > muscle (73%) > liver (70%) > hair (16%). Reliable positive correlation of mercury concentration in the all pairs of the studied tissues of the M. martes was revealed (rs=0.41-0.84, ps<0.01, n=36-135). Reliable correlation dependence of the mercury content in several marten tissues on the swap ratio, lakes, annual precipitation, average air temperature, and air humidity in the area of its habitat was revealed. Also, reliable negative correlation between the mercury content in several tissues of the M. martes and the density of the river network was revealed.

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MERCURY IN WILD GROWING MUSHROOMS AND UNDERNEATH SOILS IN POLAND: LEVELS, BIOCONCENTRATION, BIO-INDICATION POTENTIAL, POSSIBLE INTAKE

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Mercury (Hg) is a natural environmental contaminant to which humans are usually exposed in foods. The anthropogenic emissions of Hg in the last century and subsequent wet deposition of HgII and litterfall depo-
situation by plants have led to a spectacular increase of Hg content in the forest floor (organic layer of soils) in Europe and elsewhere. Mercury in soil is well absorbed by fungal mycelia of many species of mushrooms. Certain species are able to efficiently bioconcentrate Hg in fruiting bodies even if grew in unpolluted (background) soil with a small content of the element. An ability of mushrooms for efficient uptake of mercury can coincide with its elevated content in soil substrate due to anomalous soil geochemistry or pollution. This results in highly elevated content of Hg in many mushrooms and including species edible to human. We review recent progress in our understanding of the accumulation of Hg by mushrooms foraged in Poland, its content in mushroom meals and possible intake and risk.

**T.P.1.90**

**MOLECULAR EFFECTS, SPECIATION, AND COMPETITION OF INORGANIC AND METHYL MERCURY IN THE AQUATIC PLANT ELODEA NUTTALLII**

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Mercury (Hg) remains hazardous in aquatic environments because of its biomagnification in food webs. Nonetheless, Hg uptake and impact in primary producers is still poorly understood. Here, we compared the cellular toxicity of inorganic and methyl Hg (IHg and MeHg, respectively) in the aquatic plant Elodea nuttallii. IHg and MeHg regulated contigs involved in similar categories (e.g., energy metabolism, development, transport, secondary metabolism), but MeHg regulated more contigs, involved in similar categories (e.g., energy metabolism, development, transport, secondary metabolism), but MeHg regulated more contigs, supporting a higher molecular impact than IHg. At the organism level, MeHg induced antioxidants, while IHg decreased chlorophyll content. The uptake of Hg was subsequently studied in complex media. Measured uptake pointed to a contrasted impact of cell walls and copper (Cu) on IHg and MeHg. Using a speciation modeling, differences in uptake were attributed to the differences in affinities of IHg and MeHg to organic matter in relation to Cu speciation. Our data provide fundamental knowledge on IHg and MeHg uptake in a key aquatic primary producer.

**T.P.1.91**

**EXCHANGE OF GASEOUS MERCURY OVER A TEMPERATE DECIDUOUS FOREST MEASURED BY A MICROMETEOROLOGICAL GRADIENT METHOD – FIRST RESULTS AND EXPERIMENTAL CHALLENGES**

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Atmospheric Hg, emitted from anthropogenic sources as well as natural sources, deposits via various wet and dry deposition processes. While we now understand that the dominant source of Hg in many terrestrial ecosystems derives from deposition of elemental Hg(0) taken up by vegetation and transferred to soils when plants die off or shed leaves (also termed “litterfall”), the temporal and seasonal patterns of Hg(0) deposition is poorly constrained in most biomes across the globe. Here, we provide first data on annual exchange measurements of gaseous Hg(0) using a flux-gradient approach over a temperate deciduous forest in Massachusetts. The system employs measurement of Hg(0) concentrations above the forest canopy at 24 and 29 m height in conjunction with characterization of turbulent exchange parameters. Results shows substantial variability of both gradients and calculated Hg(0) exchange fluxes, indicative of particular challenges in accurately confining fluxes over rough surface elements such as forest trees. Deposition of Hg(0) was observed in early summer months, especially at nights and early mornings, while emissions dominated during middays and period prior of emergence of leaves. Compared to previous Hg(0) flux measurements over a low tundra and over temperate grasslands, the magnitude and frequency of deposition fluxes is smaller. Similarly, feedback responses of surface fluxes on boundary layer Hg(0) concentrations are seemingly weaker in this forest ecosystem. The results show that development of annual Hg(0) flux series and identification of respective environmental controls may be of particular challenge over forests. Ongoing work is aimed at improving the flux system to better constrain flux magnitudes, partitioning of fluxes into canopy and forest floor fluxes, and comparison of Hg(0) fluxes with other trace gas exchanges to determine underlying processes of flux exchange such as stomatal uptake, passive sorption/desorption, and soil contributions.

**T.P.1.92**

**ELEVATED CO2 MAY INCREASE METHYLMERCURY ACCUMULATION IN RICE GRAIN**

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BACKGROUND: Methylmercury (MeHg) in rice is a global public health concern; however there are significant knowledge gaps regarding changes in rice MeHg under increasing atmospheric CO2.

METHODS: We present a greenhouse microcosm study comparing MeHg in the soil and grain of rice plants grown at ambient (c. 450 ppm; ACO2) and elevated (c. 800 ppm; ECO2) carbon dioxide concentrations (N=14). Temperatures were held constant between treatments, while humidities were adjusted to reduce differences in transpiration. At grain maturity, we collected plant physiological measurements and analyzed MeHg concentrations in rice grain and in rhizosphere soil. Bulk soil in vegetated microcosms was also analyzed in the ECO2 treatment.

PRELIMINARY RESULTS: MeHg concentrations in the grain of plants grown at elevated carbon dioxide were approximately double the MeHg concentrations of grain grown at ambient carbon dioxide (median 0.71 ± 0.20 ng/g ECO2 vs. 0.48 ± 0.34 ng/g ACO2), although this result was non-significant (Wilcoxon rank-sum p = 0.317, n=14). We observed that ECO2 rhizosphere soil had lower MeHg compared to ACO2 rhizosphere soil (median 0.11 ± 0.05 ECO2 vs. 0.14 ± 0.05 ng/g ACO2), although again, the results were not statistically significant (p = 0.62, n=14). Additionally, rhizosphere soil was slightly reduced in MeHg concentration (median 0.11 ± 0.04 ng/g) compared to bulk soil (median 0.16 ± 0.05 ng/g) in the elevated carbon dioxide treatment (p = 0.10, n=11).

PRELIMINARY CONCLUSIONS: Our results suggest that increased plant growth in the elevated treatment, where photosynthetic rate was 62–64% greater than in the ambient treatment, potentially resulted in greater uptake of the available MeHg pool and depletion of the MeHg in the nearby rhizosphere soil relative to the bulk soil. Ongoing analyses of MeHg contents of roots and leaf tissues will assess whether plants in elevated carbon dioxide treatments accumulated higher concentrations of MeHg in photosynthetic tissues, or if the increased grain MeHg concentration of grain may be the result of carbon dioxide-mediated alterations in grain filling or MeHg translocation. Our preliminary results suggest that elevated carbon dioxide may alter rice grain MeHg concentrations by altering the physiology of the plant itself.
THE EFFECTS OF TEMPERATURE, SALINITY AND SEDIMENT CARBON ON MEHg UPTAKE IN PHYTOPLANKTON

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Phytoplankton uptake of MeHg represents a key, but understudied step in the transfer of MeHg in marine food webs. Additionally, as phytoplankton represent the first bioconcentration (~105 increase from water) of MeHg in food webs, understanding which factors influence MeHg uptake will assist in understanding MeHg bioaccumulation in marine food webs. Further, how climate change may impact MeHg uptake in phytoplankton or how this could alter marine food webs is unknown. Here, we examine how changes in salinity and carbon due to predicted increase in precipitation and changes in temperature would impact MeHg uptake in phytoplankton. We conducted a laboratory experiment, in which we used modified sediment cores with internally generated mixing to maintain cells in the water column. To these, we added ~5 cm of sediment from contaminated sites that are high in Hg (Mill Creek, NJ or Penobscot, ME) to cores. Then we added phytoplankton (Tetraselmis impellucida) and individually manipulated salinity (10 ppt, 20 ppt, or 30 ppt), organic carbon (Mill Creek: 5.3% LOI or 15.5% LOI; Penobscot: 5.2% LOI or 12% LOI), and temperature (15°C or 25°C). Phytoplankton were counted daily and harvested at stationary phase by filtering on GF/Fs in a trace metal clean room. Salinity appeared to have little effect on MeHg uptake in phytoplankton in both sediments. Significant effects of temperature on MeHg uptake was only found in phytoplankton grown over the Penobscot sediment. Lastly, lower %LOI resulted in higher phytoplankton MeHg. The results presented here highlight site-specific responses to temperature and confirm previous findings that carbon is an important driver in MeHg accumulation.

INCREASING WATER TEMPERATURE AND DISSOLVED ORGANIC MATTER CHANGE AQUATIC MERCURY BIOACCUMULATION — A MESOCOSM STUDY

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Freshwater ecosystems are warming at unprecedented rates due to climate change, likely coupled with changes in the organic carbon export from land to waters. The consequences of warming and increased dissolved organic carbon (DOC) on potentially toxic methylmercury (MeHg) bioaccumulation is still unclear. A mesocosm experiment approach was employed to investigate the combined effects of increasing temperature and terrestrial DOC on the Hg uptake by pelagic herbivorous consumers in clear, oligotrophic waters. A total number of 24 mesocosms corresponding to 6 replicates of 4 different treatment conditions (control, increased temperature, elevated DOC, and mixed condition of increased temperature and DOC) were applied in a 36-day mesocosm experiment. Aqueous and particulate MeHg, DOC, and chlorophyll-a were measured on weekly basis during the experiment. Seston (0.7–40 μm) and larger-sized algae (40–100 μm, mainly filamentous green algae), as well as zooplankton (>100 μm, mainly Bosmina longirostris) harvested at the end of the experiment showed that terrestrial DOC addition contributed to higher seston total Hg in the treatments with elevated DOC but did not stimulate significant increase in aqueous or biotic MeHg. Increased temperature also did not significantly influence on MeHg bioaccumulation. Instead, MeHg increased with increasing size fraction. The concentration of polyunsaturated fatty acids and terrestrial fatty acids in phytoplankton was the highest in the treatment with only elevated DOC (p<0.05). At the same time, zooplankton growth and reproduction (as measured by number of individuals) was greatly enhanced in the treatment which combined increased temperature and DOC. However, zooplankton size was on average smaller in the increased temperature treatment (381±91 μm) compared to zooplankton under control conditions (417±101 μm). It is likely that increased DOC stimulated algae biomass production, which supported zooplankton growth and reproduction, resulting in bio-diluted Hg bioaccumulation. The influence of increased temperature on zooplankton Hg bioaccumulation is still unclear from our investigation, but likely to exacerbate when there is oxygen depletion coupled with active Hg methylation in anoxic waters.

CONTROL OF ANTHROPOGENIC EMISSIONS AND METEOROLOGY ON VARIATIONS IN HG DEPOSITION OVER LAKE VS LAND SURFACE IN UPSTATE NEW YORK

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Atmospheric deposition is a major input of mercury (Hg) to aquatic and terrestrial ecosystems. To evaluate strategies to mitigate Hg pollution in inland lakes, the two Great Lakes adjacent to New York State (Ontario and Erie), and rural land areas of upstate New York, the relative contributions of anthropogenic emission reductions and meteorological variations to atmospheric Hg deposition were investigated using a regional three-dimensional chemical transport model with detailed Hg and bromine chemistry (CMAQ-newHG-Br). Controls on anthropogenic emission reductions did not significantly alter Hg wet and dry deposition in all study areas when averaged over time and space. However, control of emitted source emissions significantly affected spatial variation in Hg deposition and subsequent inputs to nearby water bodies. Specifically, dry deposition was elevated by 42–52% for those areas in proximity to intensive emission sources. For the Great Lakes, Hg dry deposition was enhanced by a factor of 2 – 5 within distances of <12 km downwind of intensive sources, and the enhancements decreased to negligible over distances of ~50 km. Over land, intensive emission sources contributed significantly to the spatial variation in Hg dry deposition (30%) and surface concentrations of gaseous oxidized Hg (GOM) (46%). Spatial and temporal variation in climate and foliar characteristics were found to affect Hg wet and dry deposition. Convective precipitation significantly contributed to spatial and seasonal variation (~65%) in Hg wet deposition over both lake and land surfaces, whereas dry deposition velocities of GOM and PBM, which are mainly controlled by wind speed and surface heat flux, were the main factors influencing spatial variation in Hg dry deposition over the lake surfaces. Leaf area index, which regulates deposition velocity, contributed 14% of the spatial variation in dry deposition flux over land, and variation in solar radiation, which influences photochemical formation of GOM and PBM, explained ~10% of the variation to lake and land surfaces alike. Our findings suggest that future climate change will likely serve to enhance Hg concentrations in biota via increases in Hg dry and wet deposition to varying degrees contingent on land surface type. Hence, mitigating the health risks of Hg will require more stringent controls on anthropogenic Hg emissions to eliminate hotspots and compensate for the effects of human-induced climate change.
USING ICE AND SEDIMENT CORES TO QUANTIFY CLIMATE-WARMING INDUCED INPUTS OF LEGACY MERCURY TO LAKE HAZEN, NUNAVUT

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Mercury (Hg) emitted from anthropogenic sources can undergo long-range atmospheric transport to the Arctic where it may cause health concerns for Arctic wildlife as well as Indigenous people consuming traditional country foods. Temporal trends in atmospheric Hg deposition to Arctic ecosystems have been investigated using ice cores and sediment cores. However, many sediment records do not show a clear decline in Hg deposition despite estimates that Hg emissions from anthropogenic sources have recently stabilized or declined, suggesting that Hg is being remobilized in catchments and delaying the recovery of lakes following emission reductions. To date there is little data on whether the input of legacy Hg increases Hg accumulation in lakes. We hypothesize that the climate-warming induced melting of glaciers may be remobilizing legacy Hg from glaciated watersheds into downstream lakes, providing an important subsidy of Hg in addition to modern Hg inputs. We will test this hypothesis by comparing Hg accumulation rates through time measured in an ice core and sediments cores collected within the Lake Hazen watershed on northern Ellesmere Island (Nunavut, Canada). By comparing ice and sediment core data, we can determine how post-depositional processes in the watershed controls delivery of legacy and modern Hg into Lake Hazen and whether legacy Hg inputs are increasing the rate of Hg accumulation in the lake. The temporal trends in atmospheric Hg deposition will be compared to known changes in anthropogenic production and/or emission of Hg. Our research will elucidate whether climate change may delay the benefit of decreasing Hg emissions in glaciated and Arctic watersheds, and help improve models of global Hg cycling, develop policies on Hg management, and better manage contaminant exposure for Arctic people and wildlife.

THE EFFECT OF CLIMATE CHANGE ON METHYLMERCURY IN BOREAL PEATLANDS

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Peatlands hold large quantities of atmospherically deposited Hg and can be significant sources of methylmercury (MeHg). Because they are saturated wetland systems (anaerobic) they provide conditions ideal for Hg methylation, so much so that the percentage of wetlands in a watershed is positively correlated with MeHg concentrations in fish. This study investigated how increased temperature and elevated CO2 levels may impact net MeHg in peat porewaters and subsequent export to surface waters. Global models predict a 2–4.5°C increase in temperature with more drastic increases at higher latitudes, where most peatlands are located. Peatlands are expected to become drier due to reduced precipitation. The combination of these factors may turn peatlands from mercury sinks into mercury sources. Samples were collected from 10 enclosures at the Spruce and Peatland Responses Under Changing Environments (SPRUCE, https://spruce.ornl.gov/) site located in Minnesota, USA. Each enclosure has above and below-ground heating resulting in temperature treatments ranging from +0°C to +9°C relative to ambient. Each temperature treatment has a pair of enclosures, ambient CO2 and elevated CO2. Samples were collected throughout 2017 and analyzed for total mercury and methylmercury.

Porewater: Within the surface depths (0-30cm), where most MeHg transformation occurs, there was a significant difference between +0°C and all warmer temperatures for both THg and MeHg. THg decreased with increasing temperature and MeHg increased with temperature. Throughout the whole depth profile (0-150cm) there was a significant difference between +0°C and +9°C for MeHg only and concentration increased with temperature. Elevated CO2 did not have a consistent effect. Multiple linear regression identified the following factors as important:

THg: Depth, sulfate, TOC, and season.
MeHg: Depth, temperature, watertable height, pH, sulfate, iron, season, and THg.

Outflow: There was a significant difference between +0°C and +9°C for both THg and MeHg flux. Both THg and MeHg decreased with increasing temperature. There were no significant differences between CO2 treatments. Multiple linear regression identified the following factors as important:

THg: Discharge volume and sulfate.
MeHg: Temperature, TOC, discharge, and season.

Temperature and discharge volume are negatively correlated. The trend in decreasing mercury flux with temperature can be attributed to the decrease in discharge volume.

Our findings suggest that while temperature plays a role in the production of methylmercury within porewaters, the export of methylmercury is controlled by discharge volume. Temperature will produce more MeHg but rewetting events will be required to flush MeHg into streams/lakes where it will impact aquatic wildlife.

MERCURY EXPORT AND TRANSPORT IN A GLACIERIZED MOUNTAIN ENVIRONMENT AND THEIR RELEVANCE TO ENVIRONMENTAL RISKS IN THE INLAND TIBETAN PLATEAU

SUN, Xuejun; ZHANG, Qianggong

Glaciers, particularly alpine glaciers, have been receding globally at an accelerated rate in recent decades. The glacial melt-induced release of pollutants (e.g., mercury) and its potential impact on the atmosphere and glacier-fed ecosystems has drawn increasing concerns. Two intensive sampling campaigns were conducted in Qugaqie Basin (QB), a typical high mountain glacierized catchment in the inland Tibetan Plateau, to investigate the export and transport of mercury from glacier to runoff and evaluate their relevance to environmental risks. Mercury concentration in Qugaqie River (QR) was characterized by a clear diurnal variation which is linked to glacier melt. Particulate Hg was the predominant form of Hg in all sampled environmental matrices. The estimated annual total Hg (THg) exports by ZD glacier, the upper river basin and the entire QB were 8.76, 7.3 and 157.95 g, respectively, with respective yields of 4.61, 0.99 and 2.74 μgm-2 yr-1. In comparison with other glacier-fed rivers, QB has a small Hg export yet remarkably high THg yield, underlining the significant impact of melting alpine glaciers on regional Hg biogeochemical cycles. Furthermore, the total methyl mercury (TMeHg) concentrations ranged from 0.041 to 0.115 ng·L−1, showing contrasting different distribution patterns among different environmental waters. Based on the above findings and the results from previous work, we propose a conceptual model illustrating the four Hg distribution zones in glacierized environments. We highlight that wetlands may enhance the potential hazards of Hg released from melting glaciers, making them a vital zone for investigating the environmental effects of Hg in glacierized environments and beyond.
T.P.2.1

BIOACCUMULATION OF TOTAL MERCURY IN TISSUES OF WILD BOARS: RESULTS OF THE NATIONAL MONITORING PROGRAM IN POLAND

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There is an increased interest in healthy food that includes also the low-fat meat from animals kept in natural conditions. Game meat may certainly be included among such products having high nutritional values and good sensory properties that are desired by demanding consumers. However, game animals could accumulate different contaminants like mercury (Hg) that can be present in the living environment.

The aim of our study was to summarize the results of Hg analyses in meat and liver samples of wild boars (Sus scrofa L.) that were carried out within the framework of the National Monitoring Program in Poland between 2008 and 2018. Samples of muscle tissue (N=614) and liver (N=480) of wild boars were collected by veterinary officers in venison processing plants. Determination of Hg content was performed in Official Laboratories and the National Reference Laboratory (NVRI) by atomic absorption spectroscopy techniques (DMA and CV-AAS). All of the methods used in official control were accredited according to the ISO/IEC 17025:2005+Ap1 and regularly verified by ensuring of the internal and external quality control (national and international proficiency tests).

The data was downloaded from the Central National Database and subjected to statistical analysis using R version 3.5.2.

The median of Hg concentration in muscle tissue of wild boars was 4.0 μg/kg of wet wt. and ranged from 0.5 to 48.0 μg/kg of wet wt. and in the liver was 12.67 μg/kg of wet wt. and ranged from 0.5 to 142 μg/kg of wet wt. Wild boars as omnivorous mammals could accumulate higher levels of Hg comparing to other large game animals. The diet is considered to be the most important pathway of Hg exposure that includes roots, bulbs and tubers and even small animals with higher Hg content than over ground parts of plants preferred by herbivores.

According to the Regulation (EC) No 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC, an exceedances of the maximum levels of Hg were found in 6 samples of muscle tissue and 8 liver samples in 2008-2018. Overall, low relative percentage non-compliant samples found in tissues of wild boars, animal products from wild boars and meat and offal of game animals, that could be constantly exposed to Hg in their habitat.

The aim of our study was evaluation of the concentrations of total Hg in muscle (N=489) and liver (N=394) tissue of three species of cervids: red deer (Cervus elaphus L.), roe deer (Capreolus capreolus L.) and fallow deer (Dama dama L.). All samples were collected by veterinary officers in venison processing plants throughout Poland between 2008 and 2018. The total Hg analyses were performed using atomic absorption spectrometry techniques (DMA and CV-AAS) in Polish Official Control Laboratories and the National Veterinary Research Laboratory as a National Reference Laboratory (NVRI). All analytical procedures used in the official control for determination of Hg were accredited according to the ISO/IEC17025:2005+Ap1 and regularly verified by using certified reference materials and participation in national and international proficiency tests. The data was downloaded from the Central Database and the statistical analysis was performed using R version 3.5.2 by non-parametric tests.

The results showed no statistical differences in concentrations of Hg in the liver and muscles between species of cervids. The median levels of Hg in the liver of fallow deer, red deer, and roe deer were: 1.54, 1.41 and 1.55 μg/kg of wet wt. respectively. The median concentration of Hg in muscle tissue of all species of cervids was 0.5 μg/kg of wet wt. Only one result of Hg concentration in red deer liver was higher than the applicable maximum levels (MLs) of Hg set by the Regulation (EC) No 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC. However, a small number of the MLs exceedances and low concentrations of mercury found in the liver and muscle tissue of cervids, may not pose a risk to the health of animals nor to venison consumers in Poland.

T.P.2.2

TOTAL MERCURY BIOACCUMULATION IN TISSUES OF WILD CERVIDS: RESULTS OF THE NATIONAL MONITORING PROGRAM IN POLAND

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The concentration of mercury (Hg) is annually monitored in various food commodities within the framework of the Polish National Monitoring Program that is carried out according to the European Union and Polish law regulations. The Monitoring Program covers samples of meat and offal of game animals, that could be constantly exposed to Hg occurring in their habitat.

The aim of our study was evaluation of the concentrations of total Hg in muscle (N=489) and liver (N=394) tissue of three species of cervids: red deer (Cervus elaphus L.), roe deer (Capreolus capreolus L.) and fallow deer (Dama dama L.). All samples were collected by veterinary officers in venison processing plants throughout Poland between 2008 and 2018. The total Hg analyses were performed using atomic absorption spectrometry techniques (DMA and CV-AAS) in Polish Official Control Laboratories and the National Veterinary Research Laboratory as a National Reference Laboratory (NVRI). All analytical procedures used in the official control for determination of Hg were accredited according to the ISO/IEC17025:2005+Ap1 and regularly verified by using certified reference materials and participation in national and international proficiency tests. The data was downloaded from the Central Database and the statistical analysis was performed using R version 3.5.2 by non-parametric tests.

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T.P.2.3

ACCUMULATION AND DISTRIBUTION OF MERCURY IN TRICHOLOMA SP. MUSHROOM SPECIES COLLECTED IN CROATIA AND POLAND

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Mercury is a metal that is usually present in the Earth’s, and its presence in the environment mainly origanates from antropogenic sources. Mercury is one of the most toxic and dangerous environmental contaminants, and can be efficiently bioaccumulated by many mushroom species, even if scarcely present in forest soils. Accumulation, distribution and bioconcentration potential of mercury (Hg) by mushrooms of Tricholoma columbetta, T. portentosum, T. equestre and T. terreum collected from regions within Central and South Eastern Europe are presented. In total, 121 fruiting bodies and 96 soil samples were analyzed. The mercury contents was determined by atomic absorption spectroscopy. The Hg content varied from 0.10±0.06 to 0.71±0.34 mg kg−1 dry matter for caps and from 0.04±0.02 to 0.38±0.13 mg kg−1 dry matter in stems. The Hg content of the soil substratum (0–10 cm layer) underneath the fruiting bodies were different depending on the sampling site and varied from 0.009 to 0.046 mg kg−1 dry matter with mean values varying from 0.013±0.003 to 0.028±0.006 mg kg−1 dry matter. Results showed generally low levels of mercury, both, in Tricholoma mushroom species and forest topsoil for investigated locations. In terms of the anatomical parts of the fruiting body (cap-stem), a considerably greater concentration of the mercury was found in the caps than the stems at ratio between 1.6±0.6 and 3.9±1.8. The calculated bioconcentration factors (BCF) showed that all of the mushrooms can be regarded as a mercury bioaccumulator. The T. equestre mushroom species showed moderate ability to accumulate Hg with bioconcentration factor (BCF) values ranging from 18.0±7.0 to 37±18. The consumption of analyzed mushroom species from background areas can be considered safe from a toxicological point of view because the determined concentrations of mercury are below the provisional weekly tolerance limit (PTW) of 0.004 mg kg−1 body mass. These data are important in view of toxicology, food chemistry and environmental protection.
T.P.2.4

METHYLMERCURY EXPOSURE FROM FISH CONSUMPTION IN WOMEN OF CHILDBEARING AGE IN AYAPEL, COLOMBIA

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The municipality of Ayapel is located in the department of Córdoba in northwestern Colombia on the Ciénaga de Ayapel banks, which is the main food and water pantry for the region. Unfortunately, this marsh has been impacted for decades by the artisanal and small-scale gold mining activities, as well as ferronickel and coal exploitations performed in its surroundings. This study evaluated the risk to human health from mercury exposure through fish consumption in 163 women childbearing age (18–38 years old) in Ayapel.

Questionnaire-based surveys were used to collect data on fish consumption (type and frequency), age, body weight, among other variables, and information about the weekly amount of fish consumed. Total mercury (Hg-T) and MeHg concentrations were analyzed in hair samples, and the weekly intake of Hg-T and MeHg (WI-Hg) due to the consumption of fish was also calculated. Our results show that Hg concentrations in carnivorous fish were significantly higher (p<0.05) than in the others. On the other hand, concentrations of Hg-T in women hair ranged from 0.11 to 6.71 ppm, and the mean value for the subjects under study was 1.41 ± 1.20 ppm. MeHg percentage in the hair samples ranged from 64 to 90% with a mean value of 83 ± 5 %. Values of WI-MeHg ranged between 0.004 and 13.2 with a mean of 1.4 ± 2.0. A high percentage (23%) of subjects had WI-MeHg values higher than the tolerable provisional weekly intake of 1.6 μg/kg/week. Moreover, significant correlations (p<0.01) were recorded among the concentration of Hg-T and MeHg in hair with WI-Hg (r = 0.27), WI-MeHg (r = 0.27) and the amount of fish consumed weekly (r = 0.24). In sum, our results suggest a risk scenario for health due to exposure to MeHg due to the consumption of fish in one of the most sensitive population groups. Likewise, these results on women of childbearing age revealed a worrying situation, which should serve to the competent authorities for the design and implementation of preventive actions in search of the sustainability of the well-being and health of current and future generations.

T.P.2.5

MERCURY IN FOREST SOIL AND FUNGI NEAR THE LOCAL NON-FERROUS FOUNDRY

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This study aimed to get an insight into the contamination with mercury in surface forest soil and soil cores and accumulation of the element in mushrooms grown in the forested area (ca. 150 hectares) in the vicinity of the local non-ferrous foundry. Among the studied mushrooms were both edible and inedible species important from an ecotoxicological and bio-indication perspective. The forested area studied (Sobowidz forest) is located north-east, east, south-east and south of the foundry. Between the foundry and the forest from the north, northeast and east side is a relatively narrow strip of residential buildings of the Sobowidz village. Forest soil, soil cores and mushrooms were sampled in 2016–18. The determinations of mercury concentration of mushroom and soils samples was performed using cold-vapor atomic absorption spectroscopy (CV-AAS; MA-2000, Nippon Instruments Corporation, Takatsuki, Japan) by a direct sample thermal decomposition coupled with gold wool trap of Hg and its further desorption and quantiative measurement at a wavelength of 253.7 nm. Each mushroom and soil sample was examined at least in duplicate. The analytical instrument used was a mercury analyzer (MA-2000, Nippon Instruments Corporation, Takatsuki, Japan) equipped with an auto-sampler and operated in low mode (3–20 ng Hg per sample). The limit of detection (LOD) of Hg in this study was 0.003 mg kg⁻¹ dry biomass, and the quantification limit (LOQ) was 0.008 mg Hg kg⁻¹ dry biomass. A running AC/AQ assurance was performed through the analysis of blank samples and certified reference materials such as: CS-M-1 (dried mushroom powder of Suillus bovinus), CS-M-3 (Boletus edulis) and CS-M-4 (Lecinimum scabrum). The surface layer (0-1 cm) of forest soil samples examined so far contained mercury in mean concentration of 0.18 ± 0.04 mg kg⁻¹ dry matter (the total range 0.014 ± 0.004 to 0.24 ± 0.01 mg kg⁻¹) and what substantially exceeded a typical content of < 0.05 mg kg⁻¹ dry matter in soils from the background (unpolluted) sites in Poland. The mushrooms showed a range of mercury content, and in some species and sampling points contamination with element exceeded the content typically observed in fungal materials from the reference localizations. Study supported in part by national Science center in Poland under project no. UMO-2016/23/N/NZ9/02746.

T.P.2.6

ADAPTIVE MANAGEMENT OF RESERVOIR MONITORING: METHYLMERCURY UPTAKE AND POTENTIAL DOWNSTREAM TRANSPORT

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Newly formed reservoirs associated with hydroelectric developments in Canada are monitored for standard-length total mercury (THg) concentrations in target fish species as part of the national Environmental Effects Monitoring (EEM) program. Target species are typically those of Commercial, Recreational, or Aboriginal fishery importance. Routine water analysis also accompanies EEM monitoring, but at a spatial and temporal scale that may not allow detailed evaluation of methylmercury (MeHg) evolution within the reservoir nor potential downstream transport and uptake. The latter is important to assess because communities located downstream may use fish resources located well below reservoirs. A newly flooded headpond associated with ongoing reservoir development was created in 2017, in Labrador, Canada. Monitoring has included the required fish standard-length THg assessments as well as additional, detailed monitoring of MeHg concentrations in water and young-of-year (YoY) fish species with limited home ranges to compare temporal changes. The YoY fish are being adaptively incorporated into the monitoring as early indicators of within-reservoir MeHg increases and possible downstream transport. The YoY and length-standardized fish and water data are currently being contrasted for their effective-ness and sensitivity for assessing temporal and spatial changes in MeHg from reservoir creation.

T.P.2.7

TOTAL MERCURY IN HUMAN HAIR IN FOUR RIVER-SIDE POPULATIONS, AMAZON, BRAZIL

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Total mercury (THg) is a global pollutant that affects human health. Hair is often used as a good biomarker to assess human exposure to THg. Considering the high toxicity of Hg, an investigation was conducted to determine the THg levels in hair samples from individuals that living in three districts adjacent to rivers, located in the Amazon Region, Brazil Northern. Sampling occurred in Cururupé, Acuí and Vila de Beja districts between 2012 and 2013. These districts have similar socio-demographic characteristics and fish consumption, which may increase the risk and Hg exposure. Age, gender and fish consumption were the independent variables analyzed. THg Levels were determined by induced plasma coupled mass spectrometry (ICP-MS). Participants were 298 individuals, 130 men and 168 women, with a mean age of 31 years. Regarding fish consumption, 95.6% (N = 285/298) reported consuming fish. The mean level of THg in hair was 1.06 ± 1.38 μg.g-1 in the total population studied, ranging from <0.26 to 16.51 μg.g-1. Regarding gender, mean levels of THg were 1.37 μg / g in men and 0.82 μg.g-1 in women. Individuals who consumed fish had two-fold higher mean THg levels compared to non-consumed (1.08 versus 0.46 μg.g-1). The THg levels in the hair as the weekly fish intake was higher in those consuming more than 3 fish/week meals (1.23 μg.g-1) compared to those consuming less than 3 meals / week (0.99 μg.g-1). The THg concentrations in hair of 26% of the population showed levels higher than 1.0 μg.g-1, limit of THg in hair recommended by the US Environmental Protection Agency (<1.0 μg.g-1) and may be the result of habits characteristic of the population and/or contamination of the aquatic environment. To better understand the current situation of THg levels in the hairs of riverine populations of the Amazon, human biomonitoring is necessary since elevated levels of THg can affect human health and cause irreversible damages.

EVALUATION OF THE BIOACCUMULATION KINETICS OF TOXIC METALS IN FISH (A. BRASILIENSIS) AND ITS APPLICATION ON MONITORING OF COASTAL ECOSYSTEMS

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This study proposes a pro-active approach of methylmercury (MeHg), total mercury (HgT), arsenic (As), cadmium (Cd) and lead (Pb) in situ bioaccumulation in fish (Atherinella brasiliensis) muscles from the external sector of Guanabara Bay coast, as a study case for an improvement on the risks monitoring of fishing and fish consumption by humans in coastal environments. This approach included an hierarchical sequence: analysis of the pollutants concentrations and their comparison to safety criteria; correlations between specimens concentrations vs length (as a proxy of exposure time); projections of concentrations in key lengths (sexual maturation, asymptotic, safety limits for fishing and median of fish population) through polynomial regressions, dose-response analysis (Probit), decreasing curves, and incorporation rates using only three length intervals. The results of the projections were satisfactory, evidencing the legal risks. The gradients of concentration and incorporation rates were ascending for MeHg and HgT (continued bioaccumulation) and descending for As, Pb and in lower intensity for Cd (possible bio dilution mitigating the initial high concentrations).

T.P.2.8

MERCURY CONCENTRATIONS IN COMMERCIALLY IMPORTANT FISHERIES SPECIES IN THE GULF OF MAINE, USA

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The Gulf of Maine is a complex ecosystem host to numerous productive commercial fisheries. In the Gulf of Maine, data for mercury (Hg) in sediments and in mussels have been documented along the coastline but very little is known about the concentrations in the food webs of either the inshore or offshore regions of the Gulf. To date there are no publicly available data on Hg levels in commercial species for offshore regions where most of the productive fisheries are located. The current study examined total Hg, selenium (Se), and total lipid concentrations in fillets from six commercial species: Atlantic cod (Gadus morhua), spiny dogfish (Squalus acanthias), Atlantic herring (Clupea harengus), red hake (Urophysichus chuss), silver hake (Merluccius bilinearis), and skates (Leucoraja spp.) captured in both nearshore and offshore locations. Individuals of Atlantic cod, spiny dogfish, and skate presented tissue concentrations above the US EPA 300 ppb regulatory threshold. Most species indicated a strong positive relationship of Hg with length (width for skates), as anticipated, with species-specific differences in Hg concentration observed. Se concentration was less variable among species than Hg. Relationships with catch location and feeding mode for Hg, Se, and lipids will be discussed.

T.P.2.9

EFFECT OF THE ROUND GOBY INVASION ON FISH MERCURY BIOACCUMULATION IN ONEIDA LAKE, NEW YORK, USA

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Food web structure plays a large role in the extent of contaminant exposure in fishes. Invasive species can cause significant changes in the bioaccumulation and biomagnification rate of mercury (Hg) in aquatic food webs. In New York State, several lakes have recently experienced invasion by the Round Goby (Neogobius melanostomus) including New York’s largest inland lake, Oneida Lake. Research on the effect of the Round Goby on Oneida Lake reveal this species has become abundant and incorporated into the diets of all the major piscivores in the lake. Changes in young-of-year growth rates in Walleye (Sander vitreus) and black bass species have also been observed. In 2010, sampling was conducted to measure Hg concentrations in six species including Smallmouth Bass (Micropterus dolomieu), Walleye, White Perch (Morone americana), Yellow Perch (Perca flavescens), White Sucker (Catostomus commersonii), and Freshwater Drum (Aplodinotus grunniens). Sampling of the same species was repeated in 2016 and 2017, after the Round Goby invasion in 2013/2014. Comparison of fish tissue concentrations in 2010 to 2016 showed mean Hg concentrations declined in all species, with significant declines for Walleye and White Perch. Future work will include analyses of diet composition and fish age and growth with respect to fish Hg concentrations. This study will inform to what extent the changes in fish Hg bioaccumulation patterns in Oneida Lake can be explained by the invasion of Round Goby and the mechanisms underlying those changes.
T.P.2.11

M2B DATABASE: MERCURY CONCENTRATION IN MEDITERRANEAN BIOTA

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As of its its neurotoxicity and impacts on behaviour, physiology and reproductively successful, mercury concentration in marine biota – the main entering point in the human body – has been investigated in the Mediterranean Sea since 1970s. The large number of studies has substantially advanced the knowledge on new analytical and modelling techniques but less in terms of data gaps, temporal and spatial lacks and effective trends of biomagnification process. To fill these gaps and make such big investigation digitally available and prone to be analysed with advanced statistical techniques, a large database has been constructed with data collected from available literature, both peer-reviewed and grey, from the end of 60 until 2015. The M2B - Mercury in Mediterranean Biota database includes 24465 records retrieved from 541 sources and includes organic and inorganic mercury concentration measured in different tissue of organisms from Animalia, Plantae and Chromista Kingdoms. The methodology was based on literature survey, data collection, information harmonization, unique taxon definition, assignment of geographic location and check of overlapping data. Data distribution is significantly affected by the high number of Mytilus galloprovincialis samples, which was frequently used as a biindicator. In addition, the distribution of Sardina pilchardus, Thunnus thynnus, Xiphias gladius and Diplodus sargus has been considered for an indicator. In addition, the distribution of Sardina pilchardus, Thunnus thynnus, Xiphias gladius and Diplodus sargus has been considered for a first quantitative and spatial mercury analysis, leaving more detailed analyses on trends to more specific publications.

T.P.2.13

MERCURY IS A GLOBAL CONTAMINANT IN COMMERCIAL CAT AND DOG FOODS

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Globally, businesses providing products and services to pet (cat and dog) owners are growing each year as pet ownership continues to increase annually. In 2019, the global pet care market is anticipated to exceed $152 billion USD, with pet food securing the largest product segment of the market. As demands for pet food products, especially premium and natural and organic products, increase, it is imperative that the quality of the products is held to the standards set by international and national regulators. However, studies have demonstrated that many pet food products from different international markets (e.g., USA, Brazil, Turkey) contain mercury at concentrations that far exceed the maximum tolerable limit set by various regulators, with some pet foods containing mercury concentrations orders of magnitude above the maximum tolerable limit. Limited studies to date have only quantified total mercury concentrations in pet foods, and have used analytical techniques with either high detection limits or low recoveries for mercury. Through our current research, we are determining the total mercury concentrations in 100+ commercial cat and dog foods from the USA market using a direct mercury analyzer, which has the lowest detection limit and highest recovery of all analytical techniques for mercury, as well as determining the methylmercury concentrations in the foods. Methylmercury is a potent neurotoxin that bioaccumulates in many fish species that are commonly used as ingredients in commercial pet foods. It is possible that a substantial portion of the total mercury in pet foods is present as methylmercury, especially in fish-based foods, leading to large and disproportionate health impacts on pets. Additionally, we are using molecular genetic techniques to identify the source(s) of animal proteins used in commercial pet foods to determine if one or more sources of animal protein is correlated with higher mercury and methylmercury concentrations. The results of our work will provide the public with information regarding which pet foods and ingredients pose the highest risk of mercury exposure to their pet, and animal health care professionals and pet food manufacturers with data that can be used to identify safer sources of protein for pets, and assist in establishing mercury consumption advisories for cats and dogs.
MERCURY CONCENTRATIONS IN FISHES FROM THE UPPER PARANA RIVER BASIN, BRAZIL

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Mercury (Hg) contamination is a global issue with even remote regions receiving significant inputs. This is largely due to atmospheric deposition of mercury from the burning of coal and other practices. Of particular concern are Neotropical regions with high biodiversity and fisheries of socioeconomic importance. The Paraná River is the second longest river in South America, the upper third of which is one of the most impounded river systems in the world. While the ecology of this system has been relatively well studied, few studies have addressed mercury contamination. Fish tissue samples for this study were obtained opportunistically from material previously collected for studies of carbon flow and food web structure. Fishes were collected from 10 reservoir and river sites located in and around the Upper Paraná River floodplain. The dataset for this analysis includes 467 individuals representing 63 species from 22 families. Species composition of the dataset varies significantly among sites. Samples were analyzed for total mercury content using a DMA-80. Total mercury concentrations in fish muscle across all sampling sites ranged from 0.30-1,008.69 µg/kg wet weight. Only a single fish demonstrated a muscle mercury concentration above the permissible limit for human consumption (1,000 µg/kg wet weight) in Brazil. Mean muscle mercury concentrations varied between sampling sites, due in part to differences in species compositions in the dataset. Comparing trophic guilds, standard length and mass were positively correlated with muscle Hg concentration in piscivorous Hoplias malmbericus and piranha species, but not detrivorous Prochilodus lineatus. These data represent an initial assessment of mercury concentrations within fishes, including commercially important species, of the upper Paraná River basin.

TRACE DETERMINATION OF METHYLMERCURY IN NON-PIGMENTED, RED, AND BLACK RICE USING SOLID PHASE EXTRACTION HIGH PERFORMANCE LIQUID CHROMATOGRAPHY COLD VAPOR ATOMIC FLUORESCENCE SPECTROMETRY

MANORUT, Parinda1; FELDMANN, Jörg1; KRUPP, Eva1
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Rice (Oryza sativa), one of the most important staple food worldwide, was found as the potential source of methylmercury (MeHg) exposure in human. Its growing condition particularly rises MeHg accumulation in the grains. Even though the MeHg concentration in rice grains is considered low, its high consumption can contribute to a higher risk of MeHg exposure. Previously, a simple and reliable method consisted of online preconcentration or solid phase extraction high performance liquid chromatography cold vapor atomic fluorescence spectrometry (SPE-HPLC-CV-AFS) was developed for trace determination of MeHg in rice. In this project, a different type of rice grains; non-pigmented, red, and black rice from markets and fields were analysed. The MeHg concentration in rice samples from this work did not exceed PTWI even with high rates of rice consumption present in some countries. However, a t-test showed that MeHg concentrations were significantly different p < 0.05 between types of grain. It was found higher in red rice (3.22 ± 2.77 µg/kg, n=24) compared to other varieties (1.58 ± 0.87 µg/kg, n=32).

EXAMINING DYNAMICS AND SOURCES OF ELEVATED MERCURY EXPOSURE IN AMAZONIAN INDIGENOUS POPULATIONS IN MANU NATIONAL PARK, MADRE DE DIOS, PERU

FERNANDEZ, Luis E.1; VEGA, Claudia M.1; GONZALEZ, David J.X.2; CHHABRIA, Raveena3; HAFZALLA, George3; CULQUICHICON, Carlos3; LESCANO, Andres G. (Willy)4; SILVA, Juvenal4; MUJICA, Oscar4; HOOPS, Hauke4; SANDERS, John W.1
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An estimated 10,000 recently contacted indigenous people live in the Madre de Dios region in the southern Peruvian Amazon. The primary economic activity in Madre de Dios is artisanal and small-scale gold mining (ASGM) utilizing mercury. In the past three years, two states of emergency have been declared due to environmental mercury contamination. Previous studies have reported elevated levels in indigenous populations in the Amazon basin. Contamination resulting form ASGM has been suggested as the principle source. The Machiguenga are a recently contacted indigenous people that primarily reside in the Manu River basin of Manu National Park, a relatively undisturbed protected area. This study responds to concerns by community leaders regarding possible mercury exposure. We will present the results of a multi-year study in three Machiguenga communities, which started in 2014. We assess methylmercury exposure using hair as a biomarker and admin-
MISLABELING AND MERCURY CONTENT IN SEAFOOD IN PERU

BIFFI, DanIELLA1; LOPEZ-MOBI LIA, Andrea2; KELZE, Shaleyla3; WIL LIAMS, Dean4; CHUMCHAL, Matthew5; WEINBURGH, Molly1

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Peru is experiencing a “gastronomic boom” that is increasing the demand for seafood. Several market-based initiatives have been created in order to inform consumers about sustainable choices. We chose two of these popular initiatives, Size Does Matter and BoVEDA, and investigated two implicit assumptions: seafood is not mislabeled and the recommended species contain low levels of methylmercury and are therefore healthy for consumers. Between May and July 2017, we collected 449 seafood samples, representing a minimum of 64 different species, from markets and restaurants in Lima and Tumbes, Peru. We extracted DNA from all samples and sequenced them at the mitochondrial cytochrome oxidase I gene (COI). A sub-sample of 270 samples were analyzed for mercury. The species identified were grouped into seven categories (sharks, rays, billfish, white meat, dark meat, commercially desirable species, and other). There was an overall mislabeling rate of 32.7%. Mercury content was compared to US-EPA (300 ng/g) and Peruvian guidelines (1,000 ng/g). Seventy-five samples (28%) had mercury values above the US-EPA recommendations and 13 samples had values above the Peruvian recommendation. Our results indicate that mislabeling is a common practice. Overall, if consumers bought only the recommended (“best choice”) fish for each initiative, they would receive a different species 25% and 15% of the time. Moreover, mercury concentrations below Peruvian guidelines may erroneously indicate that consumption of some predatory species is healthy for consumers. Sustainable seafood initiatives seek to change behaviors, however, mislabeling hampers the objectives of these, and some recommendations are even unsafe for consumers considering our results. Consumers’ health should be considered as part of the efforts to ensure seafood sustainability.
en daily over a week period (100 g ×7) could provide mercury in dose from 0.0019 to 0.0096 (median 0.0068) mg kg⁻¹ body mass. In view of the reference values for safe intake of inorganic mercury and moderate consumption, the fried bolete mushrooms could provide mercury in doses exceeding the safe limit.

**T.P.2.21**

**SIMULATED HUMAN EXPOSURE TO METHYLMERCURY IN POTENTIAL CONSUMERS OF SPINY DOGFISH SQUALUS ACANTHIAS HARVESTED IN SOUTHERN NEW ENGLAND WATERS**

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Spiny dogfish Squalus acanthias are small sharks, which are widely distributed on the continental shelves of six continents. Due to shifts in the marine environment as well as changes in fishery regulations, spiny dogfish have supplanted more lucrative groundfish species (Gadus morhua, Melanogrammus aeglefinus, etc.) as a target species for the day boat fishery in Southern New England, USA. However, due to the species’ long lifespan and high trophic level, concerns about mercury contamination continue to hamper the growth of a domestic market for the species in the United States. We tested fillet meat from a representative sample of spiny dogfish (n = 103) landed by commerical harvesters in Chatham, Massachusetts, a port that accounts for a substantial portion of American spiny dogfish landings, for methylmercury (MeHg; n = 14) and total mercury (THg; n = 103) during the 2018 summer fishing season. Concentrations of THg and MeHg were correlated. THg was with fish weight, with heavier fish being higher in total mercury (p = 0.025). Following the assessment methods of the United States Food and Drug Administration (FDA), we found that spiny dogfish landed in Chatham would be ranked in the “good choices, 1 serving per week” category with a bootstrapped mean mercury content between 0.348 and 0.411 ppm (wet weight). Additionally, we simulated mercury exposure for humans consuming spiny dogfish from this source, and found that all age groups could consume spiny dogfish at least twice per month with a < 5% chance of exceeding the FDA reference dose, assuming no other mercury was consumed. These concentrations of mercury are comparable to other studies conducted in New England, and show substantially lower levels of Hg levels in comparison to other locations i.e. Crete and Australia.

**T.P.2.22**

**ARTISANAL AND SMALL-SCALE GOLD MINING IN ZIMBABWE: IDENTIFICATION OF CHRONIC INORGANIC MERCURY INTOXICATION**

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**Background:**

In artisanal and small-scale gold mining (ASGM) mercury is used to extract the gold from ore. Mercury is neurotoxic and exposure to it leads to health impairments in goldminers. In ASGM chronic mercury exposure is common, leading to mercury intoxication. To identify intoxication it is necessary to assess the mercury concentration in human samples like urine and test for mercury-associated symptoms. **Objective:** Identification of chronic inorganic mercury intoxication of ASG-miners from Kadoma and Shurugwi, Zimbabwe, by applying an algorithm with mercury concentration in urine and a medical score sum. **Methods:** A cross-sectional assessment was performed in Kadoma and Shurugwi, Zimbabwe in March 2019. Urine samples and a medical assessment of 200 ASG-miners were compiled in a two-week field project. On-site mercury concentration in urine was analyzed using cold vapor atom absorption spectroscopy (CV-AAS). Neuro-motoric and medical questionnaires and examinations showed typical symptoms of chronic inorganic mercury intoxication. Both, mercury concentrations in urine and specific health symptoms were combined in an algorithm to identify cases of chronic inorganic mercury intoxication. **Results:** 200 ASG miners from Kadoma and Shurugwi were assessed. Mercury concentration in urine was increased in some miners. Typical medical symptoms were ataxia, tremor and coordination problems were observed.

**Conclusion:** Miners in Zimbabwe use toxic mercury to extract gold from ore. Their levels of mercury in urine were increased, typical symptoms of intoxication were observed.

**Acknowledgements:**

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**T.P.2.23**

**REDUCTION OF THE USE OF DENTAL AMALGAM IN THE CABINETS OF THE CITY OF COTONOU IN BENIN (WEST AFRICA)**

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In addition to the public health network, there is an emergence of a private health network of all standing with multiple dental medical centers. This study explored the problem of the use of dental amalgam and medical waste containing mercury in the dental offices of the city of Benin. The use of mercury dental amalgam is developing in the city with the expansion of the opening of dental offices. In dentistry, amalgam refers to a material used to seal cavities resulting from the removal of tooth tissue affected by cavities. Although still called “filling”, dental amalgam does not contain lead. It contains mercury bound to other metals. Although the toxicity of mercury is well established and controversial. Unfortunately, uninformed patients and even dental staff handle these harmful filling materials without the slightest precaution. However, dental mercury and its use represent a danger for the populations, in particular on their health and ecological environment. In fact, dental amalgam is a source of increasing risks to the health of producers, consumers and the environment. Patients and dental personnel are mainly exposed to dental amalgam mercury during the placement or removal of fillings and the accumulation of mercury from dental amalgam is found in the kidneys, brain, gastrointestinal system, kidney liver or tissues of the jaw. Pregnant women and children are especially the most vulnerable. NGOs denounce the anarchic use of mercury amalgams in dentistry. They advocate for a mercury-free dentistry especially that the alternative filling materials are the same color as the teeth and are increasingly popular: they allow a more aesthetic result and the dentist must remove less dental tissue. A reference study is needed to enable local, municipal, national and international authorities (SAICM) to understand the effects of using mercury amalgam, the courses on amalgams given by dental teachers in the Faculties. Health and especially the level of adoption of the Minamata Convention in Benin in order to sound the alarm. To develop the present study, the dental offices of the city of Cotonou are visited. At the level of each health facility, all categories of health professionals available to know Doctors dentists, assistants, patients are interviewed. A total of 85 actors took part in our questionnaires throughout the city. In addition, the focal point of the Minamata Convention was also interviewed in order to take stock of the implementation of the directives of this Convention on the national territory.

**POSTER ABSTRACTS • ICMGP 2019 • 14th International Conference on Mercury as a Global Pollutant • September 8-13 2019, Krakow, Poland • 191**
AIRBORNE MERCURY LEVELS AT COMPRO ORO SHOPS IN PERU

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Gold mining using the mercury amalgamation process continues to present serious community and occupational exposure problems throughout the world. Current estimates claim 30% of all processed gold is produced using mercury amalgamation with over 10 million people involved in artisanal and small scale gold mining. In Peru, there has been a 400% increase in the ASGM activities and is ranked 6th in worldwide gold production. It is estimated that one out of 28 people in Peru are associated with artisanal gold mining with Madre de Dios, an Amazonian State in Peru, accounting for 70% of mined gold.

In an effort to better understand the worker airborne mercury exposures, this paper presents the results of mercury vapor area air sampling during the amalgam burning processing step where Hg/Au amalgam is heated and the mercury driven off as a vapor-phase. Small-scale artisanal gold miners often do not have the equipment to burn off mercury from the amalgam and resort to local shops for this service. These Compro Oro (We Buy Gold) shops can be found in villages adjacent to local mining efforts in both the alluvial mining areas of the Amazon (Madre de Dios) and the hard rock communities of the Andes (Ollachea). In addition to thermal processing of the mercury amalgam, these shops sell liquid mercury to miners, supplies and at times, even portable retorts. A total of 23 gold shops were sampled in 6 mining villages between 2016-2019. In almost all cases, the worker exposure levels exceeded internationally accepted health standards. In particular concern was the finding that the women, often accompanied by their young children, operated these shops. This presentation will present the results of workplace sampling, observations of workplace practices as well as a discussion of efforts and challenges in managing occupational health risks in small-scale artisanal enterprises in low and middle-income countries.

HIGH METHYLMERCURY EXPOSURE IN HUMANS: A CONCERN FOR THE POPULATIONS OF THE AMAZON TRIPLE FRONTIER

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The Western Amazon is the most preserved part of the Amazon, however, Artisanal and small scale gold mining (ASGM) and have been spreading in this region since the beginning of the 21st century, it’s causing significant socio-environmental impacts. ASGM is the main source of anthropogenic mercury (Hg) pollution in the environment, where it can turn into methylmercury (MeHg) and cause serious public health issues. Fish consumption is the most important pathway of MeHg exposure. The Upper Solimões region, Western Amazon Basin, has one of the highest fish consumption rates of the Amazon, it’s more than 14 times higher than the global average estimated for 2017. This study was aimed to evaluate the human MeHg exposure through fish consumption in the Amazon Triple Frontier. The MeHg concentration in muscle of 7 species of fishes was determined using Gas Liquid Chromatography with Electron Capture Detector (GLC-EC). The estimated weekly intake (EWI) in adults can be above the provisional tolerable weekly intake (PTWI) of MeHg, 1.6 µg.kg⁻¹ body weight per week, for Hoploerythrus unitaeniatus, Hoplias malabaricus, Pellona castelnauana, Pimelodus Blochii, Prochilodus nigricans, and Pseudoplatystoma fasciatum. The EWI can reach 12.9 µg.kg⁻¹ bw for women of child-bearing age, when associated to the consumption of P. fasciatum, one of the most important commercial catfish in the Amazon. The high EWI of MeHg can cause many issues to human health, especially for pregnant women, infants, children, and other vulnerable groups. Fish is the main and most abundant source of nutrients for the traditional communities of the Amazon. Fish have a great social, economic, and cultural importance for the region. The reduction in the fish consumption isn’t a viable option to avoid human MeHg exposure in this region. Control measures for protecting the environment and eliminating the anthropogenic use of Hg should be adopted as soon as possible in the Western Amazon. The “gold rush” in this region is causing environmental impacts and social conflicts that can cause concerns to “One health”, the high MeHg exposure in humans is already one of them.

MERCURY IN BLOOD AS BIOMARKER OF ENVIRONMENTAL EXPOSURE FROM INDUSTRIAL POLLUTANTS IN AMAZON

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The mining and industrialization processes in Amazon are known anthropogenic sources of pollutants, as the mercury (Hg), toxic metal with harmful effects on health. Although the soil of the Amazon region presents natural levels of Hg, this study evaluated the Hg environmental exposure to individuals living in two districts in Barcarena City, Brazil Northern. The study was sectional and quantitative, involving individuals from two districts: Vila de Itupanema (VIT), located near the aluminum industries, and Laranjal (CLA), distant about 9 km from the industrial area. Blood sampling and epidemiological survey application, VIT (N=209) and CLA (N=296), occurred in the 2012 and 2013. The results were stratified by age (≤ 10 years, 11 to 17 years, 18 to 39 years and ≥ 40 years), sex, population not exposed (≤8 µg.L⁻¹) and exposed (between 8 and 30 µg.L⁻¹). The Hg analyzes were performed by mass spectrometry coupled with induced plasma (ICP-MS). The mean Hg level in VIT was 4.908 (0.130 - 22.070) µg.L⁻¹, with higher levels in youngs from 11 to 17 years old (5.643 µg.L⁻¹, N = 64). In this district, 23% of subjects presented blood Hg levels between 8 and 30 µg.L⁻¹ and, in this universe, about 40% are between 18 and 39 years old and the higher mean level was in children ≤10 years (12.410 µg.L⁻¹, N = 8). In CLA, the mean Hg level in blood of the population was 0.709 (0.067-7.530) µg.L⁻¹ and the highest mean was found in individuals in the age range ≥40 years (N=75). The mean Hg level in the blood was about 14 times higher in VIT when compared to CLA. In VIT, 43 individuals are exposure to Hg. No individuals register with levels above 8 µg.L⁻¹ in the CLA, thus demonstrating that the proximity of the industrial area increases of Hg exposure.
**T.P.2.27**

**MERCURY BIOACCESSIBILITY IN SHRIMPS MARKETED IN THE AMAZON, BRAZIL**

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In the Amazon, the shrimp specie Macrobrachium amazonicum is one of the main protein sources of the population and is expanding throughout the region. The crustaceans consumption may be exposure route to metals such as mercury (Hg). The metals bioavailability to the population also depends on the the cooking processes used. In this study, the total mercury (THg) bioaccessibility and its seasonal influences were evaluated in muscle tissues (raw and boiled) of shrimps marketed in Belem City, Amazon Region. The shrimp were purchased randomly in the in free markets and supermarkets in two season (dry and rainy) and were removed the edible portion. To evaluate the THg bioaccessibility the crustaceans were also cooked in teflon pans. Twenty-five specimens were used per treatment. 200 mL of deionized water was added and the cooking continued for another 2 minutes. The acid digestion occurred in teflon tubes, with addition of 0.1 g of shrimp tissue, 1.5 mL of nitric acid (HNO3) and 0.5 mL of hydrogen peroxide (H2O2), and was accelerated in microwaves (MARS, 5). The volume was completed to 10 ml with HNO3 (1%) aqueous solutions. The THg analysis occurred in an inductively coupled plasma mass spectrometer (ICP-MS) and for the validation of the method was used the certified reference material (DORM-3). Significant differences (p <0.05) were observed in the levels of metals found in raw and cooked shrimps, as well as between seasonal periods (p <0.05). In raw and cooked shrimps, respectively, were found 25 and 19 ng.g⁻¹ in the rainy season and 8 and 4 ng.g⁻¹. These results express reductions of 24% and 50% of THg in cooked shrimp in each season. A probable explanation for the THg reduction in boiled shrimps may be associated with high volatility of this metal, favored by heating. The WHO (World Health Organization) does not recommend the consumption of crustaceans with levels higher than 500 ng.g⁻¹. All shrimp specimens associated with high volatility of this metal, favored by heating. The WHO (World Health Organization) does not recommend the consumption of crustaceans with levels higher than 500 ng.g⁻¹. All shrimp specimens showed concentrations below this limit, however in the Amazon region the consumption of several shrimps in a single portion is recurrent. The results presented indicated a good toxicological quality of the prawns and it was found that Amazonian seasonality influences levels of bioavailable THg in M. amazonicum.

**T.P.2.30**

**BEHAVIOR OF MEHg PRODUCTION IN A HG(II) ION SPIKED PADDY FIELD SOIL DURING MULTI-YEAR RICE CULTIVATION AND THE MECHANISM OF MEHg ACCUMULATION IN RICE GRAIN**

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The use of Hg in artisanal and small-scale gold mining (ASGM) activity has increased in the rice-producing regions of many developing countries. Increasing Hg contamination of the environments surrounding ASGM activity areas, such as paddy fields, is therefore a concern. In fact, we previously confirmed that paddy soil is contaminated by released inorganic Hg owing to ASGM activity. Recent studies showed that methylmercury (MeHg) in paddy soil is efficiently accumulated to rice grain. However, the production of MeHg from newly inorganic Hg contaminated paddy soil has not been studied in detail. We therefore prepared a model Hg(II) ion contaminated soil to elucidate the changes with regard to MeHg production in soil over several years and the consequent effects on MeHg accumulation in rice grain. The experiments were performed over three growing seasons (2015-2017) using the same soil in a pot. In 2015, Hg(II) ion was added to the pot only once at 10 mg/kg and was thoroughly mixed under flooding conditions. Rice was planted once a year and flooding condition was maintained during the growing season. After each harvest, the soil was dried, sieved to remove debris, and mixed well. A surface layer (up to a depth of 3 cm) soil was collected every month and a core (1.6 cm depth) sample was also collected once a year. Rice grains were also sampled via collection of the panicle. The T-Hg and MeHg concentrations of these samples were measured.

The vertical distribution of T-Hg concentration obtained from the core sample in the first year was higher in the surface layer (50 mg/kg) and lower in the deeper layer (1.3 mg/kg). After the second year, the T-Hg concentrations in soil were almost 10 mg/kg at all layer. The maximum MeHg/T-Hg ratio of surface layer soil was 0.21% in 2015, 0.09% in 2016, and 0.06% in 2017. Correspondingly, T-Hg concentrations in un-hulled rice grain samples were 0.57 ± 0.06 mg/kg (n = 60) in 2015, 0.13 ± 0.03 mg/kg (n=25) in 2016, and 0.18 ± 0.04 mg/kg (n = 60) in 2017. These results suggest that the effect of spiked Hg(II) ion in paddy soil to rice grain is decreasing as the inorganic form of added Hg(II) ion was converted to other inorganic form leading to a reduced ability to form MeHg. In addition, a hydroponic culture study was also performed to understand the process of MeHg accumulation in rice grains.

**T.P.2.28**

**HUMAN HEALTH RISK ASSESSMENT OF EXPOSURE TO INDOOR MERCURY VAPOUR IN A GHANAIAN ARTISANAL SMALL-SCALE GOLD MINING COMMUNITY**

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People living in and around Artisanal Small-scale Gold Mining communities can be exposed to high concentrations of mercury vapour which would negatively affect their health. This study was conducted in an artisanal mining community in the Upper East region of Ghana. The concentration of mercury in air was measured inside and outside households and was related to human health risk standards. For each household, one measurement was taken from outside and three from inside. In households that burn amalgam, measurements were also made at the place where burning is done. About 91% of the households where amalgam burning is done showed concentrations higher than the USEPA reference dose of 300 [mg m⁻³]⁻¹(3) while the same figure was 64% for the households where amalgam burning was avoided. The maximal instrumental limit (50,000 ng m⁻³) was passed for the highest concentration, so, the upper 95% concentration level was estimated, using censored statistics to be up to 841,835 ng m⁻³ for the fireplaces. Estimated hazard quotients were found to range from < 1 to 108 within the households that do not burn amalgam. In the households where amalgam burning takes place, the hazard quotient had a maximum of 160. The censored data predicted hazard quotients up to 966. The results indicate that both miners and non-miners of the community are at risk of adverse health effects resulting from inhalation of mercury vapour.

**T.P.2.31**

**RISK ASSESSMENT FOR HUMAN HEALTH: MERCURY CONCENTRATION IN HAIR ASSOCIATED WITH FISH INTAKE IN MATO GROSSO, BRAZIL**

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Mercury represents a public health problem and its methylated form found mainly in fish represents a potential risk to human health. Human health risk assessment is an important tool in determining mercury exposure in food. Thus, the objective of this study was to evaluate the human risk associated with fish consumption in three municipalities of the State of Mato Grosso. The municipalities of Caceres, Cuiabá and Poconé are in the basin of the Upper Paraguay and they have varied species of fish ideal for human consumption. Three hundred people distributed in the three municipalities, among them 150 men and 150 women, participated in the study responding to the socio-demographic questionnaire and donating a sample of hair. The analysis of total mercury in 220 (two hundred and twenty) fish samples from 14 species most consumed by the population was carried out in the ecotoxicology laboratory of the State University of Mato Grosso. The analysis of total mercury and methylmercury in human hair was carried out in the laboratory of the National Institute of Minamata Diseases (NIMD). The risk assessment was determined by the frequency of weekly consumption of fish from the population groups involved. The average concentration of THg in the hair of the sampled population was 0.68 ± 1.11 μg / g, 0.56 ± 0.75 μg / g and 0.79 ± 1.00 μg / g in Cáceres, Cuiabá and Poconé respectively. In all, 90 pregnant women were included in this study and the mean concentration of THg in hair was 0.39 ± 0.29 μg.g-1. Methylmercury accounted for more than 80% of total mercury. In fish the highest concentrations of THg in μg.g-1 were found in samples of Hemisorubim platyrynchus 0.43 ± 0.074 and Pinirampus pinirampu 0.37 ± 0.06, in the rivers Paraguay and Cuiabá respectively. The estimated daily intake of Hg for pregnant women, women and men in the Pantanal population varied from 0.26, 0.27 to 0.46 μg.kg-1 pc.dia-1, respectively. Thus, the population of the municipalities of Caceres, Cuiabá and Poconé can be considered at risk and, therefore, it is necessary to consider regulatory measures and public policies regarding fish consumption.

MERGENCY IN TRADITIONAL TIBETAN MEDICINE: A STUDY OF CHEMICAL SPECIATION AND BIOACCESSIBILITY

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Mercury (Hg), a toxic element, has been identified in traditional Tibetan medicine (TTM) with high concentrations. In this study, we conducted experiments to identify the chemical speciation and bioaccessibility of Hg in TTM. The result showed that HgS is not the exclusive form of Hg in TTM, and other compounds could be in large amount, which take 2% to 52% of the total Hg in commonly used TTM s. Hg could also be released from human body into the terrestrial environment as a result of TTM ingestion. In total, an average of 12 μg of Hg (mostly inorganic)/g (range of 0.41–25 μg of Hg/g) in TTM was released into the liquid phase in simulated human gastrointestinal environments. However, different from the results from ingestion by fish, the release of Hg from TTM in the intestinal environment is larger than that in the gastric environment by a factor of 2. In the case of joint ingestion with protein-rich products, releases of methyl Hg and inorganic Hg from TTM in gastrointestinal environments could be significantly enhanced by factors of 9 and 6, respectively. Our study demonstrated that it is necessary to evaluate the clinical safety of different TTM products, as well as their environmental impacts.

EFFECTS OF MERCURY POLLUTION AND DEFORESTATION FROM ARTISANAL AND SMALL-SCALE GOLD MINING ON PEAT SWAMP FOREST ECOSYSTEMS IN CENTRAL KALIMANTAN, INDONESIA

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Artisanal and small-scale gold mining (ASGM) is the largest source of mercury emissions globally. In the Katingan River watershed, Indonesia, this practice involves the release mercury (Hg) into the environment and deforestation of peat swamp forest, putting wildlife and human health at risk. Using birds as biological indicators, we will evaluate how anthropogenic disturbance and restoration of peat swamp forest habitat affects wildlife health, diversity, and occupancy within the Katingan River watershed in Kalimantan, Indonesia. To quantify the effect of methylmercury (MeHg) in the environment on avian populations, I will examine MeHg concentrations in blood and feathers as well as body conditions of birds captured in areas upstream, downstream, and within ASGM sites. To assess how avian occupancy and diversity is affected by peat swamp forest alteration from mining activities, we will perform bird and vegetation surveys across four stages of forest growth. As the Katingan River peat swamp forest ecosystem supports over 350 vertebrate species, 33 of which are considered endangered or vulnerable by the International Union for Conservation of Nature (IUCN), the monitoring of potential disturbance from Hg and deforestation is a critical step in ensuring the peat swamp forest ecosystem remains a healthy environment for the wildlife and local communities that utilize its resources.

MERCURY IN DENTAL AMALGAM: A GLOBAL POLLUTANT

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Mercury in dental amalgam has many pathways into the environment; via respiration, cremation or burial, discharges from dental practices, sewage sludge, or sold illegally for Artisanal and Small-Scale Gold Mining (ASGM). Often referred to as “silver” fillings, they are about 50% mercury. Approximately 340 tonnes of dental amalgam is used annually, representing more than 20% of the total global mercury used in products. While the waste and release of mercury generated in the dental sector is challenging to monitor and manage, the majority of mercury in dental amalgams (about 2/3rds) ultimately enters the environment. The World Health Organization has identified dental amalgam as the principle source of human exposure. According to the US EPA, dental offices contribute the largest source of mercury into sewage treatment plants. Once treated, the remaining waste becomes sewage sludge, which is then disposed of in landfills, incinerated, or sold as fertilizer. The disposal of sewage sludge releases mercury into the ground water or the air. Dental amalgams are not inert, either chemically or environmentally, entering discharge systems that contain sanitants, cleaners, and other compounds that can generate soluble and colloidal mercury, which will be mobilized into the environment. Dental amalgam is often diverted illegally for use in ASGM, the largest source of mercury emissions worldwide. ASGM is active in approximately 70 countries. It’s estimated that 15 million people are working in ASGM, and approximately 5 million are women and children. In 2006, the UNEP reported the official amount of mercury imported in Brazil (2005) was 43.3 tonnes. While this mercury was identified for dental usage, most ended up in ASGM, even though it is illegal to mine with mercury in Brazil.
Another substantial ever-growing source of mercury pollution from dental amalgam comes from cremation. The exact amount of how much mercury released varies considerably, due to the number of dental restorations and body burden. Global cremation rates are increasing for various reasons, such as cost, less formal and less religious restrictions. The national cremation rate in the US is expected to exceed burial rates and is projected to grow to 78% by 2035. ~While measures are being taken to eliminate the use of mercury in dental amalgam, there are existing technologies that can capture and contain dental mercury waste, such as mercury amalgam separators for dental offices, or mercury scrubbers for crematoriums, that will help mitigate the continued environmental contamination from dental amalgam.

T.P.2.35

AQUACULTURE, STOCKING & MERCURY – CAN FISH INTRODUCTIONS BE A DRIVER OF MEHG CYCLING IN AQUATIC ECOSYSTEMS?

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Environmental contaminants, such as lead (Pb) or mercury (Hg), are often found in remote environments and have garnered significant interest from scientists and decision makers. Although atmospheric deposition is a key mechanism in Hg transport, biota (e.g. migrating birds or fish stock) can also act as a direct source of pollution in pristine environments. The concept of migrating biota as a source of environmental contaminants is well documented, as are the adverse ecological effects of non-native species introductions (fish stocking) to freshwater aquatic ecosystems. In addition, it is also known that commercial food pellets, such as fish feed, may act as an important source of contaminant exposure (e.g. Hg, Cd or As) to biota in aquaculture, leading to potential bioaccumulation and biomagnification of these contaminants. Given that the rate of non-native fish introductions have more than doubled over the last decades and that millions of fish are being annually introduced to fresh water ecosystems through stocking programs worldwide, these movements of biomass have an enormous potential to also alter aquatic biogeochemical cycles. Despite its importance, the interaction between fish stocking and methylmercury (MeHg) cycling and exposure in aquatic ecosystems remains largely unstudied. Few efforts have been made to look at the link between toxic metal pollution import via biota and introductions of farmed-fish to freshwater eco-systems, i.e. the humanly induced biovector transport and cycling toxic metals. Here, we discuss the introduction of farmed fish as an anthropogenic perturbation of freshwater food webs, and more importantly, as an overlooked driver of the MeHg cycle with important implications for exposure dynamics in both humans and piscivorous wildlife. Collectively the effects of fish stocking on biodiversity, ecosystem processes and geochemical cycles should be considered substantial. In light of the worldwide increasing trend of aquaculture and fish stocking, and the prioritized international interest in Hg as a global pollutant via the Minamata Convention on Mercury, it is clear that the contamination aspect related to aquacultures and fish introductions must be considered within a sustainable fishery management framework.

T.P.2.36

SPECIATION OF MERCURY IN FISH, WATER AND SEDIMENT FROM PONDS IN ARTISANAL AND SMALL SCALE GOLD MINING COMMUNITIES OF SOUTH WESTERN GHANA

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Artificial ponds constructed by Artisanal and Small-Scale Gold Miners at the sites of their operations provides water for the gold extraction process. Hg-containing effluent from the Hg-Au amalgam formation are directly discharged at the site; and subsequently washed into ponds during rains. Pond fishes are frequently harvested for local consumption. The study investigated the levels of THg and MeHg in water, sediment and fish from ponds within ASGM communities in Southwestern Ghana. THg was determined by CV-AAS (sediment and fish) and CV-AFS (water). MeHg in sediment, fish and water were determined using aqueous-phase propylation (for sediment) and ethylation (for water and fish) followed by preconcentration on Tenax, GC separation and CV-AFS detection. Pond-sediment contained 0.38-13.0 µgHg/g and 1.61-23.5 ngMeHg/g (0.14-0.42% of THg as MeHg). THg in pond-sediments including control-samples were above the USEPA (1985) recommended THg in sediment (0.2 µg/g) but comparable and in some cases higher than the 0.30 µg/g and 243 µg/g reported for pond-sediments in Brazil and Alaska-USA respectively. THg levels in sediment showed a weak positive correlation (r2 = 0.2868) with MeHg levels. Water samples contained 17.5-876 ngTHg/L and 0.45-13.1 ngMeHg/L (1.34-43.04% THg as MeHg). THg levels in water were above the USEPA (1985) recommended Hg Guideline of 12 ngHg/L for protection against toxic levels of bioaccumulation in aquatic organisms. MeHg in water were elevated; with fraction of THg as MeHg as high as 43%, indicating high risk of MeHg uptake by pond-fishes. The fish species had 70-1670 ngTHg/g and 50-1630 ngMeHg/g ww. Fractions of THg as MeHg in the Fish species varies between 32 to 100%. About 72% of fish species had THg as MeHg above 60%; signifying that virtually all the Hg in the fish species were in the methylated form. About 89% of the ponds had fish species with THg and MeHg levels below the WHO (1990) and USEPA (2001) Guideline values of 500 and 300 ng/g respectively. The low levels of MeHg in fish despite the high MeHg levels in sediment and water is as a result of the feeding habit of the fishes. Majority of the fishes are omnivorous but are fed mostly on local plant-based food made from maize and rice. The estimated weekly intake (using the minimum and maximum THg levels) showed that between 0.18 and 4.29 kg of fish has to be consumed by a person to attain the WHO PTWI limit of 300 µg.

T.P.2.37

MERCURY IN SKIN-LIGHTENING COSMETICS: A MERCURY TEST KIT AND A SURVEY IN THAILAND

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Mercury in skin-lightening products are very hazardous to health but these illegal products are widely reported in many countries. In 2018, the Zero Mercury Working Group (ZMWG) reported that 10 % of 338 skin-lightening products from 22 countries had mercury contamination ranging from 93 to 16,353 parts-per-million (ppm), while the Thai samples reached 63%. According to the Minamata Convention, the cosmetics containing above 1 ppm of mercury (including skin-lightening soaps, creams and lotions) must be phased out by 2020. However, based on Global Industry Analyst reported in June 2017, the market for skin lightening products is projected to be a US$ 31.2 billion industry by 2024. The trade of mercury-containing products is expected to grow due to the skyrocketing demand. With the Minamata Convention’s provisions on cosmetics soon to enter into force, a range of measures is emerging to end mercury use in these hazardous products. The mercury screening in cosmetics nowadays using expensive equipment such as a handheld XRF, or analyze the concentration of mercury
vapor with atomic absorption-based instruments. These methods are not practical for general cosmetic consumers. To solve this problem, a rapid test kit for mercury in cosmetics was developed. The high efficiency-screening test is provided in a dropper bottle with a single drop for a sample size of 0.2 cc. If the sample has mercury more than 10 ppm, the solution color will change and can be detected with the naked eye within a few minutes. The screening test kit is stable and can be stored for at least 6 months. The test kit has been commercially available and becomes widely used in Thailand. The positive samples were subsequently analyzed and often found in the range of 1000 to 60000 ppm. Evidently, the rapid mercury test kit for cosmetics will be an effective method to reduce the illegal use of mercury and prevent the health risks for the society as well as reduce the mercury release into the environment.
the potential efficacy of AC as a Hg-remediation tool for specific sites. Activated Carbon can be an effective tool in reducing MeHg risk by reducing MeHg in porewaters. Across the soils chemistries tested, AC efficacies ranged up to a 95% reduction in porewater MeHg. However, sediment and soil biogeochemical conditions impacted the efficacy of AC in reducing porewater Hg and MeHg concentrations. Porewater MeHg reductions were highest in sediments and soils with high dissolved organic matter (DOM), but DOM can reduce the efficacy of AC for total Hg. AC was more effective in highly organic soils than in mineral sediments. Overall, AC was more effective in reducing porewater MeHg than total Hg for most sediment and soil chemistries. AC amendments can also change the balance of MeHg production. Specifically, AC can block the degradation of MeHg in sulfidic soils, resulting in increased MeHg accumulation in the solid phase. The next critical step in evaluating AC for MeHg remediation will be to understand the bioavailability of MeHg bound to black carbons.

T.P.3.3

A PILOT SCALE REMEDIATION METHOD FOR A MERCURY POLLUTED SOIL WITH A MERCURY RESISTANT ACIDIOTHIOBACILLUS FERROXIDANS STRAIN MON-1

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A mercury resistant Acidithiobacillus ferrooxidans MON-1 can reduce mercuric ion (Hg2+) with ferrous iron as an electron donor under acidic conditions to give a volatilizable metallic mercury (Hg0). A pilot scale remediation method for a mercury polluted soil was studied with strain MON-1 to obtain basic information for the removal of mercury from a mass of mercury polluted soils by A. ferrooxidans. 3 m3 of a mercury polluted soil which contains 30 mg/kg of mercury was placed inside a soil mixer (6 m3 of volume). Also, a reaching value of the soil was 0.1 mg/L. MON-1 cells (100 mg of protein) suspended in 5 L of diluted sulfuric acid (pH 2.5) and 200 L of diluted sulfuric acid (pH 2.5) containing 5% of ferrous sulfate were added to 3 m3 of mercury polluted soil. The soil mixer was rotated for 3 minutes in a high-speed mode (approx. 5 rpm) first, and then for about 24 hours in a low-speed mode (approx. 1 rpm). The mercury volatilized from the polluted soil was trapped. The total mercury in 3 m3 soil after 24 hours treatment at 25 oC was 5 mg/kg, indicating that 83% of the total mercury in the original mercury polluted soil was removed by the treatment and a reaching value of the soil was less than 0.001 mg/L which is the Japanese soil environmental reaching standard. This remediation method using mercury resistant A. ferrooxidans cells for mercury polluted soil is promising because there was no need to consume much heat energy to volatilize metallic mercury from the polluted soil (above 360 oC) and a comparatively large amount of mercury was removed within a shorter operation time. After the treatment, the acidified and slurried soil was neutralized and dehydrated by mixing with 20 kg of Portland cement for reuse of the soil.

T.P.3.5

UTILIZING UNMANNED AERIAL SYSTEMS TO RAPIDLY ASSESS HAZARDS AT ABANDONED MERCURY MINES

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Unmanned Aircraft Systems (UASs) otherwise known as drones, are a powerful tool that scientists can use to conduct research and site hazard assessment at remote mine sites. Abandoned mercury mines have many characteristics that are well suited for assessment via UAV deployed sensors. These characteristics include distinctive color of mine tailings, waste rock, and ore processing wastes, as well as elevated air mercury concentrations. The effectiveness of UAS data collection to supplement ground-based data collection for the purpose of assessing hazards at abandoned mercury mines was evaluated by collecting data with a UAS at abandoned mercury mine sites in the western United States. Aerial mapping data from UASs is particularly useful for mine site assessments in remote areas because photogrammetry software can be utilized in the field to generate accurate base maps, profiles, and volume estimates for real time decision making. Air monitoring and sample collection via UAS eliminates the need for site workers to access areas of the mine that may be hazardous due to unsafe structures, open pits, caving sidewalls, or contamination. Several methods using UAS applications to supplement ground-based mercury assessment of various media, were tested. Mercury concentrations in mine tailings, waste rock, and ore processing wastes were determined using field portable X-ray fluorescence (XRF) in shallow soil. The extent of these mercury bearing wastes was mapped via visual identification using a UAS equipped with a high resolution RGB camera to assess the lateral impacts of mercury contamination at the mine and surrounding lands. The feasibility of use of UAS-deployed samplers to evaluate mercury vapors at mine portals, shafts, waste piles, and ore processing buildings is also evaluated. Additionally, conventional photogrammetric analysis of waste piles and excavation pits was used to estimate the volume of waste materials requiring future remediation and to estimate the volume of needed fill to eliminate safety hazards at the site. Detailed orthophotographs were used to guide implementation of site security measures, such as fencing, gates, and barriers and to estimate potential excavation volumes. This presentation will review the UAS data collection methods that were evaluated and the outcome, with discussion on practical uses of UASs and onboard sensors for site hazard assessment at other abandoned mercury sites.

T.P.3.6

INVESTIGATING SUSTAINABLE ADSORBENTS FOR MERCURY POLLUTION IN INDONESIA CAUSED BY SMALL-SCALE ARTISANAL MINING

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After years of small-scale artisanal mining, dangerous levels of mercury concentrations exist in many rural communities in Indonesia. Miners grind the extracted ore with mercury and water in order to extract the gold, which forms an amalgam with the mercury. After this, miners typically drain off the liquid, however, most becomes vapour polluting the air, soil and waterways. In the final stage of extracting the gold, miners will heat the mercury and gold amalgam with a blowtorch sending the vapour into the air. This research aims to identify sustainable adsorbents that remove mercury from both groundwater and soil. Building on research into low cost and sustainable solutions for treating legacy metal mine discharge in the United Kingdom, where the main pollution arises from lead, zinc and cadmium, we have developed scalable solutions using low cost natural materials that show greater than 95% removal of lead, and 90% of zinc in scaled-up field trials. These materials are based on the biopolymer alginate, extracted from seaweed. Owing to this, cost is lower than engineered polymers and the adsorbents are both carbon neutral and degradable. Here, we present initial data from a proof of concept data to examine the use of inclusion of co-adsorbents within the alginate matrix derived from pomello processing waste. Pomello is a grapefruit-like species indigenous to Indonesia with an inedible peel. The pomello-alginate adsorbent system is evaluated for extraction of mercury from an aqueous and a soil matrix. Using spectroscopy and electron microscopy approaches, we attempt to assign binding modes to determine how the mercury is interacting with the adsorbent material.
PERFORMANCE EVALUATION OF HYDROXYAPATITE-BASED SORBENTS FOR GASEOUS MERCURY CAPTURE AND STABILIZATION: FROM SYNTHESIS TO PELLETING

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Non-stoichiometric (Ca/P ratio of 1.51-1.58) nano-hydroxyapatite was synthesized as a mesoporous (average pore diameter around 146 Å) and a high surface area material (37-67 m²/g). Chemical modification with transition metals (mainly copper) with subsequent sulfidation makes it as an active sorbent for elemental mercury capture from gaseous streams. Based on physicochemical characteristics of the adsorbent, a phenomenological model was previously proposed and used to describe the experimental breakthrough curves allowing the establishment of a relationship between adsorbent performance and chemical nature, location, and the number of its active sites. The high removal capacity of this non-regenerative sorbent was proved by both static and dynamic adsorption results mainly to ensure the requirements for emission limits in mercury removal units (MRU). In the presence of moisture, a new phase of HgSO₄ in addition to HgS was identified by Raman spectroscopy in spent sorbents. However, adsorbent performance to mercury capture was not altered in the presence of moisture once the mesoporosity of the sorbent minimizes capillary condensation. Thus, it is worth noting that the nature of the sorbent is resistant to moisture as well as to H₂S poisoning since the active phase is a metal sulfide. Additionally, thermal stabilization results showed the Hg immobilizing, once just 4% (p/p) of total Hg amount in the spent sorbent was released during 522 hours of heating in levels of 28, 40, 60 e 80°C. Finally, a pelleting system was designed and used in the manufacture of pellets with similar size to those of commercial adsorbents, making possible future comparative tests in pilot scale.

MERGENCY RECOVERY FROM MERCURY-CONTAINING WASTES USING A PILOT-SCALE THERMAL PROCESS

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This study provides a result of mercury recovery characteristics from mercury waste using thermal technology. Mercury waste was categorized as threetyes such as waste consisting, waste containing, waste contaminated of mercoury mercury compounds. Those mercury wastes should be properly collected separatelly and recovered mercury or stabilized for environmentally soundmanagement. Thermal treatment was conducted to recover elemental mercury from mercury containing products (barometer and UV lamp) and Hg contaminated soil. A 150 L stainless steel drum filled with waste samples was pushed in and positioned inside of the pilot-scale furnace for thermal treatment. An agitator was kept rotating during thermal treatment if mixing is needied. Experiments were carried out in temperature range between 550 and 750°C with reduced pressure condition up to 10.1325 kPa. Off-gas emitted form thermal furnace was passed through a ceramic filter unit to filter out impurities in the off-gas with higher temperature than boiling point of mercury in case of necessary cleaning selectively. 100 kg of waste per batch could be treated and elemental mercury was recovered with a condensation unit by maintaining the temperature around 10°C during thermal treatment. Activated carbon trap was applied to control mercury in emitting gas to air. Also mass balance was investigated to observemercarium distribution in the pilot scale process. Treated waste could be disposed as general waste and recovered mercury could be recycled and reused as a resource.

USING SELECTIVE SEQUENTIAL EXTRACTION AND SPECTROSCOPIC ANALYSIS TO DETERMINE INSOLUBLE MERCURY SPECIES IN HIGH LEVEL RADIOACTIVE WASTE

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The United States Department of Energy’s Savannah River Site contains an estimated 60,000 kg of mercury in both salt cake and insoluble metal oxide/hydroxide solids (sludge). Inorganic mercury was used as a catalyst to aid in the dissolution of aluminum clad fuel and target assemblies associated with separation processes that supported the United States nuclear stockpile. The radioactive liquid waste is being converted into a solid glass form using a vitrification process for long-term storage and disposal. This process immobilizes the radioactivity within a solid glass phase matrix. Research has cast doubt on the baseline assumption in radioactive waste sludge processing within the vitrification plant that mercury is present only in the form of mercouric oxide. We previously reported the first application of a modified selective sequential extraction (SSE) technique to the characterization of mercury species present in a washed version of the highly radioactive component of a PUREX-based sludge in our liquid waste system that strongly suggested the presence of HgS. Insights gathered from that study informed a follow-up study that looked at the unwashed sludge component from an HM-based sludge, which was expected to have a higher mercury concentration and a different distribution of insoluble mercury species. This second study also sacrificed a SSE sample replicate and a HgS containing standard prior to the modified aqua regia extraction step expected to dissolve this species to examine the solids for the presence of HgS. The techniques applied included x-ray diffraction (XRD), x-ray fluorescence (XRF), and scanning electron microscopy (SEM). The data gathered led to different conclusions than previously predicted as there appears to be no sulfur associated with the Hg in the waste solids, as contrasted by the standard, prior to the modified aqua regia extraction. How this second study guides our plans for a third waste sludge study and modifies our previous conclusions about the nature of insoluble mercury in our high level waste system will be presented.

MERCURY ACCUMULATION AND BIO-TRANSPORTATION IN WETLAND BIOTA AFFECTED BY GOLD MINING

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Phytoremediation is a cost-effective, eco-friendly technology for the removal of metals from polluted areas. In this study, six different plant species (Datura stramonium, Phragmites australis, Persicaria lathifolia, Melilotus alba, Panicum coloratum and Cyperus eragrostis) growing in a gold mine contaminated wetland were investigated as potential phytoremediators of mercury. The accumulation of total mercury and methylmercury in plant tissues were determined during the wet and dry seasons to establish the plants’ variability in accumulation. The highest accumulation of total mercury was in the tissues of Phragmites australis with recorded concentrations of 806, 495 and 833 μg kg⁻¹ in roots, stem and leaves, respectively during the dry season. The lowest accumulation levels were recorded for Melilotus alba during both seasons. The highest amount of the methylmercury was found in Phragmites australis with recorded concentrations of 806, 495 and 833 μg kg⁻¹ in roots, stem and leaves, respectively during the dry season. The data gathered led to different conclusions than previously predicted as there appears to be no sulfur associated with the Hg in the waste solids, as contrasted by the standard, prior to the modified aqua regia extraction. How this second study guides our plans for a third waste sludge study and modifies our previous conclusions about the nature of insoluble mercury in our high level waste system will be presented.
mites australis during the dry season with a value of 618 µg kg⁻¹. The accumulation and biotransportation was not significantly different between the seasons for some plants. The results of this study indicated that plants growing in wetlands can be used for phytoremediation of mercury and suggest the choice of species for constructed wetlands.

**T.P.3.11**

**REMOVAL OF MERCURY BY IONIC LIQUIDS-FUNCTIONALIZED SILICA: EFFICIENCY AND ECOTOXICOLOGICAL ASSESSMENT**

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Mercury is a toxic and persistent metal that despite all regulations to restrict, control and phase out its use, it is still present, posing a threat to the environment and human’s health. There is still a need to find ways to mitigate water contamination, using innovative, efficient and environmentally friendly methods. In the last years, ionic liquids emerged as an alternative to common methods of removing trace elements. However, although labelled as “green solvents” very little is known about their potential toxicity, particularly on aquatic organisms. This study aimed to evaluate the viability of ionic liquids-functionalized silica (SILP) in the decontamination of Hg in saline water, under realistic conditions, i.e.: for an initial concentration of Hg equal to guideline value for this metal in effluent discharges, 50 µg/L; for a relatively low amount of sorbent (50-250 mg/L); and for a short contact time (24 h). An ecotoxicological approach is also included, by assessing the safety of the SILP and of the decontaminated water to aquatic marine organisms. For this, the marine macroalga Ulva lactuca, a very common species worldwide, and which is considered a good environmental indicator, was exposed to the following conditions: a) clean saline water; b) saline water contaminated with Hg; c) saline water previously contaminated with Hg and subsequently decontaminated by means of SILP, which was separated; d) saline water previously contaminated with Hg and subsequently decontaminated by means of SILP, which remained in solution; and e) saline water with the SILP.

After 48 h of exposure, Hg concentrations in algal tissue, as well as the impact on algal relative growth rate, chlorophyll a and b content, and several biomarkers indicative of the biochemical performance were assessed.

Results showed that silica-supported N-methylimidazolium with thiocyanate ([Si][C3C1im][SCN]) was the most efficient in removing Hg from water, leading up to 98% of reduction in Hg levels, in just 6 h. After exposure to this SILP; to decontaminated water; and to decontaminated water containing the SILP, U. lactuca did not present a significant decrease in chlorophyll content, neither a diminution in the relative growth rate, compared to the condition of exposure to clean saline water (Control). Hg concentrations in algae exposed to Hg contaminated water were significantly higher than those observed for the decontaminated water and remaining conditions. These findings, corroborated with those of biochemical analysis, support the use of SILPs as a viable and safe option for Hg decontamination.

**T.P.3.12**

**THE ELIMINATION OF INDUSTRIAL MERCURY POLLUTION IN KAZAKHSTAN UNDER THE PROJECT “CLEAN-UP OF THE NURA RIVER”**

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This report was prepared with financial support of the International Science and Technology Center (ISTC). The activity of acetaldehyde production was the source of occurrence in 1950-1993. extensive mercury-related industrial pollution in the area of the city of Temirtau in Central Kazakhstan. Perennial emissions of mercury into the environment were carried out during accidents, as well as due to the imperfection of technology during thermal regeneration of mercury from sludge, discharge of mercury-containing wastewater into the Nura river, accumulation of mercury wastes on the territory of the enterprise and beyond. The result was contaminated soil on the industrial site and around it, the river bed, banks and floodplain for about 30 km downstream from the city to the Intumak reservoir. The Government of the Republic of Kazakhstan, jointly with the World Bank have planned a number of environmental protection measures during 2007 - 2011. The main aim was the elimination of technological mercury pollution in the area of the city of Temirtau. The project of “Cleanup of the Nura river” [1] was oriented on improvement of well-being and healthcare of local population living along the Nura river. Actions were following:

- construction and operation of a hazardous waste landfill;
- removal and transfer to the landfill contaminated with mercury materials, sludge and soil from the territories associated with the industrial site of acetaldehyde production and sewage treatment plants;
- cleanup of the river bed, banks and floodplains of the river: excavation of contaminated soil and its transportation to the landfill.

In 2007 contractors from China and Supervision Engineer - Austrian company “Posch & Partners Consulting Engineers” began the implementation of the Project. The contaminated soil of the industrial territory was dug up to two meters deep and also transported to the landfill. All found metallic mercury was mothballed in concrete and plastic containers, the settling ponds of the treatment facilities were isolated. Polluted bottom sediments of wastewater treatment plants, Zhaur bogs and old ash dumps at heating station were also cleaned. The giant test site was covered with soil and, in accordance with the Project, environmental objects were monitored in its territory. The implemented Project is unique and large-scale within which one of the major environmental protection measures to eliminate the source of industrial mercury pollution within the CIS was carried out.


**T.P.3.14**

**AVAILABILITY OF A SIMPLE AND SMALL MERCURY MEASURING DEVICE, QCM-HG FOR MERCURY MEASUREMENT IN AN ARTISANAL AND SMALL GOLD MINING AREA AND GOLD DEALING SHOP**

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This study aimed to evaluate the viability of the use of QCM-HG for mercury measurement in an artisanal and small gold mining area and gold dealing shop in a highly polluted area. The study focused on the availability of a simple and small mercury measuring device, QCM-HG, for mercury measurement in an artisanal and small gold mining area and gold dealing shop. The results showed that the availability of this device can be a valuable tool for monitoring mercury levels in these areas, providing important information for environmental protection and public health.
Mercury (Hg) is a toxic element of global concern and is dispersed worldwide primarily through atmospheric long-range transport. The Minamata Convention came into force since August 2017 and active discussions regarding the Hg emission control and the reduction of environmental risks on Hg for human being and wild animals have been continued. The 1.960 tons of Hg were emitted into the atmosphere from human activities all over the world in 2010 and artisanal small gold mining (ASGM) was responsible for about 40% of the total. In developing countries, a lot of people are occupied in ASGMS. Thus, understanding on Hg exposure to the workers and residents in the vicinity of the mining area is an urgent issue. Here, we developed a simple and small Hg measuring device based on the reaction of air Hg and Au electrode of a quartz crystal microbalance (QCM). The electric resonance frequency of the oscillator changes in proportion to the mass change caused by the Hg adsorption. This device is called QCM-Hg and consists of small loggers equipped with temperature, humidity, air pressure and QCM sensors. In addition, the cost of this device is cheaper than a conventional Hg monitor including CVAAS and CVAFS. We tested the availability of the QCM-Hg in various working places including a gold mining area and gold dealing shops in Brazil by comparison with the measurement using a conventional gold amalgamation method. In a gold mining area, high Hg concentrations more than 10 mg/m3 was sometimes observed when the metallic Hg plate attached fine particles of gold ores was burned to obtained the mercury and gold amalgamation. In this time, the frequency of the QCM-Hg rapidly changed and became the plateau for several seconds. This phenomenon indicates the reaction of QCM-Hg is saturated due to the extremely high concentrations. On the other hand, in gold dealing shops, several µg/m3 of Hg were observed by the conventional Hg monitor. The concentrations increased when Hg-Au amalgamation was burned to get a pure gold (content ratio more than 90%). The frequency of QCM-Hg was also changed corresponding to the Hg concentrations in this time. In addition, the concentrations could be calculated using the slope of the frequency shift for 2 min. These results revealed that the QCM-Hg is useful device as a simpler and cheaper Hg monitor in working places and can be utilized as a personal Hg exposure monitor.

DEEPTH DISTRIBUTION OF TOTAL AND METHYL- MERCURY IN SOILS FROM SMALL SCALE AND ARTISANAL GOLD MINING COMMUNITIES OF THE PRESTEA-HUNI VALLEY DISTRICT, GHANA

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The depth (2, 4, 6, 8, 10, 15 and 20 cm) distribution of THg and MeHg in soils from Mercury-dependant Artisanal and Small-Scale Gold Mining sites in the Prestea-Huni Valley district of Southwestern Ghana has been investigated. Total mercury was determined by CV-AAS after digestion with HF/HNO3/HCl. MeHg in soils were extracted with H2SO4/KBr/CuSO4 and CH2Cl2; followed by aqueous-phase pre-concentration on Tenax, GC separation and CV-AFS detection. The concentration of THg observed at the upper 2 cm and corresponding 20 cm ranged from 0.08 to 458 µg/g and 0.05 to 3.8 µg/g; with the higher values found at commercial Hg-Au amalgam burning and ASGM sites. The lower Hg levels were observed at the upper 2 cm and the corresponding 20 cm ranging from 0.04 to 458 µg/g and 0.05 to 3.8 µg/g.

A CRITICAL STUDY OF THE THERMAL DESORPTION TECHNIQUE FOR THE IDENTIFICATION OF MERCURY SPECIES

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The ability to determine the chemical form of mercury in a contaminated environment is the key to predict its solubility, transport, behavior and bioavailability, as well as to design an effective control and remediation technology. Although there are different methods to determine mercury species in solid samples, this task is still difficult to perform. Sequential and selective extraction procedures have been the most commonly used way to determine mercury speciation due to their simplicity. However, these methods present some problems associated with mercury re-adsorption or volatile mercury losses.

X-ray absorption fine structure spectroscopy (XAFS) has also been applied to determine mercury speciation in solid samples, but this is generally effective in samples with mercury concentrations higher than 1 mg kg⁻¹ and its accessibility is usually limited. A technique with low detection limits that can be implemented without the need for complicated instrumentation and with low time-consuming
TRACING MERCURY MOBILITY AND DISTRIBUTION IN THE ABBADIA SAN SALVATORE LEGACY MERCURY MINE AREA USING MERCURY ISOTOPE RATIOS AND CONCENTRATIONS

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Persistent mercury (Hg) impact from legacy mines continues to present risk to the environment and human health globally. The Monte Amiata Hg district in Southern Tuscany, Italy was one of the five largest Hg districts in the world. Mining of Hg began in the region during the Roman era with modern mining beginning in the mid-1800s and concluding in the early 1980s which resulted in the occurrence of elevated Hg in the surrounding ecosystem. The study area focused near Abbadia San Salvatore mine (ASSM) as it was the major Hg processing facility for many mines in the district and considered a primary source for elevated Hg. The extraction of Hg from cinnabar was carried out via the roasting of ore using two primary furnace types. Initially, Čermak-Spirek shaft type and tower furnaces were used which were later replaced by Gould and Pacific type furnaces. The ore was roasted at 600–700°C to volatilize Hg to gas which was recovered via condensation. Mass dependent fractionation (MDF) of Hg isotope ratios and variation in Hg concentrations resulting from the processing of cinnabar ore have been reported for mine-waste calcines. Elevated concentrations of Hg in the extensive mine-waste calcine piles in ASSM possess the potential of releasing Hg into the local environment over a sustained period of time. The differences in extraction efficiency of Hg from cinnabar ore of different grain size and different furnace types resulted in variations of Hg concentration and isotopic composition in the mine-waste calcines (Čermak-Spirek calcine d202Hg average of 0.52% and concentration range of 32 to 1500 µg/g; Gould and Pacific d202Hg average of -0.58 and concentration range of 25 to 130 µg/g). Mass independent fractionation (MIF) has also been reported for Hg isotope ratios and is attributed to photochemical reduction of aqueous HgII and MeHg. The contribution of Hg from chemical processes and weathering of legacy mine-waste calcine piles as well as initial Hg contribution from historical Hg ore processing has resulted in a wide range of Hg concentrations (0.48 µg/g to 1500 µg/g) and D202Hg and D199Hg isotopic compositions (-1.96% to 0.95%, -0.30% to 0.25% respectively). We will present an overview of Hg distribution and mobility using concentration and isotopic composition measured for a wide range of samples (cinnabar ore, calcines, sediment, soils, geothermal water, and fish) collected in the ASSM area.

IN-SITU CAPTURE OF MERCURY IN COAL-FIRED POWER PLANTS USING HIGH SURFACE ENERGY FLY ASH

ZHANG, Yongsheng: MEI, Dongqian; WANG, Tao; PAN, Wei-ting

Coal-fired power plants represent the largest source of mercury emissions worldwide. Using fly ash, a by-product of these plants, as a sorbent to remove mercury has proven to be difficult. Here we found that the fresh surface of modified fly ash has good adsorption performance, and it declines obviously with time because of unsaturation characteristics on surface. Based on this mechanism, our study provides a method to in-situ capture mercury with high surface energy modified fly ash by mechanochemical and bromide treatment. Fresh modified fly ash with active sites is injected into the flue to directly adsorb mercury. A continuous system within a full-scale 300 MWe plant showed that the mercury adsorption performance of the modified fly ash is similar to that of activated carbon, which is the industry benchmark for the treatment of mercury emission in fossil power generation units. This is a breakthrough, and indicates that modified fly ash can become an efficient and convenient industrial sorbent for the removal of mercury.

INFLUENCE OF MICROBIAL ANAEROBIC METABOLISM ON THE MOBILIZATION OF MERCURY AND IT TOXICITY ON FORMER MINING SITES IN FRENCH GUIANA

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Successive years of alluvial gold mining in French Guiana have resulted in soil degradation and deforestation leading to the pollution and erosion of mining plots. Due to erosion and topography, alluvial gold panning sites are submitted to hydromorphy during heavy rainfall and groundwater increases. This original study focused on characterizing the physicochemical quality of rehabilitated mining sites, the impact of hydromorphic anaerobic periods on iron- and sulfate reducing bacteria, and the potential solubilisation and methylation of mercury. We sampled soil from 5 rehabilitated sites in French Guiana, including 2 sites with herbaceous vegetation (NR and Lyc) and 3 sites restored with fabaceous plants, including Clitoria racemosa (CIB) monoculture, Acacia mangium (Aca) monoculture, and Clitoria racemosa and Acacia mangium (Mix) bi-culture. We conducted mesocosm experiments where soil samples were incubated in anaerobic conditions for 35 days. To evaluate the effect of anaerobic conditions on the activity of bacterial communities, we measured the following parameters related to iron- and sulfate reducing metabolism throughout the experiment: CO2 release, carbon dissolution, sulphide production and sulphate mobilization. We also monitored the solubilization of iron oxyhydroxides, manganese oxides, aluminium oxides, mercury and its potential toxic forms in the culture medium. The results revealed two trends in these rehabilitated sites. In the Aca and Mix sites, bacterial iron-reducing activity coupled with manganese solubilization was detected with no mercury solubilization correlation. In herbaceous sites (NR and Lyc), while the measured anaerobic activity was low, it seemed responsible for sulphide production coupled with twice as much mercury solubilization. These results confirm the presence and activity of ferri and sulfate reductive communities at rehabilitated mining sites and their interactions with the dynamics of metallic elements and mercury. These results also showed the positive impact of ecological restoration applied of mining sites in French Guiana by reducing the potential mobility of mercury and its methylation.
POSTER ABSTRACTS
Thursday 12th September 2019
HIGH RESOLUTION ATMOSPHERIC MERCURY EMISSION INVENTORIES OF CHINESE CEMENT PLANTS OF 2007 AND 2015: TEMPORAL TREND AND SPATIAL VARIATION

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Mercury (Hg) has drawn global attention because of its long-range transport, high toxicity and bioaccumulation characteristics. Cement production is considered as one of the major anthropogenic sources of atmospheric mercury emission worldwide. As the largest cement producer and consumer, China has experienced significant policy adjustments on cement industry since 2007 to alleviate the pollution. Plants with dry hollow kiln and wet kiln or with an annual production of less than 0.2 Mt have been shut down. Shaft kilns were phased out gradually. This study compiled high resolution atmospheric mercury inventory of China’s cement plants of the year 2007 and 2015 with plant-level data, including raw material, coal and secondary fuel consumption and characteristics, kiln type, APCD installation, atmospheric pollutant emission and geographical location of cement plants nationwide in 2007 and 2015, respectively. Provincial industry removal efficiencies are employed to calculate individual emission. Temporal trend and spatial variation of the atmospheric mercury emission of cement industry in the policy implementation period were investigated. The results of this study could help improve the understanding on the environmental effect of policy implementation on the cement industry in China and provide useful information for developing Hg emission control strategies.

HOW IMPORTANT IS BIOMASS BURNING IN CANADA TO MERCURY CONTAMINATION?

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Wildfire frequency has increased in past four decades in Canada, and is expected to increase in future as a result of climate change. Mercury (Hg) emissions from biomass burning are known to be significant. Environment and Climate Change Canada’s mercury model, GEM-MACH-Hg, is used to quantify the impact of regional biomass burning on spatiotemporal distribution of air concentrations and deposition fluxes of mercury in Canada. Gaseous Elemental Mercury (GEM) observations (2010-2015) in North America, GEM-MACH-Hg, and an inversion technique are used to optimize the Emission Factors (EFs) for GEM for five vegetation types represented in North American fires to constrain the biomass burning impacts of mercury. The inversion results suggest that EFs representing more vegetation types in Canada – specifically peatland – are required. More measurements of Hg concentration in the air, specifically downwind of fires, would also improve the EFs using inversion techniques. Three biomass burning Hg emissions scenarios, representing a range of possible values, are used to constrain the impact of Hg emissions from biomass burning in Canada on Hg concentration and deposition. Biomass burning Hg emissions in Canada are found to be highly variable from year to year and 3 - 7 times the mercury emission from anthropogenic sources in Canada between 2010-2015 during the burning season. On average, 65% of the biomass burning emissions occur in the provinces west of Ontario. While emissions from biomass burning have a small impact on surface air concentrations of GEM averaged over individual provinces/territories, the impact at individual sites can be as high as 95% during fire events. Average annual mercury deposition from biomass burning in Canada is estimated to be between 0.3 – 2.8 t, compared to 0.14 t from anthropogenic sources during the burning season. Compared to the biomass burning emissions, the relative impact of fires on mercury deposition is shifted eastward. The local contribution of biomass burning emissions to mercury deposition in some locations (including areas downwind of biomass burning) can be as high as 80% (e.g. northwest of Great Slave Lake in 2014) from May-September. We find that northern Alberta and Saskatchewan, central British Columbia, and the area around Great Slave Lake in the Northwest Territories are at greater risk of mercury contamination from biomass burning.

FIVE-YEAR TRENDS AND MONSOON-FACILITATED TRANSBOUNDARY TRANSPORT OF ATMOSPHERIC MERCURY AT A HIGH-ALTITUDE BACKGROUND SITE IN SOUTHWESTERN CHINA

Zhang, Hui; Fu, Xuewu; Wang, Xun; Feng, Xinbin

To gain a better insight into the long term trends and influence of monsoon climate of atmospheric mercury (Hg) in southwestern China, measurements of gaseous elemental mercury (GEM) were carried out at Ailaoshan station (ALS, 2450 m a.s.l.) in southwestern China from May 2011 to April 2016, and gaseous oxidized mercury (GOM) and particulate bound mercury (PBM) was monitored from January 2014 to April 2016. The mean concentrations (±standard deviation) for GEM, GOM and PBM were 1.7±0.7 ng m⁻³, 7.6±5.2 pg m⁻³ and 31±33 pg m⁻³, respectively. Observed GEM showed a large decreases (32.8%) from 2013 to 2014 and kept a quite level (<1.6 ng m⁻³) in 2015 and the first four months of 2016. Meanwhile, a monsoon distribution pattern of GEM was observed with relatively higher concentrations (1.9 ng m⁻³) during the monsoon period (from May to September) than that (1.6 ng m⁻³) in the non-monsoon period. Conversely, GOM and PBM concentrations were higher in the non-monsoon period than that in the monsoon period. This study suggests that the decrease of coal consumption and extensive implementation of emission controls targeted at SO2 and NOx on coal-fired utilities in China should be the principal reason of GEM decline. Also, the monsoon climate have a strong impact on long-range transboundary transport of mercury from anthropogenic source regions of India and biomass burning in SouthEast Asia to remote areas in southwestern China. Some high GEM concentrations were accompanied by the occurrence of northern wind, indicating anthropogenic Hg emission from inland China could rapidly increase the GEM levels at ALS. Most of high PBM concentrations were observed under the influence of the southern wind during the non-monsoon period. This suggest that transboundary transport of Hg emitted from the frequent biomass burning in Southeast Asia during the non-monsoon period was also an important source of atmospheric Hg in remote areas of southwestern China.

FAST PHOTOCHEMICAL DEPLETION OF TOTAL GASEOUS MERCURY AFTER SUNRISE OBSERVED IN THE POLLUTED COASTAL MARINE BOUNDARY LAYER ABOVE HONG KONG

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Photochemical oxidation mechanism plays important roles in the chemical forms and cycling of atmospheric mercury (Hg). The atmospheric Hg depletion events (AMDEs) at polar regions after springtime sunrise and
that above the mid-latitude Dead Sea have been revealed as a result of drastic photochemical oxidation of Hg by rich bromine radicals followed by rapid deposition. Due to thermal decomposition of HgBr intermediate, however, the AMDEs are supposed to rarely occur in (sub)tropical regions where temperature is higher and bromine radicals are much less abundant. Here we present a comprehensive field measurement of total gaseous mercury (TGM) and Hg in ambient aerosols and cloud water at a subtropical coastal mountaintop in Hong Kong, a site near the upper marine boundary layer (MBL), from November 2016 to April 2017. Four evident TGM depletion events were observed, which were characterized by sharp decline of TGM from > 1.5 ng m-3 to near 0.5 ng m-3 within 1-3 hours after sunrise, accompanied by O3 losses of 3-35%. Enhanced solar radiation, much decreased wind speed and largely elevated anthropogenic pollutants were examined to be essential for the occurrence of TGM depletion events. Increased bromine radical (Br) which was likely released by inorganic Br precursors buildup overnight from sea salt upon sunrise was suggested to initiate Hg photo-oxidation. But the TGM decay rates could only be well matched by involving the second-step oxidation by highly elevated NO2. Significant enrichment of Hg in sea-salt aerosols compared to cloud water and seawater indicated that efficient uptake of reactive Hg by abundant sea-salt aerosols in the MBL could be a predominate fate of the depleted TGM. The results supply new insights into the atmospheric mercury cycling in the MBL under coastal anthropogenic influence.

R.P.1.6

EXPERIMENTAL RAINWATER HG SPECIATION AND PHOTOREDUCTION RATES IN THE PRESENCE OF HALOGENS AND ORGANIC CARBON

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Mercury (Hg) photochemical redox reactions control atmospheric Hg lifetime against deposition and therefore play an important role in global Hg cycling. Oxidation of Hg(0) to Hg(II) is currently thought to be a Br-initiated two-stage reaction with main end-products HgBr2, HgBrNO2, HgBrHO2, HgCl2. Atmospheric photoreduction of these Hg(II) compounds can take place in both the gas and aqueous phase. Here we present new experimental observations on aqueous Hg(II) photoreduction in the presence of dissolved organic carbon and halogens and compare the findings to rainfall Hg(II) photoreduction rates. The first order gross photoreduction rate constant of Hg(II) in the presence of 1mg L-1 of fulvic acid is 0.23 h-1, which is similar to the mean rates in high-altitude rainfall (0.15 ± 0.01 h-1 (n = 3)) and the median photoreduction rate from literature for continental waters (0.41h-1 (n=24)). Addition of bromide (Br-) progressively inhibits Hg(II) photoreduction to reach 0.005 h-1 at total Br- of 10 ¡/M. Halide substitution experiments give Hg(II)(Xn-2) photoreduction rate constants of 0.047, 0.016, 0.004, 0.002 for X = F-, Cl-, Br-, and I- respectively and reflect increasing stability of the Hg(II)-halide complex. We calculate equilibrium Hg(II) speciation in urban and high-altitude rainfall using Visual Minteq, which indicates Hg(II)-DOC to be the dominant Hg species. The ensemble of observations suggests that atmospheric gaseous HgBr2, HgCl2, HgBrNO2, HgBrHO2 forms, scavenged by aqueous aerosols and cloud droplets, are rapidly converted to Hg(II)-DOC forms due to abundant organic carbon in aerosols and cloud water.

R.P.1.8

TRENDS IN ATMOSPHERIC MERCURY FRACTIONS AND WET MERCURY DEPOSITION ACROSS THE UNITED STATES

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The creation of long-term monitoring programs has proved invaluable in assessing the efficacy of environmental policies. Two such programs, the Atmospheric Mercury Network (AMNet) and the Mercury Deposition Network (MDN), have been used to characterize the magnitude and changes in concentrations of gaseous elemental mercury, particulate mercury and gaseous oxidized mercury, and wet mercury deposition across the United States. These networks provide information on the spatial and temporal responses of air quality management aimed at reducing mercury emissions. Recently, the United States Environmental Protection Agency (USEPA) has proposed to roll back Mercury Air Toxics Standards (MATS), raising questions about the effectiveness of such polices and how the environment will respond to their removal. Presented here is an analysis of the long-term trends in concentrations of atmospheric mercury fractions and mercury wet deposition across select MDN and AMNet sites, and their relationships to changes in mercury emissions. The results of these analyses show significant decreases in concentrations of all fractions of atmospheric mercury and wet mercury deposition across the United States, but particularly in the east, with only few sites showing significant increases. Also presented are short-term trends in mercury emissions from several states measured during the course of MATS’ enforcement. These results highlight the long-term effectiveness of air pollution control and underscore the importance of maintaining these policies and mercury monitoring programs.

R.P.1.7

AIR MERCURY VARIABILITY AT LISTVYANKA STATION, SIBERIA

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The GMOS (Global Mercury Observation System) network established in 2010 has the overall goal to develop a coordinated observing system to monitor mercury on a global scale to assess its emissions, transport, atmospheric chemistry, and deposition processes. The Listvyanka monitoring station is located at a shore of Lake Baikal, Siberia, far away from the existing mercury monitoring sites in Asia, in the middle of a vast area where no observational data were available before GMOS. The station is a part of the EANET network whereby numerous parameters of the air pollution, wet and dry deposition, as well as condition of the terrestrial and aquatic environment are measured. Lumex RA-915AM mercury monitor is used for the continuous air mercury monitoring in compliance with the unified GMOS standard operational procedures. Concurrently, particulate bound mercury (PBM) was collected during 2015 – 2017. The GEM (gaseous elemental mercury) concentration through more than 7-years of measurement averages at 1.40 ng/m3. The long-term observations show a trend to decreasing of the average annual mercury concentration and obvious seasonal variation of the GEM concentration, which increases in the cold season (November – February) on the average of 1.55 ng/m3 and decreases in the warm season (June – September) on the average of 1.26 ng/m3. The same character of the seasonal variation is observed for particulate bound mercury (PBM), which amounts to 15 and 7.8 pg/m3 for cold and warm seasons, respectively. For three years of observation, the PBM averages at 9.6 pg/m3 (range 0.5 – 40 pg/m3) comprising about 0.4 – 0.8% of the total (GEM) concentration. Local short-term mercury concentration rises correlate with the SO2 and NOX rises, which are associated mainly with the N and NW wind carrying air from industrial areas where several big coal-fired power plants are located. Analysis of forward and backward trajectories obtained with the HYSPLIT model demonstrates possible revealing of mercury emissions sources based on the long-term background monitoring data.

Part of this research was carried out within the FP7 GMOS project.

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A NEW APPROACH TO NUMERICAL SIMULATION OF THE GLOBAL MERCURY CYCLE BASED ON THE MODEL FOR PREDICTION ACROSS SCALES

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It is well known that mercury (Hg) cycles through air, water and soil on a global scale. Global-scale modeling of atmospheric Hg has encountered challenges. Relatively coarse spatial discretization is needed to achieve global coverage without incurring excessive computational cost. However, gaseous oxidized mercury is known to deposit from the atmosphere rapidly. Thus, fine-scale modeling is required to address all sources of mercury depositing to specific locations. To achieve this, limited-area models have been applied within global models using various methods to treat the interface between the two. Differences in resolution of time and space, and different treatments of physicochemical processes between the global and regional models can induce unrealistic artifacts. In most cases, feedback effects from the fine scale to the coarse scale are neglected. These problems also affect global simulations of other pollutants. To provide a global air quality model to complement the Community Multi-scale Air Quality (CMAQ) model currently available for regional modeling, the U.S. Environmental Protection Agency (EPA) recently began development of a new generation of air quality model based on the Model for Prediction Across Scales (MPAS). MPAS is a global-scale modeling system comprised of separate interoperable programming components, each designed to simulate atmosphere, ocean and other earth-system media in concert. MPAS uses an irregular horizontal grid based on Spherical Centroidal Voronoi Tessellations (SCVTs) producing a mesh of polygonal elements covering the globe without the polar singularities intrinsic to orthogonal grids. During generation of the SCVTs, the mesh element size can be varied based on any desired criteria. Gradual mesh refinement avoids abrupt changes in resolution that have been difficult to treat with traditional grid nesting approaches. Additionally, the same chemical and physical treatments are used in all grid elements and all up-scale effects are included. As a first step to developing this next-generation model, it will incorporate the chemical and physical treatments for the pollutant species currently in the CMAQ model, including mercury. Recent advances in CMAQ have added bromine chemistry which could provide additional benefit to mercury simulations. Besides issues related to atmospheric modeling, MPAS could provide a consistent and seamless approach to including the oceans and other earth systems in comprehensive simulations of the entire mercury cycle. The hope for this presentation is to foster international interest in co-operative mercury model development and research using this unified framework to effectively and efficiently improve our understanding of mercury contamination around the globe.

ARE ZINC SULPHIDES AN IMPORTANT SOURCE OF HG AS A POLLUTANT IN MINING ENVIRONMENTS?

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Zinc sulphides are a known gaseous Hg source, specially during smelting process, with an estimation of 430 tonnes of Hg emitted per year. Sphalerite (ZnS) presents different concentrations of trace metals (Ag, Cd, Pb, Ge, Hg, Mn, In, Ga, Ta, Sr; among others), being Hg concentration typically in a range of 1%-10%. Main ores of ZnS corresponds to the Mississippi Valley Type, including PbS, FeS2 and amounts of other elements of interest (Ag, Cu, Sb...). It is especially important the presence of FeS2, that promotes acid mine drainage and an increase on the mobility of trace metals, particularly Zn, one of the most labile elements in this type of ore deposit. In the studied area the question is: if ZnS is labile, can Zn sulphides be an important source of Hg in Pb-Zn mining environments? In order to find an appropriate explanation to this question, we have taken samples of dumps, tailings, soil and stream sediments in San Quintín mine, a Pb-Zn mine of the Alcudia valley district (South-Central Spain). This mine presents a unique advantage to elucidate this question, because it has two different suspected Hg sources in two different working areas, sphalerite in San Quintin West (SQW) area and sphalerite and cinnabar in San Quintin East (SQE) area. Cinnabar (HgS) mineral in SQE was transported from Almadén mine to perform flotation tests, but these tests failed, and the mineral was abandoned 20 years ago. This work has search differences in total gaseous Hg between SQW and SQE areas, and their relationships with other trace metals typically present in sphalerite, especially Cd. Concerning concentration in the soils, results shows 1232 mg kg-1 in average in SQE area, and 181 mg kg-1 in SQW area, almost six times more Hg when cinnabar is present. The range in Hg concentrations were 16-20339 and 5-1066 (mg kg-1) in SQE and SQW respectively. In SQW System, is a global observational network which is to date recognized as unique global network whose activities are currently part of the GEO strategic plan (2016-2025) aimed to develop a global observing system for Hg and POPs, and particularly within the flagship on “tracking persistent pollutants” GOS4M (Global Observation System for Mercury). One of the major outcomes of GOS4M has been an interoperable e-infrastructure developed following the Group on Earth Observations (GEO) data sharing and interoperability principles, which allows us to provide support to UNEP for the implementation of the Minamata Convention. In this context, as part of the UNEP-F&T partnership area, a pilot project in cooperation with WHO, has been funded by UNEP-GEF with the aim to develop a Hg monitoring plan for “human exposure to and Environmental concentrations of mercury” to enhance the understanding of Hg concentrations in ambient air through the strengthening of the GOS4M network. The sampling pilot survey has been performed in 2017 yr over two seasonal campaigns at WHO sites, and over three seasonal campaigns at GOMOS stations, to study the potential influence of different meteorological conditions on Hg behaviour. The measurements program has been structured in order to employ a much higher number of passive air samplers (PASs) that have been co-exposed for one, two, and three weeks in parallel to cross check key parameters for the QA/QC: linearity over time, reproducibility at different climate conditions. The campaigns were carried out at six GOS4M sites, two of them in the Southern Hemisphere [South Africa (CPO) and Argentina (BAR)]. The developed PASs have been designed to give information about the average Hg levels over time periods of few weeks to months which seem to provide, as a preliminary analysis, acceptable performance compared to active samplers in terms of sensitivity at most of the monitoring sites involved.

ASSESSING MERCURY AIR LEVELS USING PASSIVE AIR SAMPLERS (PASS) AS PART OF THE GMOS NETWORK IN THE FRAMEWORK OF THE UNEP GEF PROJECT

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The overarching benefit of a coordinated monitoring network for mercury (Hg) on global scale would clearly be the advancement of knowledge of all processes characterizing the Hg distribution in the environmental ecosystems, its spatial and temporal patterns, re-emission rates from and deposition fluxes to aquatic and terrestrial receptors for different emission scenarios. GMOS (Global Mercury Observation System), is a global observational network which is to date recognized as unique global network whose activities are currently part of the GEO strategic plan (2016-2025) aimed to develop a global observing system for Hg and POPs, and particularly within the flagship on “tracking persistent pollutants” GOS4M (Global Observation System for Mercury). One of the major outcomes of GOS4M has been an interoperable e-infrastructure developed following the Group on Earth Observations (GEO) data sharing and interoperability principles, which allows us to provide support to UNEP for the implementation of the Minamata Convention. In this context, as part of the UNEP-F&T partnership area, a pilot project in cooperation with WHO, has been funded by UNEP-GEF with the aim to develop a Hg monitoring plan for “human exposure to and Environmental concentrations of mercury” to enhance the understanding of Hg concentrations in ambient air through the strengthening of the GOS4M network. The sampling pilot survey has been performed in 2017 yr over two seasonal campaigns at WHO sites, and over three seasonal campaigns at GOMOS stations, to study the potential influence of different meteorological conditions on Hg behaviour. The measurements program has been structured in order to employ a much higher number of passive air samplers (PASs) that have been co-exposed for one, two, and three weeks in parallel to cross check key parameters for the QA/QC: linearity over time, reproducibility at different climate conditions. The campaigns were carried out at six GOS4M sites, two of them in the Southern Hemisphere [South Africa (CPO) and Argentina (BAR)]. The developed PASs have been designed to give information about the average Hg levels over time periods of few weeks to months which seem to provide, as a preliminary analysis, acceptable performance compared to active samplers in terms of sensitivity at most of the monitoring sites involved.
area, Zn/Hg ratio is 82.90 in average, while in SQE area it was only 2.89, undoubtedly due to the presence of cinnabar. Nevertheless, Zn/Cd ratios are similar than Zn/Hg ratios in the west area (89.21) but noticeably higher in the east area (57.85), a finding that can indicative of notable heterogeneities in trace metals contents in sphalerites from these areas. A multivariate analysis indicate that Hg is related with Cd, Pb, Cu and Se in SQW, but only with Mo in SQE, a relationship which lacks an explanation.

R.P.1.12

APPLICATION OF PASSIVE AIR SAMPLERS FOR ATMOSPHERIC MERCURY RESEARCH: LOCAL LANDSCAPE EFFECTS, VERTICAL GRADIENTS, AND DEPOSITION AT LAKES WITH DIFFERENT FISH-HG CONCENTRATIONS

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Accurately measuring mercury concentrations [Hg] in the atmosphere is important to understand Hg deposition, sources, cycling, and spatial and temporal trends. Furthermore, airborne Hg measurements are essential for evaluating the effectiveness of the recent Minamata Convention. However, reliably determining [Hg] at ng/m3 levels is challenging, and most methods rely on active sampling, which require pumps, electrical power, operator skill, and have other constraints. An alternative approach using a passive air sampler (PAS) was introduced by McLagan et al in 2016. Gaseous Hg enters the sampler and diffuses at a known rate into a chamber where it trapped with a sorbent. Compared to active air sampling, the low-cost of PAS allows for more samplers and greater spatial resolution, albeit at coarser temporal resolution. Here, we deployed commercially available PASs (MerPAS; Tekran, Inc.) to determine their feasibility to measure: (1) [Hg] gradients between adjacent landscapes (wetland, pond, grass, and forest), (2) vertical profiles of Hg within each landscape (4 samplers each at 0.5, 3.5, and 5.5 m), and (3) [Hg] gradients at three major lakes (Grenada, Enid and Sardis) in North Mississippi. The southern-most lake (Grenada) has statistically higher fish-Hg concentrations compared to the northern-most lake (Sardis), possibly due to a nearby coal-fired power plant (CFPP). In each case, we analyzed the sorbent (sulfur-impregnated activated carbon) using a direct mercury analyzer. Preliminary results show that [Hg] increased with height at each landscape, except for the forest where concentrations were relatively uniform. At the lowest height, mean [Hg] (ng/m3) were 0.49 ± 0.06 (wetland), 0.61 ± 0.16 (pond), 0.68 ± 0.10 (grass), and 0.76 ± 0.14 (forest). Thus, the Hg-PAS is suitable for examining factors, such as uptake by vegetation, which can affect atmospheric Hg0 fluxes. For the lake study, [Hg] were highest at Sardis Lake, followed by Enid and Grenada Lakes; mean [Hg] were 1.49, 1.45, and 1.27 ng/m3 (n=22), respectively. Thus, the CFPP near Grenada Lake does not seem to be impacting the airborne [Hg] at the lake. The higher [Hg] at Sardis lake is consistent with reports that [Hg] can be elevated when the wind stems from industrial areas in the north. Hg accumulation rates in PAS were 1.06, 1.10 and 1.16 ng/week at Grenada, Enid and Sardis, respectively, over a 4 week period. We are currently repeating experiments and examining seasonal effects, and will report updated findings at the meeting.

R.P.1.13

DEVELOPMENT AND VALIDATION OF A COST-EFFICIENT MONITORING METHOD FOR THE ESTIMATION OF MERCURY DEPOSITION IN FORESTS

KOENIG, Nils; KRINNINGER, Michael

So far, only sparse information is available on the deposition of mercury (Hg) into forests. This is caused partly by the high measuring effort for the estimation of atmospheric input of elements into forests, usually requiring a multitude of samplers owing to high spatial heterogeneity of the canopy. Temperature conditioned wet-only samplers for Hg developed for open field monitoring programs are very expensive (about 20,000 Euro per sampler) and interference prone. In order to come up with a cost-efficient method for monitoring mercury deposition in forests, a new bulk sampler (about 2,000 Euro per sampler) was developed and tested. Additionally, the interference of leaves, fruits, branches, insects or bird droppings with the samples have been studied in order to estimate the uncertainty of deposition rates. First observations with 9 samplers in a beech forest and 3 samplers in the open field show promising results as to feasibility and reliability of the developed monitoring method. The open field input is comparable to results of 5 monitoring stations of the German Environmental Agency. Throughfall input of Hg into the beech forest is about twice as high as in the open field. Hg input during the foliated period is higher as compared to the leafless period. A close correlation exists between Hg input and the amount of precipitation in the forest as well as in the open field. Results of comparative observations from the cost-efficient bulk samplers, temperature conditioned wet-only and temperature conditioned bulk samplers scheduled for the coming months will also be presented.

R.P.1.14

ASSESSMENT AND ESTABLISH OF TOTAL MERCURY BACKGROUND LEVEL IN SOILS FROM DIFFERENT SITES IN LIBYA

ELGAZALI, Abdelkarem; J. FELDMANN, Eva M. Krupp

Mercury is well known as being a toxic element causing significant damage to the human beings and environment. The aim of this study is to investigate the level of mercury exposure to environment and human beings and to establish the local background levels of total mercury in Libya. Soil T-Hg concentrations were measured in 30 soil samples using CV AFS. The local background average value for T-Hg in un-contaminated soils (n = 17) was established (0.043 µg g-1). Moreover, a mercury result from contaminated soil samples (n = 13) in both forest areas and Sirte Oil Company in the east of Libya and in and around Tripoli city near Abu-Kammash Chlor-alkali plant (in the west of Libya) revealed values ranging from 0.92 to 8.52 µg g-1 mean 4.48 µg g-1. The high mercury content is indicative of the random use of Hg and the lack of control in using this element in the process of amalgamation in Abu-Kammash Chlor-Alkali plant and gas plant in Sirte Oil Company in El- Bregia city. This is leading when released in the Mediterranean Sea to an increase in the load of particulate material with long particles time (long residence time), which is accumulated and magnified in the aquatic food chain and is the major exposure route to humans. Mercury has long-range atmospheric circulation and transportation. Throughout its circulation through the atmosphere, Hg can enter the aquatic environment through diffuse and point sources. Me-Hg is taken up by fish; therefore consumption of this fish will increase the human risk.

Keywords: Mercury, Occupational risk, Chlor-Alkali plant, gas plant, soil samples, CV AFS

R.P.1.15

ASSESSMENT OF THE PRESENT MERCURY INPUT TO THE ALTAITERRITORY DURING WINTER PERIOD BASED ON HG CONCENTRATIONS IN SEASONAL SNOW COVER FOR 2014-2018 YEARS

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The sustainability of mercury in the atmosphere and the ability to be transported over long distances make it a global pollutant. Moreover mercury is an element that is largely subject to the processes of transboundary re-emission depending on environmental conditions. Seasonal snow cover is an integral conservator of pollutants allowing to assess the level of atmospheric Hg pollution during cold season.

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Snow samples were collected by researchers from the Institute for Water and Environmental Problems SB RAS on the broad territory of Altai region in March when maximum snow depth observed. Sampling, sample preparation (melting, filtering) and analyses were carried out in compliance with the clean procedure. Hg concentrations were determined in melted waters using analyzer Mercur DUO Plus accordingly US EPA 1631e. Hg concentrations in snow cover of background sites were <5 ng/L, whereas integral Hg concentrations across Altai region varied from 3 to 70 ng/L. The Hg concentration within the Barnaul city varied from 3.4 to 12.8 ng/L being comparable to the Poznan city (0.43 - 12.49 ng/L). The maximum Hg concentrations have been found in dumping snow site in the Barnaul city (1 μg/L). The interannual variability of mercury in snow cover across Altai region was analyzed from 2014 to 2018. For example, the average concentrations of Hg in integral snow sampled close to the village Sannikovo were as low as ~4 - 8 ng/L for 2014 - 2016 years and 20 and 15.7 ng/L in 2018 and 2017, respectively. A substantial increase of Hg concentrations in 2017 - 2018 may be associated to increase of Hg input and the change in precipitation intensity in winter periods that requires further study. For some sampling sites Hg concentrations in snow pack also were analyzed layer-by-layer. Hg concentrations in the layers may vary significantly (7.2 - 46.0 ng/L). Weighted average Hg concentrations calculated from the layered concentrations were compared with the integral concentration in snow cover. The estimated weighted average in the layers of snow almost coincides with integral concentration in case of low concentrations. At high Hg concentrations in some of layers and significant variability of concentration over the entire winter period analysis of individual layers provides a more objective assessment. The study allowed us to estimate the present Hg concentrations in the snow cover over all Altai territory, calculate Hg fluxes over the winter period, and also estimate their spatial and interannual variability.

ASSESSMENT OF MAJOR ANTHROPOGENIC SOURCES AND EMISSIONS OF MERCURY IN AFGHANISTAN

ASLAMY, Baktash

Goal:
To estimate emissions of mercury from major anthropogenic sources in Afghanistan.

Tasks:
1. Presentation of mercury as a toxic, persistent and global pollutant of the atmosphere.
2. Definition of major sources of mercury worldwide with a focus on anthropogenic sources.
3. Definition of major anthropogenic sources of mercury in Afghanistan.
5. Presentation of methods of reduction of anthropogenic mercury emissions in Afghanistan, particularly in the context of the UN Minamata Convention.
6. Presentation of the role of Afghanistan in the world’s pollution.
7. Presentation of the Afghanistan energy situation.
8. Presentation of the waste management system in Afghanistan.
9. Presentation of Air pollution and risks in Afghanistan.
10. Presentation of the Cement Industry and the role in air pollution of Afghanistan.

ATMOSPHERIC MERCURY OVER POLAND. THE RESULTS OF LONG-TERM AUTOMATIC MEASUREMENTS IN SELECTED INDUSTRIAL AND RURAL LOCATIONS

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CHARACTERIZATIONS AND GAS-PARTICLE PARTITIONING OF OXIDIZED MERCURY AT A TROPICAL MOUNTAIN SITE DOWNWIND OF THE EAST ASIAN CONTINENT

NGUYEN, Ly Sy Phu: SHEU, Guey-Rong; LIN, Da-Wei; HSIAO, Ta-Chih; LIN, Neng-Huei

Atmospheric deposition of oxidized mercury (Hg(II)) was found to be a major input of Hg to surface environments. The phase of Hg(II) (gaseous oxidized mercury (GOM) or particle-bound mercury (PBM)) has important implications for the biogeochemical cycles. This study reported the characterizations and gas-particle partitioning of GOM and PBM between 2014 and 2016 at Lulin Atmospheric Background Station (LABS), a tropical mountain site downwind of the East Asia continent. The mean concentrations (±s.D.) of GOM and PBM were 13.5 ± 26.0 pg m⁻³ and 4.3 ± 11.5 pg m⁻³, respectively. A distinct seasonal cycle was observed for PBM, with higher concentrations in cold months and lower ones in warm months while GOM showed unclear seasonal cycle. Concentration-weighted trajectory (CWT) indicated that East Asia was the major PBM source region, whereas the coastal area of China, West Pacific Ocean, and South China Sea were the GOM source regions. The partition coefficient for oxidized Hg (Kp = (PBM/PBM2.5)/GOM) and the Hg(II) faction in fine particles (IPB = PBM/(GOM + PBM)) obtained at LABS were 0.18 and 0.39, respectively. These values were within the range of values reported from sites in the U.S. Clear diurnal and seasonal patterns were observed. An empirical gas-particle partitioning relationship model, \[ \log(1/Kp) = 12.96 - 3409.8(1/T) \] (R² = 0.63; R² = temperature) was developed. This model was then carefully investigated, in order to estimate how the disposition of Hg(II) partitioning might be affected by different atmospheric conditions.

DETERMINATION OF MERCURY IN INDOOR DUST OF TWO CITIES OF THE NORTHERN REGION OF BRAZIL

SILVA, Barbara Caroline Pereira Da; QUEIROZ, Thais Karolina Lisboa De; CHAGAS, Brenda Rodrigues; NAKA, Karytta Sousa; MENDES, Lorena de Cássia Dos Santos; LIMA, Marcelo De Oliveira

Household dust is a bulk of organic and inorganic substances from internal and external sources, which constitute a heterogeneous and complex matrix that may include clothing, wood and glass fibers, biological components such as hair and skin fragments, and chemical contaminants such as pesticides and particles of toxic metals. These contaminants have the potential to persist and accumulate in household dust since they are not subjected to the same degradation processes that occur in outdoor dust. A continuous deposition of heavy metals in urban areas could act as a secondary source of pollution. Routes of human exposure to metals in household dust consists primarily of inhalation, non-dietary intake and skin adsorption. Mercury is a liquid metal at room temperature, its metallic form is rather volatile. It is found in air, water and soil, it appears in different compositions, both inorganic and organic. Exposure to mercury occurs mainly by ingestion of contaminated food, inhalation of mercury vapor by workers during industrial processes and people within contaminated environments. The nervous system is very sensitive to all forms of mercury, and high doses of this metal could cause permanent damage to the brain and kidneys. Mercury has been tested in workplace as an important air contaminant. In this work, the authors determined the concentrations of total mercury and inorganic mercury in indoor dust samples from two cities in the northern region of Brazil, using a combination of chemical digestion and total reflectance infrared spectroscopy (TRIR). The results showed that the concentrations of inorganic mercury were significantly higher than those of total mercury, indicating that the sources of mercury are primarily related to the use of mercury-containing products in households.

DATA QUALITY ASSESSMENT – PARALLEL CONTINUOUS MERCURY MEASUREMENT AT TWO LEVELS OF TALL TOWER KŘEŠÍN, NAO KOŠETICE, CZECH REPUBLIC

VÍTKOVÁ, Gabriela; KOMÍNKOVÁ, Kateřina; SZABÓ-TÁKÁCS, Beáta; MARTINA ČAMPULOVÁ, Martina; HANUŠ, Vlastimil; HOLOUBEK, Ivan

The Tall tower Křešín u Pacova located at the National Atmospheric Observatory Košetice in the Czech Republic ensures measurements of total gaseous mercury (TGM) as a long term continuous observation at the background conditions. For nearly a year the two Tekran 2537B devices were measuring both at the ground level and since October 2013 they have been measuring parallelly at the ground level and at the level of 240 meters. After more than six years of almost continuous operation these instruments will soon be exchanged for new ones. Data quality assessment has therefore been performed in order to revise old measurement and optimize future routines. Being a part of Global Mercury Observation System (GMOS) network measurement follows its standard operational procedures and the data are included in its database. Validation procedure consists of two steps: automatic processing, based on recorded instrumental parameters and on set thresholds, and manual processing, based on operator’s knowledge of situation and state of instrument. In some cases bad data can pass through the automatic processing without noticing. The decision about data quality is not easy to make. Using regular intercomparisons of two mentioned devices provides a general overview of the situation. It helps to decide about the data quality and whether the measured difference of two levels is caused by gradient of the Hg concentration in the air or by the instruments itself. During last four years eight periods of parallel measurements at ground level were performed. For each period outputs of the two instruments were compared by using basic statistical tests and visualized in time to identify the change in deviation. Effect of various validation flags was then carefully investigated, in order to estimate how the disposition of device influence the accuracy of measurement.
mercury concentrations were quantified by Inductively Coupled Plasma Mass Spectrometer (ICP-MS), after acid digestion process. Samples of Barcarena and Marituba, respectively, showed a mean of 0.26 and 0.06 mg/kg of mercury. The city of Barcarena, because of its diversified industrial area, is an environment favorable to the occurrence of chemical particulate emissions in the air and a greater accumulation of mercury in the household dust, which in this study is observed when presenting concentrations on average four times larger than those of Marituba's. These short and long-term emissions and accumulations can interfere with the quality of life of the populations adjacent to the industries located in this area, which makes it necessary to monitor and adopt public policies and measures regarding the risks that these populations are exposed.

**R.P.1.22**

**ELEMENTAL AND OXIDIZED MERCURY IN AN AREA WITH ELEVATED WINTERTIME OZONE**

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We measured atmospheric elemental and oxidized mercury in the Uinta Basin, Utah, U.S.A., which periodically experiences elevated wintertime ozone. The area has about 10,000 oil and gas wells and topographical and meteorological conditions conducive to strong, persistent temperature inversions (a.k.a. cold air pools) that trap pollution in a shallow layer close to the surface. Local air pollution, along with persistent inversions and abundant snow cover, allow ozone to form within the inverted layer, sometimes reaching concentrations as high as 140 ppb. Winter inversion conditions provide a strong barrier to separate the surface layer from the atmosphere above, allowing us to distinguish oxidized mercury that originated in the upper atmosphere from oxidized mercury generated via surface-level photochemical pollution.

We measured oxidized mercury using cation-exchange and nylon membranes. We pulled ambient air through the membranes at 1 L min-1 over two-week periods. We analyzed the cation-exchange membranes for total mercury using a method similar to EPA Method 1631 and analyzed nylon membranes via programmed thermal desorption to elucidate mercury speciation.

We also measured elemental and oxidized mercury using a Tekran 2537 analyzer coupled to a dual channel sampling system. One of the system's channels pulled air through a pyrolyzer to measure total mercury, and the other pulled air through a series of cation-exchange membranes to measure elemental mercury. We calculated oxidized mercury as the difference between the two channels. Sensitivity improvements and offline processing of the detector output allowed this instrument to achieve a one-hour detection limit for oxidized mercury of less than 15 pg m-3. Oxidized mercury was usually above detection during the deployment.

Oxidized mercury in the Uinta Basin was highest in the summer, and evidence points to subsidence from the upper atmosphere as the source of summertime oxidized mercury. Dual channel measurements during January-March 2019, a period with strong, persistent temperature inversions and ozone exceeding 110 ppb, showed low oxidized mercury that was weakly negatively correlated with ozone and total reactive nitrogen (NOy), and was instead correlated with warmer temperatures and lower humidity, which both indicate influence of air from above the inverted layer. The current dual channel configuration biases against collection of particle-bound oxidized mercury, and January-March 2019 data from the direct membrane collection system are not yet available. If the direct membrane measurements also show low oxidized mercury during winter ozone episodes, this will constitute evidence against mercury oxidation associated with ozone photochemistry.

**R.P.1.23**

**QUANTIFYING THE IMPACT OF METEOROLOGY ON ATMOSPHERIC MERCURY POLLUTION AT AN URBAN SITE IN EASTERN CHINA USING A GENERALIZED ADDITIVE MODEL**

**ZHOU, Peisheng**

Mercury (Hg) pollution has raised great concerns at regional or global scales for its high toxicity and bioaccumulation. Meteorological factors have important effects on Hg in terms of the emission rate of natural sources/re-emissions, transport and physicochemical process of Hg in the atmosphere. To analyze the characteristics of atmospheric Hg pollution and quantify the impact of meteorological factors in eastern China, speciated Hg (GEM/GOM/PBM), were continuously measured with the Tekran® 2537X/1130/1135 system at an urban site (NJU) from August 2014 to July 2015, relevant meteorological factors were also observed simultaneously. The average observed concentrations of GEM, GOM and PBM were 3.85 ng/m3, 43.0 pg/m3 and 127.4 pg/m3 respectively. GEM concentrations were found higher in summer and lower in winter with limited seasonal variation compared with other two species. GOM concentrations were significantly lower in winter than the other three seasons, while PBM concentrations were distinctly lower in summer. The highest concentrations of GEM and PBM occurred in the early morning (6:00-8:00) due to the near-surface inversion while GOM peaked in the afternoon (12:00-14:00) when atmospheric oxidation capacity is relative strong.

A generalized additive model (GAM) was used to quantify the impact of meteorology on the GEM concentration. The model could capture 32.8% (R2=0.328, n=3820) of GEM variations over the whole period, while 43.7% (R2=0.437, n=852) during cleaner periods. Temperature, relative humidity and wind direction were the most sensitive factors, while solar radiation, wind speed and atmospheric pressure had smaller impacts on GEM. GEM increased with rising temperature possibly because the high temperature can accelerate the evasion of Hg in soil. GEM increased rapidly when relative humidity rose at a low level (<35%), but remain unchanged when the factor further increased. Strong solar radiation may promote the photoreduction process of soil Hg, leading to higher concentration of GEM. Air masses from north-west NJU (wind direction:300°-360°) cause high GEM concentration as they pass through heavy industrial areas. GAM would be applied to quantify the effects of various meteorological factors on GEM concentration variations and predict the GEM concentrations with future climate change, especially in high polluted areas.

**R.P.1.24**

**VARIATION IN AMBIENT MERCURY LEVELS IN THE VICINITY OF COAL SEAM GAS EXTRACTION AND POWER GENERATION FACILITIES IN RURAL AUSTRALIA: SEASONAL AND METEOROLOGICAL CONTROLS**

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A total of around 205 tonnes of mercury were estimated to be emitted annually from all sources in continental Australia during 2006. Anthropogenic sources were projected to contribute around 15 tonnes, while determinations of contributions from natural sources were: soil emissions 140 tonnes; fires, 42 tonnes and vegetation, 8 tonnes. Given a small number of monitoring sites across continental Australia these
estimates have a high degree of uncertainty.
Data are presented for ambient mercury concentrations at two Australian rural sites, both of which are impacted by industrial activities with the potential to increase mercury emissions. The first location in inland Queensland was associated with an area of coal seam gas extraction of methane using hydraulic fracturing, and involved extensive gas species and metallochemical monitoring over a six month period in 2017. The second data set is for a longer term monitoring site (2013-present) located in rural New South Wales and in close proximity to both coal-fired power generators and open-cut coal mines.
At both localities, the average ambient gaseous elemental mercury (GEM) concentrations by global comparison have been found to be low (<1 ng/m³), although considerable variability occurs, and at times concentrations as low as 0.2 ng/m³ and up to 2.5 ng/m³ are seen. This variability in mercury concentration seems to be determined by local meteorological conditions, rather than by the influence of the nearby industrial operations, which appear to have little impact. A pronounced cycle in GEM concentration is seen, where overnight, under more stable atmospheric conditions mercury concentration increases only to decrease later in the day. The changes of mercury concentration determined then appear to be a reflection of processes of atmospheric reactions and deposition and re-emission from soils and vegetation in the locality. Possible mechanisms for these results are discussed.

R.P.1.26
MERCURY GEOCHEMISTRY IN THE CRYOSPHERE OF WESTERN CHINA
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Mercury (Hg) is a global pollutant as its highly adverse impacts on human health, which is among the most highly bioaccumulated toxic trace metals in the global environment. On top of the world’s highest mountain ranges and peaks of Western China is the largest aggregate of cryospheric environments outside the polar regions. Anthropogenic Hg emissions from the surrounding regions such as South Asia can be transported over long distances and deposited into the cryosphere of the Tibetan Plateau. This review synthesizes research progresses and current understandings on the Hg geochemistry from different cryospheric environments (e.g., glacier, snow/ice, permafrost) in Western China. Impacts of cryospheric processes to the biogeochemical Hg cycling and their potential environmental feedbacks are addressed in the context of climate warming at regional/global scales.

R.P.1.27
ILLUMINATING GASEOUS OXIDIZED MERCURY: BRHGONO PHOTOYSIS LEADS TO INORGANIC HG(II) AND ORGANOMERCURY COMPOUNDS
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Some global models suggest BrHgONO to be the major Hg(II) species initially formed in atmospheric oxidation of Hg(0) in most of the atmosphere. These models underestimate atmospheric concentrations of Hg(II) unless some photo-reduction process is invoked. A recent paper by Saiz-Lopez et al. assumed, for purposes of modeling, that BrHgONO photolysis led to substantial photoreduction. However, our quantum chemical calculations suggest that BrHgONO photolysis at wavelengths relevant to the troposphere produces the thermally stable radical BrHgO•. Fully relativistic calculations (or experiments) are needed to verify that BrHgO• is the sole product of BrHgONO photolysis in the troposphere. Our studies reveal that BrHgO• behaves a lot like hydroxyl radical (•OH). Specifically, BrHgO• may react with NO2 to form thermally stable BrHgONO2 or with NO to reform BrHgONO. Additionally, BrHgO• will abstract hydrogen atoms from sp3-hybridized carbons on organic compounds with a higher rate constant than does •OH. For this reason, we expect production of BrHgOH to dominate globally, although formation of BrHgONO and BrHgONO2 may compete in urban regions. BrHgO• also mimics OH in that it can add to sp2-hybridized carbon atoms, such as those of alkenes and aldehydes. BrHgO• can react with ethylene to make BrHgOCH2CH2•, which will likely react to form the compounds BrHgOCH2CH2O or BrHgOCH•O. This corresponds to formation of organomercury compounds in the gas phase. While this type of reaction is not expected to dominate the fate of BrHgO•, it could be important in regions of high biological activity, where isoprene and terpenes are relatively abundant.

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OBSERVATIONS OF SUMMERTIME OXIDIZED MERCURY IN THE COLORADO FRONT RANGE, USA, USING A MODIFIED DUAL-CHANNEL ANALYZER AND AUTOMATED CALIBRATION SYSTEM

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We collected continuous (10-min measurements of total, elemental, and oxidized mercury) during July and August 2019 in a rural/suburban area north of Denver, Colorado, U.S.A., with a dual-channel mercury speciation measurement system. The system uses a Tekran 2537 analyzer to sequentially sample air pulled through a pyrolyzer for total mercury and through a cation-exchange membrane for elemental mercury. It measures oxidized mercury as the difference between these two sample streams. The 1-hour oxidized mercury detection limit in the Colorado deployment was about 45 pg m-3. We deployed an automated calibrator as well, and we used it to calibrate the dual channel instrument routinely with HgBr2, HgCl2, and elemental mercury. Hourly average elemental mercury ranged from 1.2 to 2.3 ng m-3, and oxidized mercury ranged from -38 to 230 pg m-3. We observed diurnal trends and correlations that were similar to what has been shown in studies that utilized KCl denuder-based methods. Oxidized mercury averaged 12 ± 10 pg m-3 at night (mean ± 95% confidence interval; midnight to 4:00) and 79 ± 11 pg m-3 during the day (noon to 16:00), was anticorrelated with elemental mercury and humidity (r² = 0.36 and 0.86, respectively, for diurnally averaged data), and positively correlated with ozone (r² = 0.91). Measured oxidized mercury was on the high end of the range that has been observed at other sites around the western U.S., perhaps because other measurements were mostly made with KCl denuders that are known to have a low bias. HgBr2 and HgCl2 calibrations recovered only 43 ± 13% of injected mercury as oxidized mercury. The system had a 6 m heated inlet line prior to the dual channel unit, and oxidized mercury increased the longer the injection continued, perhaps because injected compounds did not pass efficiently through the inlet line.

This first deployment of a new, dual channel-based measurement system for mercury species was able to distinguish concentrations and behavior of elemental and oxidized mercury in the atmosphere. This system provides a new, verified method to measure mercury species in the atmosphere. We are continuing to improve the system, including injection continued, perhaps because injected compounds did not pass efficiently through the inlet line.

To examine if complete oxidation of DOM would reduce elution prior to pre-concentration. In a similar approach to what was employed to rectify interference from organic matter with persulfate, hydrogen peroxide, and UV pre-treatment. Natural water samples with low Hg concentrations (<5 ng/L) require large volumes (2-40 L) that are impractical for purge and trap methods. Cation exchange resin has proved to be a suitable alternative method for these samples, however, performance under a range of dissolved organic matter (DOM) is not well constrained. To test the oxidation of DOM using BrCl, small volume experiments (250mL) were conducted with Everglades hydrophobic acid (HPOA) DOM (5 and 25 mg/L), sulfide, and manganese. No statistical difference was observed in the MDF or MIF in comparison to the stock solution. When this technique was scaled to larger volumes (15-20L) of natural waters with high DOC concentrations (20-30ng/L) resin discoloration and increased volume for quantitative elution was observed. This indicates water samples with high DOC concentration and quality may need additional oxidation prior to pre-concentration. In a similar approach to what was employed for biological purge and trap samples, persulfate additions were tested to examine if complete oxidation of DOM would reduce elution volumes and result in accurate Hg isotopic composition.

COMPARISON BETWEEN DERIVATIZATION AND HYDROGEN GENERATION FOR THE PRECISE DETERMINATION OF METHYLMERCURY Δ13C COMPOUND SPECIFIC-ISOTOPIC-ANALYSIS BY PURGE-TRAP GAS CHROMATOGRAPHY COMBUSTION ISOTOPE RATIO MASS SPECTROMETRY

CHRISTELLE, Lagane1; SILVIA, Queipo-Abad2; MARINA, Renedo-Elizalde1; DAVID, Point1
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Mercury (Hg) is a global pollutant that impacts human health and ecosystems. Hg integrates into the natural carbon cycle, where it is transformed into methylmercury (CH3Hg), an organometallic neurotoxin with biomagnification properties in food webs. Despite significant improvements in environmental Hg science, we still lack answers to some of the most fundamental questions about Hg cycling: where and how CH3Hg is produced in aquatic ecosystems. Current Hg analytical tools offer only limited resolution to characterize and quantify complex in situ biogeochemical processes operating at ultratrace levels. The purpose of the compound specific carbon stable isotopic analysis (δ13C-CSIA) of the methyl group of CH3Hg, is to explore the interaction mechanisms between the carbon cycle and Hg sources and its contribution to CH3Hg formation. The stable isotopic composition (δ13C) of the carbon atom embedded in the CH3Hg toxin holds key information about its source origin and fate. This analytical challenge requires the development and optimisation of new high-resolution analytical tools. In this study, we propose an advanced and original technique based on purge and trap system (PT) coupled to a gas chromatography combustion isotope ratio mass spectrometry (GC-C-IRMS) with the objective of determining the total amount of CH3Hg available in a low nanogram scale. For this purpose, two analytical approaches were developed and compared: (i) an

INVESTIGATION OF ORGANIC MATTER INTERFERENCES FOR LOW LEVEL HG PRE-CONCENTRATION TECHNIQUES

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Measurements of mercury (Hg) isotopes are continuously expanding to better resolve processes and pools of Hg in the environment. As the focus expands to natural sites, uninfluenced by direct point source contamination, new challenges arise with making Hg isotope measurements in media with ever lower Hg concentrations and increasingly complex matrices. In this study, we have optimized two pre-concentration methods to deal with these challenges; a rapid thermal desorption system and cation exchange resin. For solid samples with low Hg concentrations or limited mass a rapid thermal desorption system was designed to allow for increased sample throughput and a smaller trapping volume (2mL), compared to traditional furnace methods. Following acid digestion, solids were purged onto gold traps that were then desorbed step-wise over a 40-minute heating program and collected into an oxidant trap. No mass dependent (MDF) or independent fractionation (MIF) was observed and Hg mass percent recoveries were consistently greater than 95% for natural water and sediment samples with this method. When the rapid desorption method was applied to biota, simple matrices, such as fish tissue, were successful. Digestion procedures were sufficient to accurately measure Hg concentration of plankton and plant matrices, however, interferences due to organic matter prevented quantitative trapping when applied to larger sample masses. More aggressive digestion protocols were employed to rectify interference from organic matter with peroxide, hydrogen peroxide, and UV pre-treatment.

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indirect technique based on the derivatization (ethylation) of CH$_3$Hg and, (ii) a direct technique based on hydride generation, with the formation and analysis of a CH$_3$HgH compound. The obtained δ13C-CH$_3$Hg values for a standard solution prepared from the same CH$_3$HgH salt were similar for both the derivatization method (-53.5 ± 1.9 ‰) and the direct CH$_3$Hg hydride generation technique (-54.8± 0.4 ‰), which are consistent with previous isotopic values obtained in our previous study (-53.8 ± 1.1 ‰). Although both methods exhibit δ13C-CH$_3$Hg isotopic values in good agreement, the hydride generation technique provides a significantly higher precision, even when varying the quantity of CH$_3$Hg analysed (from 200 to 600 ng). This result highlights a good reproducibility in terms of hydride generation yields, independently of the concentration of the standard solution, then permitting the precise determination of δ13C-MeHg across a wide range of concentrations. These new developed methodologies are encouraging towards their application in natural biological samples displaying CH$_3$Hg concentrations in the low-mid ng/g range, and represents a substantial analytical advance in order to explore the meaning of the carbon stable isotopic signature of CH$_3$Hg in the environment.

R.P1.32

WHAT IS NEW IN THE WORLD OF NATURAL HG MINERAL SPECIES?

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There are 103 approved naturally-occurring mercury-containing minerals in the International Mineralogical Association (“IMA”) master list as of November 2018. A 104th published mineral with no IMA status is azarkite, the bromine end member with corderoite, Hg3S2(Br,CI)2. Goldamalgam, (Au,Ag)Hg, a poorly described mineral, is not assigned an IMA number or status, but brings the total of HG minerals in the list to 105. Approximately twenty as-yet-unpublished naturally occurring mercury minerals are in the process of being described. Over the last 40 years, Mr. Gail Dunning of Sunnyvale, California, with both professional and amateur associates, has pursued new mercury mineral discoveries. Twenty-one uncharacterized mercury minerals have been found at the Clear Creek mine, San Benito County, California, USA, and about half have been named and accepted as new minerals. Mr. Dunning and his associates are also pursuing twelve uncharacterized mercury minerals from northern Humboldt County, Nevada. The discoveries, and those in process, add significantly to a family of mercury minerals with the general formula Hg3S2X, where X may be any of several simple or complex anions capable of forming a compound with a strongly-bound cationic structural unit [Hg3S2]**+, made up from 3Hg2+ + 2S2-. A revised mineralogical classification is proposed for these minerals.

This information is relevant to pollution research and abatement that explores the meaning of the carbon stable isotopic signature of CH$_3$Hg in the environment.

R.P1.33

AN IMPROVED AUTOMATED CALIBRATOR TO VERIFY ATMOSPHERIC MERCURY MEASUREMENTS

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Previously, we developed a calibration system that used permeation tubes to deliver stable concentrations of elemental and oxidized mercury (HgBr$_2$ and HgCl$_2$) to atmospheric mercury measurement systems (Lyman et al., 2016). We have improved this calibrator by (1) moving the electronics and data logging indoors to improve performance and heat management, (2) using capillary tubing to reduce residence time of mercury compounds in the device for less contamination and breakdown of oxidized mercury compounds, (3) adding the capability to introduce mercury-free air to measurement systems and inject calibrant gas into mercury-free air, and (4) adding a second outlet so the calibrator can verify the performance of multiple instruments. We have also developed techniques to independently verify the permeation rate and speciation of oxidized mercury permeation tubes, and these will be discussed in a separate presentation. We present results from use of the automated calibrator to verify elemental and oxidized mercury measurement instrumentation, including (1) a dual-channel mercury analyzer, which utilizes a pyrolyzer channel for total mercury and a cation-exchange membrane channel for elemental mercury, and (2) a system that pulls air at low rates through nylon and cation-exchange membranes, which are then analyzed for total mercury content in the laboratory. We will discuss the calibrator’s features, level of reliability, output stability and speciation, and how calibration results with independently-verified permeation tubes compare against traditional calibration methods (i.e., elemental mercury vapor injections) in field settings.

R.P1.34

PROFICIENCY TEST PT MUSHROOM - TRACE ELEMENTS IN MUSHROOM

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In the framework of the of the “ERA Chair ISO-FOOD for Isotope Techniques in Food Quality, Safety and Traceability”, we organised a proficiency test (PT) for the determination of trace elements in edible field mushroom (lat. Xerocomus badius, family Boletaceae).

The PT Mushroom was prepared from mushrooms collected from a non-contaminated rural area as part of an IAEE project (H. Polkowska-Motrenko, M. Rossbach, Accred. Qual. Assur., 2007, 12:343-350).

In summary, whole mushrooms were cleaned, chopped up with a stainless steel knife, air dried, milled and sieved. The sample size was small enough to be measured in a fraction of a millimeter (less than 1 mm). The samples were then milled, using a zirconium planetary ball mill, sieved (125 μm) and homogenized. Care was taken to avoid contamination. After homogenization, the particle size was determined, and tested for homogeneity. The material was then subsampled into HDPE bottles, containing 2 g of sample.

Fifteen laboratories from eleven countries registered to the PT. The exercise and reported results for 13 elements. The quality requirement expressed as relative standard deviations for proficiency assessment (rpt) were set according to modified Horwitz equation: 15% for Ag; 18% for As; 16% for Br; 14% for Cd; 11% for Cs; 8% for Fe; 20% for Hg; 3% for K; 19% for Mo; 6% for Na; 6% for Pb; 18% for Se; 7% for Zn. Most of the participating laboratories reported satisfactory results (according to the z score) which confirms their overall good performance. Noticeable deviations are mostly found for toxic elements such as As, Cd and Hg. Speciation data for Hg were reported by two laboratories with significant differences. Speciation of As was not reported. Performance of accredited laboratories was compared to non-accredited labs. Wet digestion using microwave was practised by most laboratories, but the results were similar to conventional wet digestion techniques. In case of mercury two methods were used, combustion followed by CV AAS method (DMA) and wet digestion followed by CV AAS. Both methods provided comparable results. In case of microwave wet digestion lower results were obtained for Hg, most probably due to losses. For other elements no significant differences were observed among the most commonly used detection methods (ICP MS and NAA).
DETERMINATION OF METHYLMERCURY IN SCOT-TISH BIRDS OF PREY (RAPTORS) USING LC-PVG-AFS

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A new, simpler sample preparation and analysis technique for methylmercury has been recently developed for seafood and hair matrices. The method combines a simplified methylmercury extraction and photochemical vapor generation (PVG) of Hg0 with liquid chromatography and atomic fluorescence spectrometry (LC-AFS). This reduces the number of reagents required to methanol and APDC for offline extraction and online separation of Hg species, and acetic acid combined with UV photolysis, which generates volatile Hg0 in one single step. Since then, the method has been applied to a study of methylmercury in the livers of Scottish birds of prey (raptors). The extraction was optimised for liver matrix using dolphin liver CRM DOLT-4 as proxy, giving good recoveries within 90–110%. A preliminary study has been carried out to assess the methylmercury concentrations in Scottish raptor livers using 33 samples from a broad range of raptor species. All samples were dried by lyophilisation, powdered, and homogenised. The samples were tested for reproducibility, which was found to be below 5% RSD in all cases, and to establish a methylmercury concentration range in the livers of Scottish birds of prey, which was found to vary over two orders of magnitude from 0.216–20.8 mg kg−1 across the 33 samples analysed.

APPLICATION OF DIFFUSIVE GRADIENT IN THIN FILMS (DGT) METHOD TO ASSESS BIOAVAILABLE Hg IN ARTIFICIAL AND NATURAL SOILS

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The technique of diffusive gradient in thin films (DGT) has been used as a potential tool for predicting metal bioavailability in soils mostly under laboratory conditions. In this study, we have examined the influence of soil properties (e.g., pH, ORP, organic matter content, labile Hg, and water holding capacity) on the accumulation of Hg in binding gel embed in DGT device and in the earthworm species Eisenia fetida, deployed in OECD artificial soils and natural river soils. The exposure of DGT and earthworm to Hg contaminated soils has been conducted using artificial soils prepared with different percentage of peat moss (i.e., 5, 10, 15, and 20%) and varying pH values (i.e., 4.6, 5.6, and 6.2). As a result, the DGT-soil accumulation factor (DSAF) and biota-soil accumulation factor (BSAF) increased as the peat moss content decreased and the pH increased. Across diverse soil properties, the apparent steady state of Hg concentration in earthworm was found to be correlated with the DGT-measured Hg flux, while there are no significant correlation between Hg in earthworm and labile Hg concentrations measured by chemical extraction methods. The result indicates that DGT-measured Hg flux is a better tool than conventional methods for predicting Hg bioavailability by earthworms. In order to evaluate the applicability of DGT technique to natural soils, DGT and earthworms were deployed in eight surface soils collected from Hyeongsan River, along with the measurements of conventional soil properties. The experimental results revealed that the Hg concentration in earthworm was able to be predicted by DGT-measured flux, and moreover, 71% of BSAF and 64% of DSAF variations were explained using a multiple linear regression model applying soil properties. Overall results demonstrate that the DGT-measured Hg flux, roughly predictable by related soil properties, is a practical tool for evaluating Hg bioavailability for earthworms inhabiting diverse types of soils.

ISOLATION AND ISOTOPIC DETERMINATION OF METHYLMERCURY USING PRETREATMENT ACID EXTRACTION OR DISTILLATION COUPLED TO ANION-EXCHANGE CHROMATOGRAPHY FOR BIOTA AND SEDIMENTS

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It is well understood that the chemical speciation of Hg controls its mobility and toxicity in the environment, furthermore this can also impact the Hg isotopic composition and fractionation processes it undergoes. Thus, the isotopic determination of methylmercury (MeHg) and inorganic mercury (HgII, Hg0) has the potential to provide a better understanding of Hg cycling and biogeochemistry in comparison to bulk isotope measurements alone. Various techniques have been developed for the analysis of MeHg isotopes, with the goal of producing reliable and precise measurements. Despite these analytic advances, few isotopic measurements of naturally occurring MeHg pools exist, due to the lack of an accepted approach for both biological and sediment matrices, as well as other analytical complications.

In an attempt to overcome some of these challenges, our technique employs anion-exchange resin chromatography for species separation of MeHg. Using optimized, matrix-specific pretreatment steps, consisting of either distillation or acid extraction, coupled to resin separation, we liberate matrix-bound MeHg and take advantage of the species’ characteristics in acidified aqueous solutions containing chloride to separate it from inorganic Hg. Further, isotopic spike experiments of MeHg standard show no fractionation is imparted via resin separation. We demonstrate the effective concentration recovery of MeHg in biological CRMs (DOLT-2, TORT-2) and MeHg spikes in synthetic and natural waters and sediments, down to 5 ng of MeHg.

Application of MeHg separation techniques to natural sample matrices (sediments, invertebrates, plankton, and fish) have also been successful. Results for sediment show that acid extractions, coupled to resin separation, allow for breakthrough of HgIII species, whereas distillation showed >90% recovery and preservation of the isotopic signature of the MeHg spike added to the matrix. Lipid-washed biological CRMs, separated using acid extraction coupled to resin, showed acceptable recoveries and comparable isotopic values to previous literature methods, with similar variability. However, further application of acid extraction coupled to resin separation, as well as previously cited toluene extractions, did not perform well for natural plankton and fish matrices. Due to the higher mass requirements and lipid content of natural tissues, distillation was employed prior to resin separation, which improved method performance. This method has been successfully applied to ambient MeHg fractions in sediments, invertebrates, plankton and fish from a contaminated system. By examining the isotopic composition of the methylated, bioaccumulated fraction of Hg, we aim for an improved understanding of Hg cycling, sources, and bioaccumulation through aquatic food webs.
LONG - TERM STUDY OF ATMOSPHERIC MERCURY DEPOSITION AT MONITORING STATIONS IN LITHUANIA

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The results of long-term study of atmospheric mercury concentrations in the rain water carried out at the Auksštaitija (Highland) and Žemaitija (Samogitia) integrated monitoring stations are presented in this work. The bulk precipitation samples at both stations were collected every week during the 2007-2017 periods. The mercury measurement method is based on the absorption of radiation by mercury vapor at the 253.7 nm line. Monthly samples of precipitation after preparation were analyzed using the mercury analyzer “Gardis-7” developed at our institution. The average annual concentrations, deposition amounts and trends of mercury in the precipitation over the period of 2007-2017 were analyzed. The tendency of average monthly mercury concentrations in the precipitation at the Žemaitija station was continuously increasing before 2011, however, after 2012 it has a decreasing tendency which was contrary to that at the Auksštaitija station. At the same time, the tendencies of average monthly amounts of mercury deposited with precipitation showed decreasing amounts, especially at the Žemaitija station. Explanation of the above mentioned phenomenon is complicated and the main reasons are changeable air mass trajectories and irregularity of precipitation.

PECULIARITIES OF MERCURY DISTRIBUTION IN SHUNGITES

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Shungite is a mineraloid consisting of up to 99 % of carbon. The first deposit was found near Shunga village (Karelia, Russia) within the Paleo-proterozoic host rocks. Karelian shungites represent the greatest accumulations of carbon with reserves of up to one billion ton. Shungite matter is considered as a specific allotrope of carbon having complex globular supramolecular structure with the globules size of 5-10 nm and including 0.0001 – 0.001 % of natural fullerenes. There are two opinions on the shungite origin: the deep metamorphism of the organic-rich sedimentary rocks and the pyrolysis of the mantle methane jets. Association of mercury and hydrocarbons (coal, gas, oil) is quite fairly studied. E.g., in coals, the mercury content varies in a range from ppb to few hundreds ppm with a world average of 100 ppb. Mercury, as an informative geochemical indicator, can help throw light on the shungite origin; however, so far almost no data on mercury in shungites are available. Zeeman AAS was used for determination of the total mercury concentration in shungites. Surprisingly high concentration up to 12,000 ppb with an average of 2,200 ppb was found in all samples, which is much higher even as compared with the mercury concentration in coal of the Donetsk basin located within the mercury belt with an average level of 450 ppb. The thermoscaning technique was applied to study mercury thermospecies. This technique revealed a high-temperature form of mercury in shungites releasing at a temperature above 640 oC and comprising 39-45% of the total mercury. That drastically differs from the thermospectra of anthracite with the main portion of mercury being released at a temperature below 480 oC. The loss of mass for anthracite and shungite during heating to 900 OC is practically identical, whereas the loss of mercury from anthracite is much faster. As both substances consist mainly of carbon, the difference in mercury binding energy can be explained by a specific globular structure of the shungite matrix. Additional experiments on the shungite exposure to mercury in the liquid and gaseous phases showed the increased mercury release at a low temperature and no increase in the high temperature species. The occurrence of a significant portion of the uncommon high temperature species suggests that this mercury can be transported with the mantle methane jets and captured inside the firm carbon globules of the shungite.

DETERMINATION OF TOTAL HG IN NATURAL WATERS AFTER AMALGAMATION OF HG2+ ON CU POWDER AND HG0 ON AUNPS

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Determination of total amount of mercury (Hg) in natural waters is usually carried out after chemical restoration of Hg2+ ions to elemental mercury Hg0, using cold vapour generation technique with atomic absorption detection (CV-AAS). The limit of detection (LOD) of Hg determination in natural waters using (CV-AAS) is approximately 0.2 µg L-1. At present, to reduce the value of LOD of Hg determination in natural waters is only possible by analytical methods in which a step of preconcentration is involved. The most promising method of preconcentration could be the sorption of Hg0 on golden nanoparticles. For this, all Hg2+ ions in water samples must be reduced to elemental mercury. This step of chemical pretreatment is connected with additional time of analysis and could be the reason of either losses of Hg or contamination of samples. To...
avoid the problem of samples chemical pretreatment, we proposed the method of determination of Hg in water samples by preconcentration of Hg(II) on copper powder and Hg on golden nanoparticles impregnated into membrane filters. The reaction between different chemical forms of mercury with Cu and Au are the following:
Hg^{2+} + Cu → Hg + Cu^{2+} (1), Hg + Cu → CuHg (2), Hg + Au → AuHg (3).

The measurement of Hg were carried out by thermal desorption of Hg from filters, using a RA-915+ mercury analyzer (Lumex, Russia). The determination of Hg by thermal desorption does not involve any additional chemical reagents and sharply reduces risk of samples contaminations. The LOD calculated using the calibration graph function (y=332x + 2, R^2=0.9983) and corresponding standard deviation (3.2 %) for the calibration line was found to be 0.2 ng L⁻¹. The validation method was done by analysis of CRM TORT-2, which was obtained after chemical decomposition in HNO_3 and H_2O_2 using microwave digestion, Mars-5 were in good agreement with certified value 0.27±0.06 µg g⁻¹. The results of recovery test, which was conducted with samples of tap water collected in Pretoria, were in the range of 94 – 104 % for Hg concentrations of between 0.5 and 1.0 ng L⁻¹. The greatest advantage of this method is the possibility of samples collection on the spot, without transportation of large amounts of water for the analysis in the laboratories due to high efficiency of simultaneous collection of Hg(II) and elemental Hg(0) from aqueous phase on membrane filters.

**R.P.1.42**

**EFFECTIVENESS OF DGT TECHNIQUE WITH OPEN AND RESTRICTED GELS IN PREDICTING MERCURY UPTAKE BY PLANTS**

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Peri-urban agriculture provides environmental benefits to the nearby urban areas. However, domestic and industrial infrastructures can be sources of pollution that can affect agricultural production. On the other hand, worldwide concern regarding mercury (Hg) toxicity and the associated risk for human beings calls for an easy tool to determine the bioavailable Hg which would be able to predict the transfer of Hg from soils to crops. In this work, the diffusive gradient in thin film (DGT) technique was used to assess the bioavailability of Hg in organic-amended agricultural soils, and uptake by lettuce. Therefore, two different amendments were studied individually in three different sets using a wood-based biochar at two rates (3% and 6%), and compost at one rate (30%). The effect of the amendments on Hg bioavailability, mobility and uptake was investigated by means of both DGT analyses and accumulation of Hg by lettuce. DGT manufactured in-house devices with polyacrylamide gel using both open and restricted diffusive layers were used to determine organic and inorganic Hg labile species in soils, respectively. The Hg concentration in lettuce leaves and roots were analysed and compared with DGT measurements to predict the uptake of Hg from the different organic-amended soils and the non-amended soils. To interpret DGT measurements, CDGT can be converted to an effective concentration (CE) using different equations and applying the 2D DIFS model (DGT induced fluxes in sediments), considering the kinetic properties of each soil. Results show that the application of biochar reduces the bioavailability of Hg in soil and, in consequence, the Hg uptake by lettuce. Inorganic Hg species were predominant in all the different sets of the experiment (62-97%), although the addition of the different amendments reduced the free ionic species in soil. Finally, it should be highlighted that Hg obtained by DGT measurements in the soil matched the Hg concentration found in lettuce roots, confirming the effectiveness of this technique in predicting Hg uptake by plants.

**R.P.1.43**

**STUDY TO DETERMINE A RELIABLE MERCURY ANALYSIS PROCEDURE ON SULFURNATED-PASSIVE SAMPLER TRAPS**

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With the Minamata Treaty on Mercury officially enforced, the necessity to measure and monitor the global atmospheric and dry deposition of Mercury is important for better understanding on the emission sources and the migration. Passive sampler is one of the dry deposition sampling techniques used for collection of mercury in the air. Absorbants employed in such samplers are used either Sulfurinated or Halogenated which presents difficulties to the analysis. Therefore, it is key to have an easy and reliable analysis procedure to produce qualitative and accurate data.

**R.P.1.44**

**ANTAGONISTIC MECHANISM BETWEEN MERCURY AND SELENIUM IN RICE (ORYZA SATIVA L.) STUDIED USING 1, 2-DIMENSIONAL ELECTROPHORESIS AND SR-XRF TECHNIQUES**

**GAO, Yuxi**²

(1)Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Mercury (Hg) is a hazardous heavy metal in the environment and can accumulate and amplify in the food chain. Selenium (Se) is a necessary element for human health and has antagonistic effects on Hg toxicity in humans and animals. The antagonistic effects in plant was confirmed in our previous researches. But the antagonistic mechanism between Hg and Se in plant remains elusive. In this work, we investigated the effect of Se on Hg containing and Hg-responsive proteins in rice using 1, 2-dimensional electrophoresis combined with SR-XRF techniques. Two weeks old rice seedlings were exposed to Hg and/or Se compounds. After 21 days proteins in the rice roots were separated by electrophoresis and their metal contents were determined by X-ray fluorescence to identify Hg and Se responsive biomolecules. The results show that under Hg stress alone Hg is bound to proteins with molecular weights of 15–25 kDa. With the addition of Se, a new containing protein band in the 55–70 kDa range was also found, while the content of Hg in the 15–25 kDa proteins decreased. Ten and nine new protein spots were identified after adding Se to inorganic Hg and methylmercury exposed roots, respectively. Adding Se regulates the abundance of proteins associated with carbohydrate and energy metabolism, stress response, cell cycle, and DNA replication indicating that these proteins mediate the antagonism of Se against Hg toxicity. This study helps us to better understand the molecular mechanism of Hg tolerance as well as the molecular antagonism between Hg and Se in rice plants.

**R.P.1.45**

**DESIGN AND DEVELOPING OF PASSIVE SAMPLERS BASED ON NANOCOMPOSITE TiO2NPS/AUNPS MEMBRANES FOR TOTAL GASEOUS MERCURY MONITORING**

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Passive sampling systems (PASs) represent an approach to measure Hg concentration in the air in different environments and over variable periods from a few hours to weeks/months. A large variety of materials based on nanotechnology have already been used on purpose, even if state of the art in those nanomaterial-based passive samplers is still at infancy. For this reason, we have designed and developed passive samplers for total gaseous mercury based on innovative and robust nanostructured materials consisting of an adsorbent thin film made of titania nanoparticles (TiO2NPs, ≤25 nm diameter) finely decorated with gold nanoparticles. Because of the strong affinity between Au and Hg, an amalgam of the two elements is usually generated upon contact. This property was here exploited to create an efficient sampler for gaseous mercury. The TiO2NPs functionalization with AuNPs was obtained by exploiting the photocatalytic properties of titania-anatase when UV-irradiated and submerged in an aqueous solution containing HAuCl4. The resulting blue-violet suspension of TiO2NPs was deposited by drop-casting on a microfibrous and microporous thin quartz disk and then dried. The resulting nanodecorated composite support was stable and easy to be handled without suffering from apparent damages or detachment of the deposited thin film that was withheld by the microstructured substrate. The various PAS samples obtained upon this processing were then incorporated into an axial sampler, designed on purpose to be used as a potential PAS device.

The morphological characteristics of the PAS samples were analysed by High-Resolution-TEM, AFM and Optical Microscopy. The mercury adsorbed after exposure was thermally desorbed for a few minutes and then quantified by a mercury vapor analyzer (Tekran 2637A). Such a sampling system reported an efficiency of adsorption that was equal to ≈95%. Temperature and relative humidity seemed to affect the membrane performances very slightly. The developed PASs were tested both indoor and outdoor for more than six months, and the relative performances in terms of the sampling rate (SR), reproducibility and restoration were investigated and the results compared. Moreover, PASS loaded with different amounts of sorbent material were investigated in order to correlate their efficiency, as well as their lifetime, to the layer thickness and arrangement. Therefore, because of the ease of preparation, high sensitivity to gaseous elemental mercury deriving from the strong affinity of Au for Hg, high efficiency, and long lifetime, the AuNP/TiO2NP-based passive sampler here proposed sounds to be a promising candidate for passive monitoring.

FIT FOR PURPOSE ANALYTICAL PROCEDURES FOR DETERMINATION OF METHYL MERCURY IN SEAWATER

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Mercury is a global pollutant released into the environment from both natural and anthropogenic sources. Various Mercury species differ greatly in their bio-physico-chemical properties such as toxicity and rate of bioaccumulation by organisms. Therefore, the analysis of samples only for total mercury is no longer completely acceptable and provides only partial information about their impact on human health and the environment. As a consequence, considerable progress has been made in the development of techniques, which are capable of quantifying various mercury species. Future regulations on methylmercury (MeHg) will require the standardized procedures for quantitative determination of alkylmercury species, therefore there is a strong need for development of robust analytical procedures providing reliable data on both, total mercury and its chemical species in the complex marine matrices.

Among its multiple tasks, IAEA Environment Laboratories (IAEA EL) in Monaco acts as the analytical support centre for IAEA Member States laboratories and is the pillar of the Quality Assurance program for determination of contaminants in the marine environment. Several recommended methods for mercury and MeHg, based on the application of different analytical techniques are set up. Development and validation of reliable and sensitive method based on gas chromatographic separation and pyrolysis-atomic fluorescence spectroscopy (GC-py-AFS) in was developed and validated according to the recommendations of ISO-17025 standard and Eurachem guidelines.

Since reliable results are still mostly dependent on sample preparation step, special attention was payed on the development of the efficient extraction procedure for preconcentration of MeHg and seawater matrix separation. The full validation process following international guidelines is presented and described in detail. Preliminary forecast of the uncertainty budgets was used as a strategy to ensure that the determination of MeHg in seawater can be achieved with demonstrated traceability to a stated system of reference within less than 20 % expanded uncertainty (k=2).
MERCURY METHYLATION AND METHYL MERCURY DEMETHYLATION IN SULPHATE-LIMITED AND SULPHATE-RICH BOREAL LAKE SEDIMENT

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Sediment organic matter and porewater dissolved organic matter (DOM) play significant but heterogeneous roles in methymercury (MeHg) formation in freshwater lake sediment. Controls on MeHg formation can be further complicated where increased sulphate concentrations are present. This may be because of the stimulation of sulphate reducing bacteria (SRB) and potentially because of impacts on mercury bioavailability. This study used sediment from both sulphate-impaired and unimpacted boreal lakes in northern Ontario, Canada to investigate the importance of initial sulphate exposure and concentrations on the ability of sediment to methylate mercury and demethylate MeHg, using enriched isotope approaches (Kmeth and Kdemeth). Samples were further manipulated in laboratory incubations in a full factorial design using inputs of sulphate, Suwannee river fulvic acid standard II (SRFA, sulphur%=0.46%), Suwannee river natural organic matter (SRNOM, sulphur%=1.78%), and molybdate as a SRB inhibitor. Demethylation was relatively consistent across experimental treatments except where molybdate and sulphate were concurrently added to sulphate-limited sediment, resulting in significantly lower Kdemeth. Our results indicate that Kmeth was significantly greater in sulphate-impaired lake sediment, a finding consistent with many other studies. Addition of sulphate depressed Kmeth in sulphate-impaired lake sediment but increased Kmeth in low sulphate sediment, suggesting that sulphate only stimulates methylation in sulphate-limited sediment. The addition of molybdate resulted in significantly less mercury methylation, but methylation was not entirely depressed, suggesting a broader community of microbes methylate mercury in this system. Additions of DOM, especially the higher sulphur-containing DOM, stimulated methylation in sulphate-impaired sediment, but not in unimpaired sediment unless additional sulphate was added simultaneously. These results suggest that Hg methylation was more likely to be limited by SRB activity in less sulphate-impaired sediment, but probably regulated by Hg bioavailability in elevated sulphate sediment. This study suggests that methylation of mercury methylation change across a spectrum of sulphate exposure history. One less understood control may be the accumulation of sulphur into DOM.
Does the community structure of Hg-methylating microbes impact Hg methylation rate? Or is some other factor – perhaps the overall activity of Hg-methylating microbes, or Hg complexation and bioavailability – the main driving factor? How does the community structure of Hg-methylating microbes change in response to environmental conditions? In this study we enriched a freshwater microbial sediment community with different terminal electron acceptors to help address these and other questions. Key goals included evaluation of the types of hgcAB+ microbes enriched by select terminal electron acceptors (TEAs; nitrate, sulfate and ferrous iron); an assessment of the types of hgcAB+ microbes most related to net and gross MeHg production under each condition; and the correspondence between hgcA expression, gene abundance and diversity.

The starting community was taken from bottom sediments in Hg-contaminated East Fork Poplar Creek, in Oak Ridge, TN. Rotting leaf litter from the nearby creek bottom was used as organic substrate. Anaerobic sediment slurries were constructed using water with similar composition to the creek, degassed and reduced with Ti-NTA. Triplicate microcosm bottles were created for each of four starting conditions: 10 mM sulfate, nitrate or ferrous iron (as iron citrate), or no TEA addition. Overall heterotrophic activity (as estimated from the sum of DIC+CH4 production) was highest in Fe(III) and sulfate amendments. The control bottles had the highest ratio of CH4:DIC production.

Gross methylation rates (measured with stable isotope spikes) were highest in the sulfate enrichments, and lowest in nitrate enrichments. Initial- ly, net MeHg accumulation was also highest in the sulfate treatments, but declined after sulfate accumulated. Gross demethylation rates were high in all treatments. After a month, nitrate amended bottles contained the most MeHg. The balance between methylation and demethylation was a strong driver of MeHg accumulation in these enrichments. Quantitative qPCR using clade specific primers suggested that methanogen hgcA sequences were most abundant in the control bottles, while deltaproteobacterial hgcA sequences were most abundant in the sulfate bottles and least abundant in the nitrate enrichments. We will compare methylation rates and net MeHg accumulation to the abundance and diversity of hgcAB+ organisms in the enrichments over time, using high throughput amplicon specific sequencing for hgcA. We are developing techniques for assaying hgcA expression in these enrichments using the same approach from RNA.

R.P.1.53

COMPARISON OF THE MERCURY REACTIVITY IN TWO DEEP SEA CANYONS (CAPBRETON, ATLANTIC OCEAN AND MONTEREY, PACIFIC OCEAN)

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Submarine canyons are important stocks of commercially important fisheries whose consumption is responsible for the main monomethylmercury (MeHg) human exposure. Currently, biogeochemistry of mercury in those biologically productive systems is unknown. Here, inorganic mercury (Hg(III)) and organic mercury (MeHg) distributions as well as the Hg reactivity were measured in surface sediments of two submarine canyons: Monterey Canyon in NE Pacific Ocean and the Capbreton Canyon in the NE Atlantic Ocean. First results have shown total mercury levels are up to seven times higher in the Capbreton than the Monterey Canyon (ranging from 18.2 to 975 ng g-1 dw and from 9 to 134 ng g-1 dw, respectively). Positive correlations between organic matter content, fine grain size content and mercury concentrations were shown, suggesting canyon sediments accumulate fine particulate matter and concentrate mercury. The reactivity of mercury species was investigated in sediments along a canyon transect using isotopic tracers during sediment slurry incubations in order to compare the specific methylation and demethylation rate constants (kM and kD) between those two submarine canyons. Results showed that MeHg levels in sediments are controlled by competing and simultaneous methylation and demethylation processes mainly mediated by biotic process. The mercury species levels and estimated kM and kD measured for the first time in these ecosystems suggests submarine canyon sediments could be significant in the global mercury cycle and should be considered in further studies.

R.P.1.54

KINETICS OF METHYL-MERCURY PRODUCTION IN PERiphyTON AND SEDIMENTS FROM A CONTAMINATED FRESHWATER STREAM

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Methylmercury (MMHg) produced by periphyton biofilms presents a substantial fraction of the overall MMHg flux in East Fork Poplar Creek (EFP), an industrially contaminated creek in Oak Ridge, Tennessee. We conducted experiments using mercury (Hg) stable isotopes to determine periphyton MMHg production rates across four seasons, two EFPC locations, and two light conditions. 201Hg and MM202Hg were added to intact periphyton samples from EFPC, and the formation of MM201Hg and the loss of MM202Hg were monitored over time. These data were used to calculate methylation and demethylation rate potentials using a transient availability kinetic model. This model incorporates kinetic expressions for multisite sorption of Hg and MMHg and Hg(II) reduction with methylation/demethylation kinetics to account for these competing processes when estimating methylation/demethylation potentials. Our experiments showed that, for methylation, light exposure and sea-
son were significant predictors of rate potential, with greater methylation rate potential in full light exposure and in the Summer. For demethyla-
tion, season, light exposure, and location were all significant predictors of rate potential. Demethylation rate potentials were highest in dark
conditions, in the Spring, and at the upstream location (closer to the Hg-contamination source). Net MMHg production was driven by light
exposure, with positive production occurring in periphyton grown under full light exposure and net loss of MMHg occurring in periphyton grown in
the dark. On average, transient availability rate potentials were 15x higher and 9x higher for methylation and demethylation, respectively,
compared to first-order rate potentials calculated at 1d. Our data show that light exposure is the controlling factor of periphyton net MMHg
production in EFPC, and our results underscore the importance of ap-
plying transient availability kinetics to MMHg production data to obtain accurate estimates of MMHg production potential and flux.
Our current work applies the transient availability kinetic model to metabolically active transient storage zones within sediments from
East Fork Poplar Creek. Experiments are underway to determine Hg and MeHg sorption and methylation/demethylation rates in the sedi-
ments. Sediments from different regions of the creek will be compared, and MeHg production rates will be correlated with measures of geo-
chemistry and sediment microbial activity.

R.P.1.55

PROGRESS TOWARDS UNDERSTANDING THE ROLE OF HGCA\(B\) IN HG-METHYLATION IN PURE CULTURES AND IN THE ENVIRONMENT

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Substantial progress in understanding microbial Hg-methylation has taken place since the discovery of the gene pair hgc\(AB\) and their use as a predictive biomarker for the ability of an organism to methylate mer-
cury (Hg). To date both qualitative (PCR) and quantitative (qPCR) tech-
niques have been developed to determine the abundance and diver-
sity of Hg-methylating populations. When combined with meta-omics approaches, the number and variety of Hg-methylators continues to
increase and encompass ever more physiological types of microorgan-
isms. We have recently improved our broad-range PCR primers and
have incorporated direct DNA sequencing of the PCR amplicons to im-
prove efficiency as well as throughput. While assessment at the DNA
level has been essential to further understand Hg-methylation, it is
unknown whether and to what extent are hgc\(AB\) expressed, as well as if particular geochemical conditions warrant an increase or decrease in expression at the community level. The ORNL group has developed
and used some of these techniques to ascertain a more comprehensive
picture of the local Hg-methylating community and are continuing to
do so with sequencing at both the DNA and mRNA levels.

Using these techniques and metagenomics, we have discovered sev-
eral new and novel putative Hg-methylators which we are attempting to
isolate, while also beginning to construct and assess multi-species
communities using cultured, highly prevalent Hg-methylators from our
site in highly controlled chemostats so as to better understand the ef-
fect of lifestyle (syntrophic versus competitive) as well as geochemistry
on the activity of Hg-methylation. These results will begin to inform
modeling efforts in an effort to accurately describe as well as eventual-
ly predict Hg-methylation potential.

While we are studying the community levels aspects of Hg-methyla-
tion, several questions remain as to the mechanism of Hg-methylation
by hgc\(AB\). Their abundance in microbial communities where Hg is lim-
iting, and the widespread diversity of hgc\(AB\), suggests that it may code
for an enzyme with a native physiological function beyond Hg-methyla-
tion and act as a methyl group carrier to facilitate acetyl-CoA gen-
eration as part of the Wood-Ljungdahl carbon fixation pathway for ac-
etate production and/or convert homocysteine to methionine. While
small differences in growth and metabolites are observed when hgc\(AB\)
is deleted in D. desulfuricans ND132, recently acquired transcriptomic
and metabolomic data suggests a complex compensation to reroute
carbon and electrons. This suggests that hgc\(AB\) codes for a membrane
protein complex involved in single-carbon metabolism and likely in-
cludes the formation of acetate from CO\(_2\) for biosynthesis.

R.P.1.56

TRACEABLE DETERMINATION OF GASEOUS ELEMENTAL MERCURY USING IMPREGNATED ACTIVATED COAL AS AN EFFICIENT TRAPPING SORBENT

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Mercury (Hg) in the atmosphere has a crucial role in the global cycle, where it mostly exists as gaseous elemental mercury (GEM). Gold traps
are most commonly used for the collection of GEM samples. Howev-
er, they are prone to passivation during longer sampling periods or in
the presence of chloride ions. Impregnated activated carbon (AC) have
been used in the industry for the removal of Hg from the flue gas. The advantage of AC is its resistance to passivation, while the major
drawback is possible high procedural blank. In this work, we have as-
essed the use of AC traps as efficient trapping sorbents for GEM by
comparing two methods traceable to the certified standard solution
(NIST 3133). In addition, we compared the performance of the com-
mercially available iodinated AC with the in-house prepared iodinated
and brominated AC traps.

In-house AC traps were prepared by heating virgin AC for 5 hours at
500°C, equilibration in the solution with known concentrations of
iodide (bromide), and stirred for 48 hours at 300 rpm. Following im-
pregnation, AC was washed with Milli-Q water and quickly dried under
reduced atmospheric pressure (rotavapor) to avoid desorption of im-
pregnating salt. Approximately 150 mg of AC (commercial or in-house)
was packed into each quartz trap.

Certified standard solution of mercury was loaded onto AC using two
methods. First, a known amount of mercury was reduced to Hg(0) using
\(\text{Hg}^{2+}(-\text{II})\) chloride solution and quantitatively purged onto the AC traps.
For the second method, direct spiking of AC with a known volume of
certified standard solution was used. Mercury content in AC was de-
termined using atomic absorbance spectrometer (AAS) equipped with
Zeeman background correction. AC was carefully transferred from the
quartz tube to the analytical boat, heated at 700°C in the pyrolytic unit
to release Hg which was determined by AAS.

Commercial AC and the in-house AC impregnated with 0.01 M iodine
solution obtained quantitative recovery when comparing both loading
methods at 1000 ng Hg level. In addition, commercial AC was tested
for a wider range of Hg concentrations (100 – 2000 ng) and showed
good correlation \(r^2 = 0.9984\) between two loading methods. Results

demonstrate that impregnated AC could be used for traceable deter-
mination of GEM in the air samples. However, the use for its determi-
ations in the unpolluted atmosphere might be limited, due to relatively
high procedural limit of detection (<1.98 ng per trap).

R.P.1.57

A STUDY ON THE SPECTROPHOTOMETRIC ANALYSIS OF HG(II) USING DITHIZONE UNDER CONDITIONS PERTINENT TO HG(II) REDUCTION IN AQUATIC SYS-
TEMS

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The reduction of mercuric mercury (Hg(II)) in aquatic systems to the
more volatile elemental mercury (Hg(0)), operationally defined as dis-
solved gaseous mercury (DGM), is of environmental importance because
it can potentially lessen the pool of Hg available for methylation and ulti-
mately bioaccumulation and biomagnification in the food web. Photo-re-
duction of Hg(II), which is primarily bound to organic ligands (Hg(II)L), has been hypothesized as the fundamental mechanism for DGM generation in surface waters. However, more research is required to gain a better kinetic and mechanistic understanding of these reactions.

Spectrophotometric analysis of Hg(II) using dithizone is a useful and effective analytical method in various research on environmental Hg redox chemistry. We investigated the applicability of the dithizone method for spectrophotometric analysis of Hg(II) under different environmental conditions pertinent to the study on aquatic Hg(II) reduction, particularly superoxide-mediated Hg(II) reduction. We examined the effects of (1) aqueous systems (pure water vs. bicarbonate buffered solutions), (2) ligands, and (3) pH on the dithizone-Hg(II) analysis method. Results showed that the method was valid and applicable under the different conditions studied as none of the three variables were found to affect the sensitivity of the method. This suggests that the dithizone method is suitable for the study on the superoxide-mediated Hg(II) reduction. Upon verification of the dithizone analysis method, an experimental setup was developed to obtain the redox kinetics of Hg(II) and Hg(II) L complexes in the presence of superoxide (O2•−/HO2•) and potentially its conjugate acid, hydroperoxy (HO2•). Our preliminary research suggests that O2•−/HO2• appears to be able to reduce mercuric complexes under certain environmental conditions.

R.P.1.58

SPATIOTEMPORAL DISTRIBUTION OF ANTHROPOGENIC HG EMISSION IN PAKISTAN

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Pakistan is facing severe environmental pollution like neighbouring countries in South Asia. This study reviews the current state of knowledge regarding emissions of mercury (Hg) in Pakistan and investigates the intensity and spatial distribution of Hg emissions to the atmosphere from anthropogenic sources. The largest sources of Hg emissions are industries, combustion of fossil fuels and coal, gold mining, electronic devices, medical and agricultural waste. Pakistan has been experiencing polluted atmosphere in recent decades and lethal impacts on human health and the environment. This research has been carried out to study the trends of Hg in Pakistan both spatial and temporal. Country wide gridded model based anthropogenic Hg emission data is retrieved from Global Mercury Observation System (GMOS). GIS interpolation techniques were used to generate maps to show the horizontal distribution of Hg climatology over Pakistan. It is noted that high emission areas of Hg (0.0164pg/m2/s) is eastern boarder of Pakistan and Baluchistan has the lowest emission of Hg (0.0074 pg/m2/s). In addition, cumulative seasons are studied along with wind to find the direction of polluted air mass of Hg. The correlation between Hg and relative humidity (%) shows a significant relation however, with other meteorological parameters such as temperature, precipitation did not show any correlation. The seasonal mean Hg show high emission in pre-monsoon and post-monsoon seasons (0.003-0.01 pg/m2/s) due to dry weather conditions. In monsoon, the emission is very low (0.0005-0.0055 pg/m2/s) due to monsoonal rainfall in the country. The temporal trends of Hg emission have shown the increased rate throughout the selected years. This study also illustrates that the different climatic conditions during different seasons create a different scenario for transportation and accumulation of Hg in Pakistan.

R.P.1.59

GEOTRACES INTERCALIBRATION EXERCISES AND DEVELOPMENT OF REFERENCE MATERIAL FOR THE COMMUNITY

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(1) MIO

Mercury is one of the least concentrated elements in the oceans. Low concentrations, in addition to different collection procedures, storage and preservation methods, and analytical techniques, result in poor reproducibility of marine mercury measurements. Sound analytical methods are needed to understand and interpret global Hg distribution and trends. To evaluate analytical performance, we organized three international intercalibration exercises for total mercury (tHg) and total methylmercury (MeHg) determination in seawater collected during the 2013 GEOTRACES MEDBlack cruise (Black Sea), the 2014 GEOTRACES GEOVIDE (North Atlantic Ocean), and the 2015 GEOTRACES TranSArC (Arctic Ocean). Each laboratory received a single sample bottle that had undergone the same cleaning procedure prior to sampling and each sample was preserved in the exact same manner. The 2013 exercise was intended as a broader screening with 25 participating laboratories. Results indicated substantial disagreement between the participating laboratories, for both total mercury and methylmercury determinations. For the 2014 exercise we could only invite the 10 best performing laboratories from the 2013 exercise. Intercomparability of this second exercise was considerably better. For the 2015 exercise we invited again a larger panel of laboratories and received results from 24 laboratories. Results indicated again substantial disagreement between the participating laboratories for both target species. The results call for a more thorough investigation and continued efforts to obtain better intercomparability. Intercalibration exercises based on preserved samples can only address total mercury and total methylmercury, but not the gaseous dimethylmercury and gaseous elemental mercury species. This is why we organized, together with 20 participating laboratories, the 2017 GEOTRACES Hg species intercalibration cruise. As part of this cruise we sampled reference seawater into 1200 pre-combusted glass bottles. For now, the only commercially available certified reference materials for total mercury in seawater are ERM-CA 400 (European Reference Materials) and BCR-579 (Institute for Reference Materials and Measurements), which have total Hg concentrations of 82 ± 5 and 9.5 ± 2.5 pM, respectively. Those Hg concentrations are much higher and are associated with a high uncertainty, compared to average Hg levels and variability (1 ± 0.8 pM, n = 5352) observed in the open ocean. No certified reference material for ambient methylmercury in seawater is available yet. We also sampled 30 kg of marine sediment. The sediment has been dried at 60°C, sieved at 300 micrometers and ground to obtain a homogenous reference material. Both in-house reference materials are now freely available.

R.P.1.60

TOTAL HG IN SAMPLES FROM CEMENT PRODUCTION USING PYROLYSIS COUPLED TO AAS – METH-OD VALIDATION

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Cement is an indispensable material used for construction. It is obtained by heating a mixture of limestone, clay and other materials at high temperatures to obtain clinker. The raw materials and fuels used in cement production contain mercury (Hg) as an impurity, for which emission limits are already in place. Controlling the input of Hg through raw materials as a dominant source of Hg, is one way cement industry complies with the emission limits. The objective of this work was to assess the suitability of portable Lumex RA-915+ for quantification of total mercury in raw materials and intermediate products in cement production process and to validate such method so it will fulfill the analytical quality control requirements and aid cement industry in monitoring mercury inputs in the process. With respect to solid nature of the samples, two different calibration approaches were employed: (1) calibration of the standard matrix under study. The method provides a lin-
ear working range up to 250 ng absolute Hg mass and the detection limit of 0.9 ng, which is satisfactory for the materials used for cement production. The expanded uncertainty (k = 2) obtained with the second calibration approach were in a range of 25 – 32 %, and were lower compared to the results obtained with the matrix CRM calibration approach. Overall, the method proposed has an advantage that it does not require sample preparation, which minimizes mercury loss that occurs when the sample has to be digested.

R.P.1.61

METHOD DEVELOPMENT FOR TOTAL MERCURY AND MERCURY SPECIES DETERMINATION IN SORBENT TRAP MATERIALS OF RELEVANCE TO ENVIRONMENTAL MONITORING

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The work presented here discusses method development and validation for the determination of total mercury (Hgtot) and mercury species ([Hg]I, CH3Hg+) in a variety of solid state materials, often used as sorbent traps of relevance to environmental monitoring. Activated carbon (AC), and chemically modified carbon materials (e.g. iodized and brominated AC) were examined. The quantification of Hgtot in these samples was accomplished by microwave-assisted digestion, followed by ICP-MS analysis with either quantification by external calibration or by double IDMS, the latter leading to lower uncertainty and improved accuracy. The accuracy of the developed methodologies for Hgtot was demonstrated through the analysis of certified reference materials (halogenated activated carbon SRMs 2445 and 2448). The obtained mass fractions for Hgtot agreed with the certified ones within the method measurement uncertainty. The method applicability has been further demonstrated through the analysis of a candidate CRM bituminous mineral coal, produced by CENAM (Mexico) and used for intercomparison studies. The mercury species analyses were performed using a gas chromatography system (GC), coupled to ICP-MS/MS via a heated transfer line. The GC-ICP-MS interface was modified by extending the GC capillary column within the heated interface. With this setup, sharper Hg-species peaks with improved signal-to-noise ratio were obtained. The derivatisation of Hg(I) and CH3Hg+ was performed from acidified aqueous solution, using NaB(C2H5)4, followed by the extraction of the respective ethylates in organic solvent and direct injection into the GC-ICP-MS. The potential of using isotopically enriched 199Hg(I) and 201CH3Hg+ to monitor species conversion will be demonstrated. In an effort to quantitatively extract the mercury species from widely used sorbent trap materials for further GC-ICP-MS determination, a variety of extractants including sulfydryl containing chelating reagents (L-cysteine, 2-mercaptoethanol, NaDDTC etc.), organic solvents, acids and acidic buffer solutions have been tested. The suitability of the used reagents in variety of extraction conditions (e.g. combined with heating or ultrasonication), along with the Hg species stability, will be discussed. The research activities presented in this work are part of the MercOx EMPIR project, supporting the Industrial Emissions Directive (IED) 2010/75/EU, the Air Quality Directive 2004/107/EC, the Waste Incineration Directive 2000/76/EC and the Minamata Convention adopted in 2013.

R.P.1.62

A UNIQUE INTERACTIVE NANOSTRUCTURE KNITTING BASED PASSIVE SAMPLER ADSORBENT AT THE MICROSCALE FOR TRACE LEVEL MONITORING OF Hg2+ IN WATER

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This work reports the development of a nanostructure material based passive sampler, which binds trace concentration of mercury (Hg2+) by employing ultrathin graphite carbon nitride (g-CN) nanosheets as effective adsorbent. The g-CN nanosheets were obtained by exfoliating the bulk g-CN which was synthesized via a thermal polycrystallization process. The as-prepared samples were characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), fourier transform infrared (FTIR) spectroscopy and atomic force microscopy (AFM), which confirmed graphite-like structure. The results showed high recovery capacities for Hg2+ in different matrices in the following order: Sea < River < Rain < Milli Q water of 89%, 93%, 97% and 100 %, respectively. Ion interference studies (Ca2+, Zn2+, Fe2+, Mn2+, Ni2+, Bi3+, Na+ and K+) were also performed to check the specificity and selectivity of g-CN towards Hg2+. There was minimum or no effect of the presence of ions on the binding efficiency of Hg2+ on g-CN nanosheets. The effect of pH (2.4, 4, 7 and 9) on the binding efficiencies of Hg2+ on g-CN was also studied. It was found that g-CN nanosheets showed enhanced binding response to Hg2+ in comparison to its bulk counterpart, which could be ascribed to the strong affinity between g-CN and Hg2+ through its -NH and -NH2 groups. This allows detection of Hg2+ in aqueous solutions with high sensitivity and selectivity. A mercury analyzer used in present work to quantify Hg2+ retained on g-CN and supernatant. Such a sampling material reported an efficiency of adsorption that was equal to ~99%. Temperature and relative humidity only mildly affected the material performances. These defined nano-interwoven structures “knitting” seem to be promising candidates for mercury samplers. The nano-knitting structures seem to be promising candidates for mercury samplers, due to the strong affinity with Hg2+, and the wide adsorbing surface. These results demonstrated that the g-CN was a potential candidate for detecting trace levels of Hg2+ in water and can be used as reference material for inter laboratory comparisons.

R.P.1.63

TRACEABILITY OF MERCURY CHLORIDE PERMEATION TUBES FOR THE CALIBRATION OF GAS PHASE OXIDIZED HG MEASUREMENT SYSTEMS

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(1)IPS Analytical

The use permeation tube devices are a commonly used technique for producing gas standards for instrument calibration. Certification by the vendor or supplier is normally performed by establishing the gravimetric loss from the permeation tube over a period of time, at a specified temperature which is accurately and precisely controlled. Suppliers claim that the permeation devices are capable of generating a SI traceable calibration gas that is stable for a long period of time provided that the compound within the permeation tube is still present and the conditions of use are carefully controlled. This however is not the case for mercury chloride. Although this compound is thermally stable and exhibits sublimation it is difficult to transport and the permeation rate is highly dependent on the conditions of use such as temperature and flow. Required permeation rates are in the picogram or low nanogram per minute range which means that certification using gravimetric loss takes a considerable amount of time and the uncertainty can be high. One further complication is that the commercially available apparatus for permeation tube operation are not compatible because the transportation of mercury chloride gas requires a close coupled heated sample line. The determination of oxidized mercury in ambient air and from thermal combustion sources is a critical and important measurement. Despite the recognition importance, measurements are mostly performed without calibration simply because of the lack of SI traceable calibration devices available. As part of the EMPIR 16ENV01 MercOx Metrology project we have been conducting research on the use of HgCl2 permeation tubes. We will investigate their optimal operational conditions in relation to temperature and flow and how these influence permeation rates. A newly developed permeation tube apparatus and two channel direct
mercury analyser based on AFS will be described. This system offers a real time Hg fractionation measurement of total and elemental Hg. These results will be compared using KCl/brominated carbon sorbent traps which are commonly used for Hg fractionation in stack gas. A bottom up expanded uncertainty budget on the use of permeation tubes will be also be presented.

R.P.1.64

SOLUBILITY AND OXIDATION OF ELEMENTAL HG IN KCL TRAPPING SOLUTIONS USED FOR THE DETERMINATION OF OXIDIZED HG IN FLUE GAS.

DE FEO, Gianmarco1; DEXTER, Matthew1; CORNS, Warren1 (1) P S Analytical

Mercury fractionation data in flue gas from thermal combustion sources is of great value to the mercury research community. Results are used not only for the development and optimization of mercury control technologies, but also to provide emissions data which are ultimately used for modelling the fate and transportation of Hg species in the environment. The most commonly used and approved method for the fractionation of Hg in Flue Gas is the ASTM D6784-16 “Standard Test Method for Elemental, Oxidized, Particulate Bound and Total Mercury in Flue Gas Generated from Coal Fired Stationary Sources” (Ontario Hydro). The method applies the use of 1 mol/l KCl trapping solutions to selectively preconcentrate oxidized Hg from the flue gas matrix. The main concern with this approach is related to the selectivity of the trapping solution. Trace levels of impurities present in the trapping solution and dissolved acid gases introduced from the flue gas matrix may cause oxidation of elemental Hg thereby producing a positive bias in the measurement of the oxidised Hg fraction.

An analytical method was developed to determine the degree of oxidation of elemental Hg and the solubility of elemental Hg in the KCI solution. The dimensionless Henry’s Law constant was used to determine the solubility of elemental Hg in the KCl trapping solution at the experimental conditions typically used during flue gas sampling. Experiments were conducted by injecting a known mass of mercury vapour into a gas stream purging a temperature-controlled extraction vessel containing a known volume of trapping solution. The rate of oxidation and solubility profile was studied using different gases at concentrations typically found in flue gas. The rate of release of Hg was then measured using amalgamation-AFS by installing gold traps at the gas exit of the extraction vessel and this data was used to establish the dimensional Henry’s law constant. The constant is directly related to the solubility of elemental Hg in the KCl trapping solution. The uncertainty associated with the concentration of generated calibration standards used can have a substantial impact on the overall uncertainty of a measurements made using the associated technique. This in turn can affect the fitness for purpose of those measurements.

As no metrological infrastructure exists for traceable, validated and accurate measurements of oxidised mercury species in the atmosphere and emission sources, there is an urgent need for development of Hg(II) calibrators traceable to SI at ambient and industrial levels. Novel He plasma oxidized mercury Hg(II) source was developed that link the Hg(II) traceability chain to gravimetry instead of the currently used elemental mercury (Hg(0)) vapour concentration techniques and followed equations. Non-thermal or cold high energetic He plasma was produced at room temperature and atmospheric pressure. Traceable quantity of Hg(0) derived from NIST 3133 Hg standard solution was introduced in flow of He gas where within production of He plasma Hg(0) was quantitative converted to Hg(II). Hg(II) is very quickly bonded to any available surface and thus in plasma production area and immediately further quarc wool and KCI traps were used to trap Hg(II). Efficiency of Hg(0) to Hg(II) conversion and trapping is 100 % as no breakthrough was detected either by Lumex measurements or trapping of Hg(0) by gold coated traps or impinger solution traps.

Measurement step consist of heating KCI traps to high temperatures and thermal decomposition and reduction of trapped Hg(II) to elemental Hg, Hg(0) is then detected by CVAAS or CVAFS techniques. Method was tested for production of ambient and industrial sources Hg(II) levels from few pg to few hundreds of ng. System and oxidation of Hg was also checked by radioactive 197Hg which was used as a tracer for chemical conversions and efficiency of the system. He plasma produced Hg(II) on KCI solid traps can be used for traceable calibration purposes for low level QGM ambient air measurements or industrial applications. As Hg(II) in He plasma was produced at room temperature and atmospheric pressure the method is appropriate for applications where heating of the treated gas or sample is unwanted at Hg levels typical for ambient air and industrial sources (levels from few pg to few hundreds of ng).

R.P.1.65

MEASUREMENT OF OXIDISED MERCURY IN GAS PHASE EMISSIONS AND THE ATMOSPHERE: UNCERTAINTY BUDGETS FOR CALIBRATION GAS SOURCES

DEXTER, Matthew2; CORNS, Warren1 (1) P S Analytical

Traceable determination of total gaseous mercury, elemental Hg and oxidised mercury in gas emissions and in the atmosphere depends upon the use of traceable calibration methods. European Metrology Programme for Innovation and Research’s (EMPIR) Project 16ENV01 MercOx is focussed on the development of SI traceable measurement for the different mercury species in emission sources and in the atmosphere. In order to perform a SI traceable measurement there is a requirement for an SI traceable calibration method. Calibration gases for oxidised mercury are notoriously difficult to generate and to transport due to the adsorption and desorption phenomena, requiring them to be generated at the point of use. The practicality of introducing these gases to sampling and measurement systems is problematic especially when considering the vast array of analytical approaches that are utilised for this application.

The MercOx project is considering and developing a range of mercury(II) chloride calibration gas generators, based on methods including: oxidation of elemental mercury calibration sources, permeation devices, evaporation of liquid standards and dilution of mercury(II) chloride saturated vapour.

The estimated uncertainty varies by technique and required concentration. Typical expanded uncertainties for calibration gases in the 20 µg/m³ range are less than 20 %.

R.P.1.66

NOVEL PLASMA OXIDIZED MERCURY SOURCE

KOTNIK, Jože; ŽIVKOVIĆ, Igor; GAČNIK, Jan; JUROV, Andrea; CVELBAR, Uroš; HORVAT, Milena

As no metrological infrastructure exists for traceable, validated and accurate measurements of oxidised mercury species in the atmosphere and emission sources, there is an urgent need for development of Hg(II) calibrators traceable to SI at ambient and industrial levels. Novel He plasma oxidized mercury Hg(II) source was developed that link the Hg(II) traceability chain to gravimetry instead of the currently used elemental mercury (Hg(0)) vapour concentration techniques and followed equations.

Non-thermal or cold high energetic He plasma was produced at room temperature and atmospheric pressure. Traceable quantity of Hg(0) derived from NIST 3133 Hg standard solution was introduced in flow of He gas where within production of He plasma Hg(0) was quantitative converted to Hg(II). Hg(II) is very quickly bonded to any available surface and thus in plasma production area and immediately further quarc wool and KCI traps were used to trap Hg(II). Efficiency of Hg(0) to Hg(II) conversion and trapping is 100 % as no breakthrough was detected either by Lumex measurements or trapping of Hg(0) by gold coated traps or impinger solution traps.

Measurement step consist of heating KCI traps to high temperatures and thermal decomposition and reduction of trapped Hg(II) to elemental Hg, Hg(0) is then detected by CVAAS or CVAFS techniques. Method was tested for production of ambient and industrial sources Hg(II) levels from few pg to few hundreds of ng. System and oxidation of Hg was also checked by radioactive 197Hg which was used as a tracer for chemical conversions and efficiency of the system. He plasma produced Hg(II) on KCI solid traps can be used for traceable calibration purposes for low level QGM ambient air measurements or industrial applications. As Hg(II) in He plasma was produced at room temperature and atmospheric pressure the method is appropriate for applications where heating of the treated gas or sample is unwanted at Hg levels typical for ambient air and industrial sources (levels from few pg to few hundreds of ng).
The most frequently used method for pre-concentration of Hg is based on amalgamation of elemental Hg using gold (Au) traps, which is followed by thermal desorption of Hg at a temperature of 500 °C and detected by CV AAS or CV AFS techniques. The method is suitable for lower masses of mercury (up to 1000 ng). The precision of measurements is less than 15 %. Memory effects and passivation of Au traps can lead to loss of mercury or reduction in the amalgamation efficiency. Au coated silica sand is widely used as absorbing media, however other noble metals as Au and Pt can be used to pre-concentrate Hg. Instead of silica AI2O3 can be used as AI2O3 is more stable at high temperatures. Different noble metals coatings of different carrier materials result in different temperatures of Hg collecting and different temperatures of Hg desorption from gas.

Conventional Au – silica, Au and Au-Pt coated AI2O3 sand were used during experiment. Commercially available conventional Au silica traps were used to compare efficiency of Hg collection from ambient air, Hg derived from standard solution or Hg saturated air. Au and Au-Pt coated AI2O3 were prepared from solution of gold chloride hydrate and/or platinum chloride hydrate, followed by heating in inert atmosphere. Prepared traps were tested and compared for Hg collecting efficiency to commercially available Au coated silica traps by concentrating Hg from ambient air, Hg saturated air and NIST 3133 Hg standard solution in range of few tens of pg to about 1 μg. Au and Au-Pt coated AI2O3 traps were also tested and compared to gravimetric Hg standard generator developed at VSL. Hg thermally desorbed from traps was detected either by CV AAS with Zeeman background correction or CV AFS.

In all repeated tests, the trapping efficiency and the linearity of the results was excellent. The repeatability of the testing was about 5 % on average, expressed as relative standard deviation of at least three measurements. Au and Au-Pt coated AI2O3 traps had same Hg trapping efficiency as conventional Au – silica traps, however Hg thermal desorption temperatures can differ for almost 150 °C, which mean that also trapping temperatures interval rises at same level. Higher Hg trapping and desorption temperatures can be very useful for many purposes where higher collecting and desorption temperatures are required.

SYSTEM FOR THE SIMULTANEOUS MEASUREMENT OF TOTAL AND ELEMENTAL MERCURY CONCENTRATIONS IN THE FLOW OF THE OXIDIZED MERCURY GENERATOR

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Nowadays, continuous emission monitors (CEMs) are widely used to measure mercury in automatic mode in stack gases of thermal power plants, metallurgical facilities, etc. The correctness of measurements should be periodically validated by introduction of a known concentration of mercury both in the elemental and oxidized forms, because the concentration of oxidized mercury in stack gases can be up to 90% of the total mercury concentration. Whereas the generators and methods for elemental mercury calibration are better known, the generators for oxidized mercury are still being developed and tested. One of the ways to produce a flow of oxidized mercury is evaporation of a liquid solution of mercury species, e.g., HgCl2. However, since the oxidized mercury is partially reduced on the surfaces of the generator, a mixture of elemental and oxidized mercury is produced in the generators when only oxidized mercury solution is used. The addition of HCl to the reference solution leads to partial re-oxidation of the elemental mercury. The oxidized mercury is partially thermally converted even at a temperature of the surfaces below 200 °C. The properties of the heated generator surfaces vary during operation, which, along with the above factors, results in variation of the elemental-to-oxidized mercury concentration ratio. Hence, it is impossible to assign a certain exact value of concentration of the oxidized mercury to the output of the generator. Moreover, the chemical uncertainty caused by transition of mercury from the oxidized to elemental form in the solution should be added to the instrumental uncertainty. Therefore, to optimize the oxidized mercury generator and to rule out this uncertainty, we propose to use a system of Zeeman mercury analyzers to measure simultaneously the elemental and oxidized mercury concentrations in the output of the generator in real time.

The proposed system consists of a heated input unit and two gas channels for determination of the elemental and total mercury concentrations. Both channels comprise a mercury Zeeman spectrometer (LUMEX RA-915F), a suction pump and a heated cell. The temperatures of the heated cells are maintained at 130 and 750 °C, respectively, in the channels for elemental mercury and total mercury. Testing with oxidized mercury generators (HovaCal, Optoseven) it was found that the elemental mercury concentration ranges within 1 – 2 % relative to the oxidized mercury concentration. Results of tests of the system with different HCl and H2O concentrations are reported.

HUMAN BIOMONITORING IN NORTHERN CANADA: ASSOCIATIONS AMONG CONTAMINANT AND NUTRIENT BIOMARKERS

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Traditional foods, such as locally caught fish, are important food sources for Indigenous communities in Northern Canada. These foods have important nutritional, social, cultural, and economic benefits for Indigenous communities. However, fish consumption can be a significant route of mercury exposure. Conducting human biomonitoring projects in remote northern communities allows for the assessment of mercury exposure in populations who may be at increased risk due to their diet. For example, in the Northwest Territories, Canada, in the Mackenzie River Valley, elevated levels of mercury have been measured in fish samples prompting the release of consumption advisories. To address the concerns of First Nations communities in the region, a human biomonitoring project was implemented and biological samples and dietary data were collected for use in risk assessments. Since these foods are of such importance, the benefits of their consumption should also be considered along with the risks of mercury exposure. Therefore, along with total mercury (whole blood; hair), levels of the essential nutrients omega-3 fatty acids (blood plasma) and selenium (whole blood) were also determined.

For those participants who provided blood samples (n=136) and hair samples (n=231) (Dehcho region data) the majority had levels below the relevant health guidelines. Blood and hair mercury levels were positively associated (ρ_spearman=0.63). Blood mercury levels were also positively associated with plasma levels of omega-3 fatty acids (ρ_spearman=0.34) and blood selenium levels (ρ_spearman=0.28). Hair mercury levels were positively associated with plasma omega-3 fatty acids levels (ρ_spearman=0.36). However, blood mercury and the most recent segment of hair samples (2 cm approximating two months of exposure) only provides information about recent mercury exposures. Fish consumption patterns vary seasonally and human mercury levels could vary significantly throughout the year. Therefore, mercury concentrations were also measured in additional hair segments from the long hair samples. In a subset of the hair samples (n=96), six segments approximating a year of mercury exposure in bi-monthly periods were measured. There were significant differences in mean hair mercury
MATERNAL MERCURY LEVELS: MEASURING VARIATION BETWEEN AND WITHIN INDIVIDUALS DURING PREGNANCY

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Methylmercury (MeHg) is a persistent environmental toxicant that accumulates in fish and seafood. MeHg selectively targets the developing nervous system and is of great concern for pregnant women and the developing fetus. Human metabolism and elimination of MeHg has been shown to be highly variable, with half-life values of 11/2 ~ 30 to >120 days. This variability underscores the uncertainty that is inherent in the dose calculations used to formulate federal fish consumption advisories for pregnant women. Yet, the mechanisms of this variability are poorly characterized and, remarkably, the half-life of MeHg in pregnant women has yet to be determined in a controlled study. In this study we assessed the feasibility of measuring the MeHg elimination rate in pregnant women via a non-invasive longitudinal Hg analysis methodology in hair samples collected near delivery. Subjects with >10 cm of hair length were recruited near delivery and divided by retrospective food diaries into fish eaters (FE) and non-fish eaters (NFE). Hair strands were sampled and analyzed with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Ablations at 333 μm increments (approximately 1 day of hair growth) achieved measurements of daily MeHg levels for at least 266 days of pregnancy and 30 days prior. Periods of Hg decline over time, indicating MeHg elimination after a recent fish meal, were modeled with first-order kinetics to determine elimination rates and half-lives at intervals spanning all three trimesters of pregnancy. Longitudinal MeHg hair profiles of three FE subjects revealed a distinct profile of elevated Hg levels relative to a NFE subject. Hair from FE subjects produced profiles of several events of “peak and decay” of Hg over time. Kinetic determinations showed a wide range of values with 11/2 ~ 25 to 131 days. Remarkably, in two subjects, elimination rate significantly increased (shortened half-life) in third versus first trimester. Our data reinforce the capabilities of LA-ICP-MS to detect small changes in hair Hg attributable to fish intake, making determination of elimination rates during pregnancy feasible. Moving to a prospective protocol to capture accurate fish consumption data will facilitate future kinetic studies of MeHg metabolism during pregnancy and ultimately contribute to improved individualized fish consumption advisories.

THE APPLICATION OF TWO MINIMALLY INVASIVE MICROSAMPLING METHODS FOR MERCURY BIOMONITORING IN ARTISANAL GOLD MINING AREAS IN ZIMBABWE

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Background:
Artisanal small-scale gold miners use mercury for the extraction of gold. Therefore, the miners and their families are exposed to high levels of mercury. This is reflected by increased levels of mercury in urine and blood. Biomonitoring of exposed individuals is important for the assessment of miner’s health. The results can be used for protective and treatment measures. However, biomonitoring in remote areas is associated with many problems, e.g. unavailability of staff with appropriate medical training, difficulties to transport samples with a continuous cool chain, and lack of regional laboratory infrastructure.

Objective:
Our goal was the development, validation and field application of two minimally invasive microsampling methods for mercury biomonitoring in artisanal gold mining areas. The first application of those methods took place during a field project in Kadoma/Zimbabwe.

Methods:
The first goal of this study was the evaluation of the feasibility of microsampling methods for mercury biomonitoring under laboratory conditions. All analyses were carried out with a direct mercury analyser. Two microsampling devices were investigated: Dried-Blood-Sampling (DBS) and Volumetric-Absorptive-Microsampling (VAMS). Certified reference materials were used for method development. Both devices were tested for accuracy, reproducibility and stability. Therefore, both devices were tested under simulated field conditions with a small number of subjects. Finally, this method was used for mercury biomonitoring of nearly 200 miners from using mercury for gold extraction during a field project in Kadoma, Zimbabwe, in early 2018. From all miners venous blood samples as well as DBS and VAMS samples from finger pricks were collected and analysed in our laboratory in Germany.

Results:
Both DBS and VAMS proved to collect sufficient amounts of blood for quantification by direct mercury analyses, even at levels lower than 1 µg/l blood. VAMS showed to more reproducible compared to DBS, especially when authentic blood samples were used. Both devices showed a satisfactory correlation with venous blood samples which were considered as gold standard as well as good storage stability. The results of the field study are still under ongoing investigation.

Conclusion:
Microsampling methods are a valuable tool for the biomonitoring of pollutants in remote area. The simplicity of such devices allows blood sampling from finger pricks without extensive medical training. Furthermore, cold chains and other infrastructural issues are less important compared to generally used venous blood samples. Our preliminary results demonstrate the feasibility of such microsampling devices under laboratory conditions. The applicability for remote areas is under ongoing investigation.

VALIDATION OF METHOD FOR METHYL MERCURY DETERMINATION IN BLOOD BY LIQUID CHROMATOGRAPHY – INDUCTIVE COUPLED PLASMA MASS SPECTROMETRY

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Methyl mercury is a toxic mercury formed in the environment which can lead to serious health problems and threats to the development of children in utero and early life. Methyl mercury tends to build up in living tissue. The analysis of methyl mercury in blood may represent the accumulation from daily diet intake and biomonitoring of occupational environmental exposure. In Malaysia, despite the importance of monitoring methyl mercury in blood, there is a serious dearth of research that has been performed in this area due to limitations in instrument setup to analyse methyl mercury in human blood. Thus, a simple, fast and cost-effective extraction procedure is presented in this paper for
the determination of methyl mercury in blood by a hyphenated method
of Liquid Chromatography – Inductive Coupled Plasma Mass Spectros-
copy (LC-ICPMS). The objective of the work is to validate methods used
for analysis of methyl mercury in blood samples. Prior to instrumental
analysis, blood samples are extracted using a mixture of 2- mercaptoeth-
anol, L-cysteine and hydrochloric acid. The liquid chromatography (LC)
separation was achieved by using Zorbax Eclipse XDB-C18 4.6 x 150
mm, 5 um column with mobile phase containing 0.05% 2-mercaptoeth-
anol, 0.4% L-cysteine, 0.06 mol/L ammonium acetate, and 5% methanol.
Method validation was performed according to guidelines published by
EUREACH. The validated method was selective with a limit of detec-
tion (0.242 ug/L), limit of quantification (0.807 ug/L), bias (5.91%), and
linear method working range (1 – 200 ug/L). The repeatability of the
method is determined with 2.38% RSD and intermediate precision with
3.22% RSD. This method was validated using actual human blood sam-
ple and Standard Reference Material (SRM) 955c in Caprine Blood with
recoveries ranging from 94-113%. As a conclusion, the validated meth-
od is suitable to analyse methyl mercury in human blood for the study of
daily intake and occupational environmental exposure.

R.P.2.8

DEVELOPMENT OF HUMAN URINE AND HAIR REF-
ERENCE MATERIALS FOR HUMAN BIOMONITORING
OF MERCURY

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The purpose of the development of new human urine and hair reference
materials are to support human biomonitoring for general populations
with exposure to elemental mercury (HgO) and MeHg, respectively. HgO
and inorganic Hg exposure can result from dental amalgams, inhalation
of indoor air, broken thermometers, and fluorescence lights. MeHg ex-
posure can result from seafood consumption. The requirements for cer-
tified reference materials for assessing human Hg is growing with an
increasing body of research from surveys to evaluate the effectiveness
of the Minamata Convention. We collected human urine and hair from
Japanese males and Vietnamese males, respectively, without occupa-
tional exposure to Hg compounds. The urine was immediately sterilized
by 80Co radiation, filtered, and blended. We prepared 4,000 bottles of
urine, each containing 4 g. The inter-bottle homogeneity was confirmed
by measuring the concentrations of THg and cadmium in the material
and by subsequent statistical analysis. The hair was incrementally pul-
vzerized with 3 mills with liquid nitrogen. The homogenized hair powder
was divided 3 g each into 1,200 bottles and sterilized by 80Co irradia-
tion. Value for total mercury and methylmercury, as well as other trace
elements (Cu, Zn, As, Se) was presented. We are characterizing property
values to developed reference materials using a collaboratively studied
method. Hair reference material will be distributed this year. The present
reference materials will be of value to the parties to the Minamata Con-
vention to assure the analytical quality of their monitoring.

R.P.2.9

A NEW UNDERSTANDING OF SKIN AS AN INDICA-
TOR FOR HUMAN EXPOSED TO METHYLMERCURY

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Developing indicators for human exposure to methylmercury (MeHg)
is critical in assessing health risk of MeHg. A number of indicators, in-
cluding hair, EDI (estimated daily intake), urine, and nail, have been
commonly used to assess human exposure to MeHg within short (e.g.,
days) or mid-term (e.g., months) period. However, indicators for long-
term (e.g., years) MeHg exposure are lacking, which may hinder under-
standing of risk of MeHg associated with chronic exposure (e.g., di-
etary MeHg exposure for general populations). The objectives of this
study are to (1) try to validate a new indicator, i.e., dermal tissue, to
assess long-term dietary exposure to MeHg; (2) explore the relation-
ships among different indicators, i.e., hair, dermal tissue and EDI. The
validity of the new indicator was examined by correlating MeHg levels
in tissue samples (human skin and hair) collected from 144 patients
in China and their dietary exposure to MeHg. Given that the growth
rate of hair is 1 cm/month, the hair samples were further divided into
different sections to indicate MeHg exposure during various time peri-
od. Methylmercury concentrations in tissue samples were determined,
while dietary exposure to MeHg was assessed by questionnaire survey
(to obtain ingestion rates for fish and rice, the two principle dietary
sources of MeHg for Chinese). Methylmercury levels in hair or skin
tissues are equally sensitive to estimated MeHg uptake: (1) According
to Pearson correlation coefficients, MeHg contents in 6-12 cm hair
were significantly correlated with MeHg EDI, indicating that MeHg EDI
could indicate mid-term (up to 12 months) MeHg exposure. (2) Methyl-
mercury contents in >24 cm hair had significant relationship with those
in human skin, suggesting that MeHg levels in skin might indicate long-
term (more than 2 years) MeHg exposure. The new indicator validated
in this study would help assess long-term dietary exposure to MeHg,
and identify sources of MeHg exposure for general populations.

R.P.2.10

CURRENT EFFECTS OF METHYLMERCURY ON HEALTH
AROUND MINAMATA

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Methylmercury injures neurons in the central nervous system. The
pathophysiologic processes of methylmercury toxicity are caused by
spotty neuronal necrosis or apoptosis and structural damage can occur
in the living neurons before cell death. As a result of this damage, neu-
rological, neuropsychological, psychological, and psychiatric symptoms
can occur, depending on the amount and duration of exposure, as well
as the characteristics of the exposed person (age, intelligence, charac-
ter, and so on).

As there are literally billions of neurons in the CNS, the onset and
progress of symptoms happens gradually and symptoms can fluctu-
ate. There is also a very wide-range in the variety of symptoms among
affected patients. There is a variety of complaints, with various levels
of intensity, but the most common symptom is sensory disturbance in
the limbs’ extremities. If the symptoms become more serious, truncal
ataxia, limb ataxia, dysarthria and visual constriction can occur.
Evident neurological abnormalities, which can be recognized not only
on an epidemiologic level but also as individual abnormalities, have
been reported only in geographical areas that have been subjected to
moderate to severe pollution, like Minamata and the Niigata areas in
Japan, Ontario in Canada, the Amazon River in Brazil and the Songhua
River area in China.

In this poster session, we will present a patient with symptoms of Mi-
amata disease. He was born in January 1954. He developed four-
limb sensory disturbance and cramps around 1994. 26 years after the
Chisso Corporation had stopped dumping mercury polluted waste wa-
ter. Then, finger dexterity became clumsy. Around 2004 he began to
stumble easily. These symptoms began very slowly. He had not only
the specific symptoms such as numbness of four limbs, ataxia, prob-
lems tasting and detecting smells, but also non-specific symptoms such
as general fatigue, shoulder stiffness, and so on. Neurological exami-
nations showed he had systemic somatosensory disturbance, truncal
and four-limb ataxia. The range of sensory disturbance and the degree
of ataxia changed several times. Bilateral visual constriction was not observed. They say that a picture is worth 1,000 words. We will go one step beyond by introducing this actual patient who exhibits symptoms of Minamata disease.

R.P.2.11

ASSOCIATIONS AND SIGNIFICANCE OF MERCURY LEVELS IN URINE, BLOOD AND HAIR IN A SPANISH HBM STUDY

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Selecting the appropriate sampling matrix is critical when assessing human exposure to mercury from different sources. Mercury levels in blood reflect recent exposure to this heavy metal, however speciation is required for identifying the source. The mercury species varies in that exposure. The majority of human biomonitoring (HBM) studies does not include speciation analysis but collects different of the preferred matrices, blood, urine or hair. Both hair and urine are non-invasive matrices and therefore attractive to use in large scale human biomonitoring programs. Exposure to methylmercury (MeHg) is usually estimated from measurements of total Hg in hair, while exposure to elemental mercury (Hg0) and inorganic Hg is estimated from analysis of total Hg in urine. Therefore, the study of total mercury levels in these three matrices could be an alternative to speciation analysis for having a complete information about the extent of the exposure.

In BIOAMBIENT.ES, a Spanish national wide HBM study with more than 1900 participants (18–65y), total mercury was determined in urine, blood and hair. The correlation of mercury levels in different matrices has been studied in a subsample of 527 individuals. Information about mercury exposure was collected by a self-administered epidemiological questionnaire with specific questions on diet and fish consumption and other determinant factors of mercury exposure. The GM (95% CI) for total mercury in urine were 1.17 µg/L (1.95%: 0.20 – 6.74) and 0.90 µg/L after creatinine adjustment (95% CI: 0.17 – 4.91) and 6.68 µL/L (95% CI: 1.48 – 30.07) and 1.87 µg/L (95% CI: 0.46 – 7.69) for blood and hair respectively. 1% of the urine samples were above the HBM l-value (5 µg/g creat) defined by the Human Biomonitoring Commission of the German Environment Agency. In contrast, 68% and 11% of samples were above the HBM I and HBM II values defined for whole blood (5 µg/L and 15 µg/L respectively). All correlations among matrices showed significant Pearson coefficient (p<0.001) with the highest values for blood and hair (r=0.85).

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R.P.2.13

METHYLMERCURY TARGETS MUSCLE DEVELOPMENT

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Methylmercury (MeHg) has long been understood to target the developing nervous system. Several decades of laboratory animal studies reinforce observations from human population studies that early life MeHg exposure can elicit both motor and cognitive deficits. Mechanistic studies of MeHg toxicity have therefore predominantly focused on neuronal targets. As a result, the possibility that motor function deficits can stem from MeHg alteration of muscle development has largely overlooked. In prior transcriptomic and genome-wide screens for developmental MeHg susceptibility genes with Drosophila we have identified a number of gene candidates that constitute core muscle developmental pathways, namely, the Notch receptor pathway and myoblast fusion and muscle attachment genes such as Kirre (vertebrate Kerrel) and Sticks and Stones (vertebrate Nephrin) and Kon-tiki (chondroitin sulfate proteoglycan 4, CSPG4). In parallel, we have observed overt MeHg muscle phenotypes including perturbation of myogenesis in the fly embryo that parallel adverse effects on developing motor neurons. At later developmental stages, MeHg perturbs formation of adult indirect flight muscles during pupal metamorphosis, which also results in deficient eclosion and flight behaviors. Using a transgenic strategy of tissue specific expression of the MRP1 (ABCC1) transporter to induce MeHg export and cell autonomous protection we see that targeted MRP1 expression in muscle lineages gives a much greater overall developmental tolerance to MeHg than MRP1 expression in neural lineages. Additional functional assays in transgenic flies have
identified a downstream target gene of the Notch receptor, the bHLH transcription factor Enhancer of Split mDelta (E(Spl)mδ) that mediates MeHg toxicity in muscle development. We have further investigated effects of MeHg on mammalian myotube formation using the C2C12 mouse myoblast model. We find that MeHg inhibits both myoblast differentiation and fusion events in a concentration-dependent manner. MeHg is seen to specifically and persistently affect expression of myogenin (MyoG), a core transcription factor involved in myocyte differentiation. By characterizing a myopathic component of MeHg neurotoxicity our studies are expanding the current understanding of how motor deficits are likely to arise from early life MeHg exposure.

R.P.2.14

LOW LEVEL MERCURY EXPOSURE AND ELECTRO-CARDIOGRAPHY CHARACTERISTICS AMONG YOUNG ADULTS

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Previous studies report associations between mercury exposure and cardiovascular risk factors. The cardiovascular effects of mercury, however, are not limited to increased blood pressure and hypertension. Although the mechanisms of how mercury induces hypertension are not fully understood, it has been hypothesized that altered cardiac excitability may play a role in cardiovascular disease. In this study we investigated the effects of low level mercury background exposure (assessed in hair by atomic absorption spectroscopy) in Tomsk Polytechnic University on electrocardiography (ECG) changes in one hundred fifty-four 17-19 years young adults (63 males). ECG was evaluated from analysis of three-lead electrocardiography 1-minute recordings. Mercury concentration in hair was 0.15±0.14 (min-0.02, max-0.95) µg per g with no significant gender difference. ECG data analysis revealed that the average heart rate was 74.3±12.21 beats per min with significantly higher values in females. Moderate tachycardia was revealed in 14 cases, while 14 young adults had moderate bradycardia. The duration of the intervals R-R, P-Q, Q-T and QRS complex and P wave were within normal ranges along with all the amplitudes. Gender differences showed that the duration of QRS complex was significantly longer in males, as well as the amplitudes of all the waves. No significant correlations were found between mercury concentration and ECG intervals’ duration. However, statistically significant negative associations between amplitude of R in II and III standard leads and in AVF and mercury and negative for the amplitude of T in III standard lead and AVF and mercury were observed, showing that exposure to mercury may be one of multiple factors that might influence cardiac activity. These results suggest that altered cardiac activity may play a role in pathogenesis relating to the harmful effects of mercury exposure on human health. Mercury analysis was funded by RFBR according to the research project № 18-29-24212.

R.P.2.15

EPIDEMIOLOGICAL ANALYSIS ON THE HISTORICAL DATA OF HEALTH EXAMINATION SURVEY CONDUCTED IN MINAMATA FROM 1975 TO 1981

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An outbreak of Minamata disease was observed mainly during the 1950s and 1960s in the coastal area of the Yatsushiro Sea including Minamata, in Japan, where methylmercury had been discharged into the water environment from a chemical factory synthesizing acetaldehyde. Methylmercury had been generated as a by-product in the reaction chamber from inorganic mercury compounds used as catalysts, and accumulated in fish and shellfish at extremely high concentrations in the sea. By 2018, 2,282 patients, in the coastal area, have been officially diagnosed as Minamata disease who is eligible to receive the compensation from company responsible, and more than 65,000 inhabitants have been recognized as having partial symptoms of the intoxication and recipient of financial aid. A large scale health examination survey was conducted in Minamata, from 1975 to 1981, to find latents patients. In this survey, 33,445 inhabitants participated in primary questionnaire survey with a participation rate of 90.0% of the city population. Although 387 patients were confirmed in the survey, no epidemiological analysis has been performed on the data obtained. The author retrieved and statistically analyzed the primary self-reported questionnaire data that had been collected from 27,621 participants with recovery rates of 82.6% and 74.4% of total participants and population, respectively. On 23 neurological complaints, crude odds ratios of high fish consumption in the past were found to increase significantly, for examples, at 8.46, 7.34 and 7.19 on fine movement of the hand, perioral sensory disturbance and sensory disturbance in the hands/feet, respectively. Since it was shown that fish consumption frequency was closely associated with age, and age was one of significant determinants of health, the effects of age then should be excluded on the evaluation of association between fish consumption and health impairments. Age specific prevalence of 23 neurological complaints, hypertension and diabetes apparently increased depending on fish consumption. The logistic regression analyses indicated that age-adjusted odds ratios of fish consumption, classified as four categories, were 1.25 to 2.91 and significantly increased on the 25 health outcomes including hypertension and diabetes. Additionally, fishery engagement, residence in a fishing village, and duration of residence in Minamata were partially but significantly associated with the health status. In conclusion, a large part of inhabitants in Minamata in the 1970s was considered to be affected by a broad spectrum of adverse health effects of methylmercury through the previous daily consumption of contaminated fish.

R.P.2.17

FASUDIL, A ROCK INHIBITOR, RECOVERS METHYL-MERCURY-INDUCED AXONAL DEGENERATION BY CHANGING MICROGlioL PHENOTYPE IN Rats

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Methylmercury is an environmental neurotoxicant that induces neuro-pathological changes. In this study, we established chronic methylmercury-intoxicated rats. These rats survived, and sustained methylmercury-induced axonal degeneration, including the dorsal root nerve and the dorsal column of the spinal cord; these changes persisted 12 weeks after methylmercury withdrawal. We demonstrated for the first time the restorative effect of Fasudil, a specific inhibitor of Rho-associated coiled-forming protein kinase, on axonal degeneration and corresponding neural dysfunction in the established chronic methylmercury-intoxicated rats. To investigate the mechanism of this restorative effect, we focused on the expression of Rho protein families. This was supported by our previous study, which demonstrated that co-treatment with Fasudil prevented axonal degeneration by mitigating neurite extension/retraction incoordination caused by methylmercury-induced suppression of Rac1 in vitro and in subacute methylmercury-intoxicated rats. However, the mechanism of the restorative effect of Fasudil on axonal degeneration in chronic methylmercury-intoxicated rats differed from methylmercury-mediated neuritic extension/retraction incoordination. We found that the restorative effect of Fasudil was caused by the Fasudil-induced change of microglial phenotype, from pro-inflammatory to anti-inflammatory; moreover, Fasudil suppressed Rho-associated coiled-forming protein kinase activity. Treatment with Fasudil decreased the expression of pro-inflamma-
GENETIC MECHANISMS UNDERLYING METHYLMERCURY TOLERANCE AND SUSCEPTIBILITY: EVIDENCE FROM THE SEYCHELLES CHILD DEVELOPMENT STUDY.

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Results from studies investigating the association between prenatal exposure to methylmercury (MeHg) and child neurodevelopment are heterogeneous. Underlying genetic differences across study populations are likely to contribute to the variation in response to MeHg and presumably denote an intrinsic range of tolerance and susceptibility to MeHg among individuals. Despite knowledge of numerous cellular processes that are affected by MeHg, a consolidated picture of mechanisms that are most influential for tolerance or susceptibility to MeHg in the developing fetus remains to be resolved. We have undertaken a multidisciplinary approach to resolve moderators of MeHg toxicity at the genetic level within the Seychelles Child Development Study (SCDS). Our investigations have built upon the fundamental notion that MeHg toxicokinetics and toxicodynamics can vary widely stemming from genetically encoded differences in underlying enzymes mediating these processes. Our approach is guided by the concept that glutathione (GSH) modulates MeHg toxicokinetics and thus “protective” mechanisms may reside in a core pathway we refer to as the “GSH axis”. To elucidate the foremost genetic players in this pathway we have used a combination of unbiased genetic screening and functional assays of candidate genes in transgenic Drosophila in parallel with SNP-based genotyping of polymorphic variants in DNA of the mothers and children of the SCDS cohort. We have resolved concerted action of GSH axis genes categorized in Phase I (CYP3A family), Phase II (GCLc, GCLm, GSTP1) and Phase III (ABCC1, MRP1) metabolism that moderate, to various extents, MeHg levels and toxic action in both Drosophila and people. Notably, we see instances where MeHg effects on neurodevelopment can be moderated without an associated change in body burden, indicating that certain components of the GSH axis are capable of acting preferentially, and protectively, via toxicodynamics. These results have consolidated a rationale for examining a master regulator of these gene candidates; the NRF2 antioxidant response pathway. Knowledge of these genetic players, and strategies to probe for them, will serve to enhance interpretation of observed outcomes in existing and future prospective studies of MeHg effects on human development and health.
Mercury is a potentially toxic element for fungi, however many species efficiently accumulate it in fruiting bodies in high concentration. Aim of this study was to investigate accumulation of mercury in stems and caps of the fruiting bodies of mushroom Amanita muscaria at different developmental stage. Mushrooms were collected from the forested area in northern Poland in 2015. Fruiting bodies were grouped in six size classes regarding to their developmental stage. Next, they were cleaned-up from soil particles and litter debris, separated for caps and stems, pooled accordingly, dried and pulverised in a porcelain mortar. The pooled fungal materials depending on a class contained from 16 to 54 individuals in a pool. Subsamples were extra dried to a constant mass at 65 °C directly before analysis. The determinations of mercury concentration was performed using cold-vapour atomic absorption spectroscopy (CV-AAS) by a direct sample thermal decomposition coupled with gold wool trap of mercury vaptours and its further desorption and quantitative measurement at wavelength of 296 nm. Each sample was examined in triplicate. The analytical instrument used was a mercury analyser (MA-2000, Nippon Instruments Corporation, Takatsuki, Japan) equipped with an auto-sampler. The mercury concentrations remained stable in A. muscaria as the fruiting bodies matured. Clearly, mercury is continuously absorbed by mycelia and translocated at similar rate to stems and caps of the fruiting bodies of A. muscaria from their emergence to maturation. This observation may suggest that non-essential is absorbed/co-absorbed and translocated via the same pathway as some essential elements to fungi.

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Methylmercury (MeHg) is a neurotoxicant that exists widely in the natural environment, and is accumulated in seafood through the food web. Because of fears regarding the adverse effect of MeHg contained in seafood on the developing fetus brain, pregnant women have been warned against consuming fish and shellfish in many countries. The biotransformation of MeHg is a modifying factor in its toxicity. Intestinal flora plays an important role in the decomposition and fecal excretion of MeHg. Since Bifidobacterium, Lactobacillus and Bacteroides isolated from the human and rat intestinal tracts have been shown to be able to transform MeHg into inorganic mercury in vitro, we hypothesized that daily intake of indigestible saccharides decreases the total mercury (Hg) concentration in tissues after MeHg exposure. Female BALB/c mice were fed diets containing 0%, 5% fructooligosaccharide (FOS) or 2.5% glucomannan (GM) in a basal diet (AIN-76) for 6 weeks before oral administration of MeHg chloride (5 mg/kg), and then urine and feces were collected for 28 days using the metabolic cages. At the end of the experiment, mice fed the FOS diet showed different intestinal bacterial structure. These results imply that FOS was modified the biotransformation of MeHg by intestinal flora. In conclusion, our findings suggest that dietary FOS reduces the Hg level in the brain through fecal Hg excretion after MeHg exposure and might therefore reduce the neurotoxic effects of MeHg.

DETERMINANTS OF METHYLMERCURY AND PCBs IN CORD BLOOD AND DHA IN MATERNAL BLOOD IN TOHOKU STUDY OF CHILD DEVELOPMENT

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Adverse effects have been reported by exposure to methylmercury and polychlorinated biphenyl (PCB) in the fetal period. Although these chemical substances are derived mainly from fish intake, it is known that DHA which is a n-3 unsaturated fatty acid is taken through consumption of fish and shellfish. These findings suggest that seafood consumption is associated with both risks and beneficial effects to human health. We have been conducting a birth cohort study (Tohoku Study of Child Development; TSCD) in urban and coastal areas in Tohoku district in Japan to examine the adverse effects of prenatal exposures to chemical exposure, and reported the associations of child neurobehavioral development with PCB (Environ Res, 133: 321-326, 2014) and methylmercury (Tohoku J Exp Med, 242: 1, 2017) in cord blood. In the present study, the determinants of methylmercury, PCB and DHA were analyzed. The subjects were 749 pregnant women of coastal area in TSCD. Plasma fatty acids in maternal blood collected immediately after birth were measured by gas chromatography (GC). Maternal hair and cord blood mercury (Hg) were determined by cold-vapor atomic absorption spectrometry. Eleven indicator PCB isomers including highly chlorinated PCBs in cord blood were determined by GC-mass spectrometry, and total PCB on wet weight basis was used in the present study. Fish intake correlated positively with DHA, maternal hair Hg, and cord blood Hg, but there was no significant relation with total PCB. DHA was positively related to academic background and prepregnancy BMI. DHA was also positively associated with birth weight. Maternal hair Hg increased with alcohol consumption during the pregnancy. Umbilical cord blood Hg was positively correlated with alcohol consumption and prepregnancy BMI. On the other hand, total PCB was positively related to maternal age, and negatively related to number of deliveries. These findings will be useful to generate the fish intake recommendations in Japanese women of childbearing age to take DHA while avoiding methylmercury exposure.

MERCURY AND MICROPLASTICS, TWO POLLUTANTS OF ENVIRONMENTAL CONCERN FROM A BAY IN THE CARIBBEAN: ENDANGERING HOT SPOT FOR BIODIVERSITY?

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Microplastics (MPs) are the anthropogenic particles, most abundant in the world’s oceans. They have sizes <5 mm, and are distributed
through the water column, sediments, mangroves, open sea and fresh-water ecosystems. Its size implies they can be ingested by a wide range of organisms, from plankton to humans. The main goal of this study was to investigate the levels of mercury present in surface MPs found on beaches of Cartagena in Colombian Caribbean. Samples were manually collected between the tide line and the vegetation zone, parallel to the shoreline during dry season. After removing debris, pellets were classified according to their surface degradation/oxidation features. Industrial samples were also analyzed. Total mercury levels were determined using a Direct Mercury Analyzer® (Milestone Inc., Shelton, CT, USA), following the USEPA method 7473. T-Hg quantification was performed by measuring the mercury released by the pellets after a digestion process. For each sample, three replicate measurements were performed to ensure the accuracy of the results.

Data were presented as mean ± standard errors and normality and variance homogeneity were checked using Kolmogorov-Smirnov and Bartlett tests, respectively. Statistical analyses were performed using Stagraphics Centurion XVI-II. For all statistical purposes, the criterion of significance was set at P<0.05. According to its color, seven MP categories were obtained (industrial, white-new, gray-sand, amber-brown, black, white-degraded and secondary MPs). An interesting finding in this work is the uptake of Hg by those plastic pellets undergoing degradation processes: T-Hg levels (µg/g) were significantly greater in black pellets (96.1±19.4) or secondary MPs (21.3±2.0) than industrial pellets (15.4±0.8); mercury concentrations in White-Degraded (33.8±2.2) were greater than those found in Gray/Sand pellets (16.3±3.0) and secondary MPs displayed T-Hg concentrations that were different from all other pellets except Black and White Degraded. Human activity is the main cause of mercury releases, particularly for this study area the Dique Channel may carry Hg from gold mining areas that discharge effluents into Magdalena River. Besides, at Cartagena Bay, more than forty years ago, there was a Chlor-alkali plant leaving behind elemental mercury in the sediments. The presence of organic matter and oil, trapped while floating in the bay, could explain the higher T-Hg values detected in Black pellets, whereas the extended surface area may be the critical factor responsible for Hg accumulation in White-Degraded pellets.

**MERCURY LEVELS IN INVASIVE LIONFISH, PTEROIS SPP. (SCORPAENIDAE), FROM THE CARIBBEAN COAST OF COLOMBIA**

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The invasive Lionfish (Pterois spp.), a voracious and opportunistic predator native to Indian and Pacific Oceans, was reported along the northern coast of Colombia since 2009. Some impacts of its presence on ecosystems are the structure and composition alteration of the biological communities of the reef systems and decrease of biodiversity by the displacing and even cause the extincion of the native species from their natural habitats for space and trophic network competition. Considering the scope and complexity of the challenge of controlling invasive species, some of the strategies proposed to control Pterois spp. abundance, dispersion and to limit ecological damage, include the hunting and consumption of this species. Coastal zones in the study area are influenced by incoming flow from the Canal del Dique Channel which drains 7% of Colombia’s main watershed and largest river, the Magdalena, placed in the top ten most polluting rivers in the world as predicted by the global river plastic inputs model, heavily influenced by land-based sources of pollution, runoff, industrial effluents, domestic wastewater and also sediments, loaded with high levels of Mercury, that is impacting marine organisms and human populations in the surrounding communities. Hence negative stressors on the water quality can damage tourism economy since they can affect the adjacent marine protected area, like the Rosario and San Bernardo Corals Natural Park, a landmark in the Caribbean. This document corresponds to a preliminary study that documents for the first time, total mercury levels in dorsal muscle tissue from 15 lionfishes collected along Rosario and San Bernardo Corals National Natural Park located on the Caribbean Region of Colombia. Morphometric measurements and meristic characters were determined on the specimens. Fish ranged in size from 15.4 to 28.5 cm standard length (mean = 19.54 ± 1.05 cm), and mercury levels ranged from 0.01 to 0.30 mg kg–1 (mean = 0.11 ± 0.005 mg kg–1). Mercury levels did not show an increase proportional to the fish length. Mercury levels did not differ between males and females. Total mercury levels in fish complied with legislation, low concentrations of mercury indicate lionfish from Rosario and San Bernardo Corals National Natural Park are safe for human consumption.

**MERCURY IN FISH FROM U.S. NATIONAL PARKS – CONCENTRATIONS, SOURCES, AND ECOLOGICAL RISK**

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Mercury (Hg) emissions to the atmosphere can transport at global scales and subsequently deposit anywhere, including pristine national parks. As Hg accumulates in the ecosystem it can be toxic to natural resources the U.S. National Park Service is mandated to protect. Possible deleterious effects include reduced foraging efficiency and reproductive success of wildlife, and the issuance of fish consumption advisories to protect human health. Given the natural presence, it can be challenging to distinguish Hg sources. Therefore, we measured Hg in more than 3,900 fish from 239 remote lakes and rivers (spanning 51 fish species and 56 national parks in 33 states), analyzed composite samples for Hg isotopic signatures to assess sources, and compared fish Hg concentrations to health benchmarks. Preliminary findings suggest that across all parks, sites, and species, fish Hg concentrations ranged from 7.3 to 2,663 ng/g ww with a mean of 149.6 ng/g ww. Fish Hg levels varied greatly both among and within parks, suggesting that patterns of Hg risk are driven by processes occurring at site specific, local, and continental scales. Measurements of δD/Hg, δ15N/Hg, δ202Hg, and D200Hg have been shown to be effective indicators of Hg source, photo-chemical processing, and atmospheric transport, respectively. Preliminary data indicate that the atmospheric tracer D200Hg was observed in most sites, but to a lesser extent in the east, suggesting regional Hg sources that have not undergone long range atmospheric transport. Western sites show enhanced D199Hg likely tied to precipitation inputs and increased photochemical processing, whereas, lower D199Hg and tightly clustered d202Hg data from the eastern sites suggests a different Hg input pathway, likely dry deposition driven by regional Hg emitters. These trends are clearer when constrained to a single fish species. Preliminary results also indicate that Hg concentrations were below EPA’s fish tissue criterion for safe human consumption in 81% of the fish sampled. However, Hg levels in individual fish at some sites from 21 of 35 eastern national parks exceeded the human health criterion. Mercury concentrations in at least one individual exceeded the most conservative fish toxicity benchmark at 45% of all sites, and the most sensitive health benchmark for fish-eating birds at 76% of all sites. Much of the mercury found in these mainly remote areas is likely the result of air pollution from outside the parks. Future research would help identify patterns of Hg distribution and facilitate informed management decisions aimed at reducing Hg in the environment.
FEATHERS OF ADÉLIE PENGUIN AS A TOOL FOR THE MONITORING OF TOTAL AND MERCURY METHYL IN THE ANTARCTIC ENVIRONMENT

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Penguins are long lived and occupy high levels in the marine food web, turning them susceptible to accumulate elevated quantities of Hg through the processes of bioaccumulation and biomagnification and making them useful sentinels for the assessment of Hg contamination in the environment. Feathers are well studied and known as the main route of Hg elimination in birds. Studies sampling chicks and adults can provide a comprehensive picture of bioaccumulation and local contamination. Adélie Penguin, Pygoscelis adeliae, has circumpolar distribution and depends on the Total Mercury (THg) and Methylmercury (MeHg) concentrations in feathers of P. adeliae. Fieldwork was carried out in March 2014 during the Austral summer at King George Island, South Shetlands Archipelago, Antarctica. Chicks (n=8; 4 males and 4 females) and adults (n=16; 9 males and 7 females) were captured and feathers samples were collected. Total Hg concentrations were determined by cold vapor atomic absorption spectrometry (FIMS-400, Perkin-Elmer) and MeHg concentration by atomic fluorescence spectrometry (MERX System, Brooks Rand Labs). The gender of each individual was molecularly identified. The concentration (± standard deviation) of THg ranged from 73 to 111 (± 11) ug.kg-1 in chicks and 233 to 658 (± 134) ug.kg-1 in adults and MeHg ranged from 55 to 100 ug.kg-1 (± 17) in chicks and 145 to 489 (± 104) ug.kg-1 in adults. Adults had THg and MeHg levels higher than chicks (Mann Whitney; p=0.0001). There was no gender difference in THg and MeHg levels for adults or chicks (T test; p=0.405). THg and MeHg concentrations were highly correlated in chicks and adults together (r=0.97). MeHg corresponded to 76% (±12%) of THg levels. THg and MeHg concentrations increased with age but did not differ with gender of penguins. This pattern has already been reported for some birds that do not present gender differences in diet. Most of the mercury in P. adeliae feathers is accumulated in the form of methylmercury regardless of age. Our results on THg levels are consistent with the literature. Previous studies have reported THg or MeHg in adults of this species, but to our knowledge this is the first to report MeHg levels in P. adeliae chicks’ feathers. Our study demonstrates the bioaccumulation of mercury by age and describes the close correlation between THg and MeHg in penguins’ feathers.

RELATING DIET AND HG EXPOSURE IN A GENERALIST SEABIRD

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Mercury is a globally distributed pollutant whose toxicity depends on its molecular speciation. Species positioned higher in the trophic chain are considered to be more exposed to the most toxic form methylmercury (MeHg). Seabirds are long-lived birds occupying high trophic levels and permit non-lethal sampling through feather collection, hence could be good candidates to assess Hg pollution. Besides Hg species concentrations, feathers allow us to obtain information on diet based on stable isotopes δ13C and δ15N analysis. In this study we worked in ten yellow-legged gull breeding colonies in the south-eastern bay of Biscay, 4-6 dorsal feathers were taken from ten chicks of each colony, during the breeding period of 2016 and 2017. We aimed to address whether chicks’ concentrations of MeHg are related to the consumption of certain feeding resources. High mercury species concentrations were found with MeHg and inorganic Hg (I(Hg)) mean values of 3065±1398 ng/g and 625±544 ng/g respectively, and percentage of MeHg from the total Hg was 85±19 %. In some preliminary models, individuals foraging more on marine prey presented higher concentrations of MeHg. In seabirds, marine prey has been found to have several advantages regarding reproductive output, then a cost-benefit balance may exist with respect this feeding resources. In the same way, individuals foraging more on terrestrial or landfill resources had lower concentrations of total Hg, which includes MeHg and inorganic Hg. Additionally, an effect of chicks’ age was found to affect Hg concentration levels. Finally, we discuss the suitability of this species and sampling method as bioindicator, taking into account its wide range of feeding habits depending on the resources available, its variability among colonies and sampling accessibility.
RISK ASSESSMENT OF MERCURY CONTAMINATION TO ECOSYSTEM IN AN OIL EXTRACTION FIELD

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Mercury (Hg) particularly methylmercury can be accumulated through food webs which results in higher risks for the species with higher trophic levels in the food web. We developed a conceptual model to conduct ecological risk assessment based on the food web structure. The model could not only identify which species are at risk but also elucidate the sources of risks through diet. Risk rating criteria is developed based on the food web structure to categorize the different levels of risks for different species. The results indicate increasing risks for biota higher in the food web hierarchy. Grasshoppers in the whole area are generally at no risk, while earthworms at the immediate vicinity to mine tailings are at high risk and moderate risk further away due to still high soil concentrations. Spiders as insect predator are at high risks within 3 km radius from the tailings. Herbivorous birds similar to grasshopper are at no risk at the whole area, while omnivorous and insectivorous birds are at high risks. The conceptual model is a helpful tool to improve pollution remediation and risk control strategies based on ecological risks in the food web rather than just Hg concentrations in environment.

SURVEY OF TOTAL MERCURY CONCENTRATION LEVELS IN EGGSHELLS OF BLACK STorks

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Wildlife can successfully be used as a pollution monitoring tool to assess presence of various contaminants in different parts of ecosystem. Non-invasive methods, for instance, measurements of feathers and hatched or failed eggs, are useful to investigate problems connected with locally and globally endangered species. The object of our interest is Black Stork (Ciconia nigra), as it is rare species in Europe and its population is decreasing, especially in Baltic States. Ornithologists for years are trying to find the cause for that. One of the hypothesis that it could be connected to mercury pollution as previous research has shown that young storks have high levels of mercury concentration in blood.

In this work we measure total mercury concentrations in eggs shells of black storks. Samples are collected from various nesting sites in Latvia. Analysis are done with spectrometer RA-915M and its attachment pyrolyzer PYRO-915+ (Lumex, Russia) by means of thermal decomposition. Samples were divided in three groups – eggs shells, inner eggshell membranes and eggs shells with attached inner membranes. The determined concentrations in analysed samples confirmed that various parts of eggs have different mercury concentrations. For hard outer shells they varied from as few as 5ng/g up to 35 ng/g; but for inner membranes concentrations reached over 200 ng/g, overall showing that the difference of mercury concentration in shells and membranes is about 5-10 times, depending on sample.

Results indicate that juvenile storks receive some amount of mercury from their mothers, as it is known that mercury concentrations in embryos is even higher than in eggs shells. However it is expected that major source of contamination could be their food items, so we plan to continue this study with measurements of mercury concentration levels in food samples.

RELATIVELY UNAFFECTED NESTING SUCCESS OF TWO SONGBIRD SPECIES IN Hg MINING AND NON-MINING AREAS OF GUIZHOU PROVINCE, CHINA

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Mercury (Hg) is known to have serious effects on reproductive of animals, and songbirds in particular, but field studies remain rare, especially in Asia. China is an important study region because of high emissions and various local pollution sources, and a recent report has shown high Hg concentrations in inverteivorous songbirds, both in Hg mining (Wanshan Hg Mining District) and non-mining (Leigongshan National Nature Reserve) areas of Guizhou Province. We worked in the same two areas on the reproduction of a granivorous (Russet sparrow, Passer rutilans) and inverteivorous (Great Tit, Parus major) species. We found that egg volume was lower in the mining area for sparrows (201 eggs compared to 223 in non-mining area, t = 2.90, P = 0.004), and egg weight and volume was lower in the mining area for tits (44 eggs compared to 54 in non-mining area, t < 2.99, P < 0.004), although these differences were not significant when averaged at the nest level. These results could also be due to clutch size being significantly larger in the more northerly mining site for sparrows, although not for tits. No other measure of reproduction was different between the two areas at the nest level for either of the two species (considering fledgling weight, hatching success and fledgling success; sample size for sparrows for these analyses, 26-38 nests in mining area, 26-51 nests in non-mining area; for tits, 6-8 nests in mining area, 7-12 nests in non-mining area). However, the concentrations of Hg in the birds in the mining area were much lower than in the previous reports: 2.33 (±0.88 SD) µg/g in feathers, 0.67 (±0.23 SD) µg/g in blood for sparrows (n=18), and 2.99 (±1.44) µg/g in feathers, 1.48 (±0.42 SD) in blood for tits (n=7). Our study shows that not all birds in China are at risk for adverse effects of Hg, and confirms the idea that low levels of Hg (previously considered < 4 µg/g in feathers and < 0.7 µg/g in blood) might not present difficulties for reproduction of songbirds in the field. In continuing work, we aim to sample more tits, and more birds at more highly Hg-contaminated sites of the mining district.

HG ELIMINATION BY THREE SIZE CLASSES OF GOLDFISH (CARASSIUS AURATUS)

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Fish are of special concern in the field of mercury (Hg) toxicity because they are a primary source of Hg exposure to the human population. Model development for accurately predicting Hg concentration in fish requires better understanding of the factors regulating Hg uptake and elimination dynamics in fish. Previous studies suggested that for older, larger individuals, toxicokinetic parameters including chemical elimination rates would slow down as they age. To investigate size- and physiology-related changes in chemical toxicokinetic relationships, three size classes (13.18±5.90 g, 21.62±5.26 g, and 73.93±17.28 g) of Goldfish (Carassius auratus), were dosed with Hg and allowed to depurate the chemicals over 3 months under ambient water temperature (1-20°C). Two hypotheses were addressed in this study: 1) Hg elimination in small and younger fish is faster than older and larger fish; 2) Hg elimination by Goldfish is slower in colder water than warmer water. Preliminary results showed that the initial Hg dosing level was 529±112, 677±30, and 622±560 ng g-1, and the Hg elimination rates
Piscivorous birds are top predators in aquatic ecosystems and are vulnerable to mercury (Hg) exposure and associated adverse health effects. In some areas of North America, the health risk posed to piscivorous birds by Hg contamination has not been characterized because concentrations of Hg in bird tissues have not been extensively monitored. When data on Hg in tissues of piscivorous birds are not available, the concentration of Hg in the blood of piscivorous birds can be estimated from the concentration of Hg in prey fish. We used concentrations of Hg in different lengths of a proxy prey fish, bluegill (Lepomis macrochirus), to estimate the concentration of Hg in the blood of 4 species of adult piscivorous wading birds (little blue herons [Egretta caerulea], green herons [Butorides virescens], great egrets [Ardea albus], and great blue herons [Ardea herodias]) in 14 ecoregions of the south central United States. The 4 species of birds consume different sizes of fish with different concentrations of Hg and were predicted to have different concentrations of Hg in their blood. For each species of bird, there were significant differences in average estimated concentrations of Hg in blood between ecoregions, with estimated concentrations of Hg in blood increasing with Hg deposition. The level of predicted risk varied with ecoregion and bird species and was highest for great blue herons. We recommend that future studies of Hg contamination of piscivorous wading birds of the southern United States focus on great blue herons in water bodies within ecoregions that have high Hg deposition.

RELEVANCE OF ACTIVE BIOMONITORING OF MERCURY USING FRESHWATER BIVALVES

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Mercury pollution is a widespread global issue. Due to its high persistence, mercury is present in the environment over a very long period of time. This is why monitoring of this component is necessary. However, because of its hydrophobic characteristics, mercury is difficult to measure in the water column and it is better to measure this metal in biota. Zebra mussels (Dreissena polymorpha) are a commonly used monitoring species in fresh water ecosystems. In the present study accumulated mercury concentrations in these freshwater bivalves were compared to water and sediment concentrations, using multiple regressions. In these models additional abiotic characteristics of water (temperature, oxygen, conductivity) and sediment (clay content and TOC) were included. Furthermore, we investigated the relationship between accumulated concentrations and ecological water quality of the studied water bodies. The latter was determined using MMIF indices. An index value of at least 0.7 represented a good ecological water quality. In this way we investigated if a threshold could be identified for the accumulated concentrations above which an EQS value of 0.7 is never reached. Zebra mussels were exposed in 28 sampling locations for a period of 6 weeks. Afterwards mercury analysis was performed on pooled samples. The results of this study will underline the importance of using biota in monitoring of mercury. Finally we will be able to evaluate if high accumulated mercury concentrations result in a poor ecological quality.

MERCURY POLLUTION IN DISTINCT GEOMORPHOLOGICAL COMPARTMENTS IMPACTED BY MINING DAM BREAKING IN MARIANA (MINAS GERAIS STATE, BRAZIL): TOXIC EFFECTS ON EARTHWORMS

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The breaking of the Fundão dam is considered the most important environmental accident ever recorded in Brazil, and induced the contamination of soils, sediments and biota with iron mining wastes. This study examines mercury concentrations in a small village (Paracatu de Baixo, MG) impacted by the dam breaking in order to identify geomorphic compartments where the wastes could be preferentially deposited. This preliminary study was conducted in the small area of the Gualaxo do Norte river, and surface samples from bottom sediments, floodplain and fluvial terrace were collected. Samples from a reference area were also collected for further comparison. In addition, a sample of waste (taken from the interior of the houses impacted by the dam breaking) was collected. Acute bioassays with earthworms (Eisenia andrei) were performed with such materials. Mercury determination was performed by LUMEX equipment. The results revealed that mercury contents in the bottom sediment (0.0622 mg/kg), floodplain sediment (0.0636 mg/kg), fluvial terrace (0.0604 mg/kg) and waste (0.0589 mg/kg) were significantly different from the contents found in the control area (~0.020 mg/kg). The increase of mercury concentrations was correlated with the increase of Fe, As and Pb contents. The most ecotoxic material was the one collected in the fluvial terrace. This observation may be associated with weathering processes that are more intense in this geomorphologic compartment, stimulating the leaching of mercury and other metals to soil solution. Finally, the dam breaking increased metal contents in the sediment and may be a good indicator to identify depositional environments most impacted by the wastes.
Blacknose dace along with any microevolutionary processes shaping their genetic variation. We hypothesized that: H1), abiotic factors such as Hg concentrations in sediments, suspended particles or water are less important predictors of body burdens than biological factors (i.e. feeding); and H2), Hg body burdens inversely correlate with fish genetic diversity. To test these hypotheses, we combined environmental measurements of total mercury (THg) and methylmercury (MeHg) with genetic and evolutionary toxicology approaches. Overall, there were substantial differences in Hg concentrations in the Still River sediment, particulates and water column between sites. These differences often exceeded an order of magnitude (e.g. particulate THg 0.90 – 11.63 ppm). Concentrations of THg in fish muscle tissues ranged from 0.09 to 1.42 ppm wet weight and were significantly higher in historically contaminated Still River populations in comparison with a reference site. Fish Hg concentrations did not correlate with any of the environmental Hg measurements. Using delta-15 N, we showed that diet type could not explain the variation in Hg concentrations in fish muscle. Hg concentrations however did positively correlate with body mass. This result suggests that diet intake is a better predictor of Hg bioaccumulation under the assumption that fish achieve greater mass per length and higher Hg concentrations in relation to higher rate of food intake. Moreover, based on microsatellite analyses, a common genetic marker, we found that fish with higher Hg accumulation had a lower allelic diversity. Our preliminary results suggest that in Blacknose dace Hg burdens are related to dietary intake rate and not directly to environmental Hg concentrations, and that the degree of Hg accumulation can influence the allelic diversity in these fish.

**R.P.2.39**

**RECONSTRUCTING AVIAN MERCURY CONCENTRATIONS THROUGH TIME USING MUSEUM SPECIMENS FROM NEW YORK STATE**

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4) Cornell University Museum of Vertebrates

In this study, we examined how variation in MeHg concentrations through time is reflected in birds, a taxon commonly used as a biological indicator of ecosystem health. Using museum specimens collected from 1880 to 2016, we measured feather MeHg concentrations in six species of New York State breeding birds with distinct dietary and habitat preferences. We predicted that MeHg concentrations in feathers would mirror Hg emission patterns in the Laurentian Great Lakes and increase through time until 1980, and then decrease thereafter in response to increased regulation of anthropogenic Hg emissions. We found that MeHg concentrations increased with trophic position as indicated by delta-15 N, and that MeHg concentrations in some individuals from four of the six species were indicative of negative sublethal effects in birds. In contrast to our prediction, MeHg concentrations through time did not show consistent trends and varied by species, even after correcting for possible changes in diet and habitat through time. We also found substantial variation within species and individuals, suggesting that trends through time may be obscured due to high within-individual variation in feather MeHg concentrations caused by spatiotemporal variation in molt or environmental Hg exposure. Our study provides an important assessment of feather MeHg in six species not typically analyzed using this retrospective approach.

**R.P.2.40**

**LAND DISPOSAL OF DREDGED SEDIMENTS FROM GUANABARA BAY (RIO DE JANEIRO, BRAZIL): SEASONAL VARIABILITY OF MERCURY POLLUTION AND TOXIC EFFECTS ON EARTHWORMS**

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3) Centre for Mineral Technology
4) Fluminense Federal University

Guanabara Bay (GB) is highly impacted by the discharge of metal-polluted wastes, leading serious effects on surrounding human populations and biota. This study examines the seasonal variability of mercury (Hg) concentrations in dredged sediments from GB and its contribution in the toxicity related to the disposal of such sediments in soils. The sediments were collected in August 2014 (winter) and February 2015 (summer) in five areas: Port of Rio de Janeiro, Port of Niterói, Meriti River mouth, Iguacu River mouth and the Environmental Protection Area (APA) of Guapimirim. To simulate land disposal, the sediments were mixed with a ferralsol (a representative tropical soil) in proportions varying between 0-100% and their toxicity was analyzed. The results showed that the toxicity of sediments increased with the proportion of sediments used, and that the toxicity was higher in the winter sediment. Moreover, based on microsatellite analyses, a common genetic marker, we found that fish with higher Hg accumulation had a lower allelic diversity. Our preliminary results suggest that in Blacknose dace Hg burdens are related to dietary intake rate and not directly to environmental Hg concentrations, and that the degree of Hg accumulation can influence the allelic diversity in these fish.

**R.P.2.41**

**POTENTIAL ECOLOGICAL RISK AND MERCURY DISTRIBUTION IN BOTTOM SEDIMENTS FROM RODRIGO DE FREITAS LAGOON (RIO DE JANEIRO, BRAZIL)**

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Over the last the decades, the Rodrigo de Freitas Lagoon (RFL) has been impacted by the discharge of domestic wastes and metals, such as mercury (Hg). RFL is commonly used for the practice of aquacultural sports, including during the 2016 Olympics. This study examines...
Mercury concentrations in the studied samples ranged from 0.025 to >3 kg, n=28. Total mercury (THg) concentration was determined in dried AMA 254 mercury analyzer (Altach Ltd, Czech Republic).

Results and discussion

Mercury concentrations in the studied samples ranged from 0.025 to 52.12 mg/kg. The highest hepatic THg levels were found in adult specimens (8.065 mg/kg) and the lowest in pupples (0.108 mg/kg). Mean nephric THg levels in pupples, juveniles and adults were as follows: 0.136, 1.917, 4.154 mg/kg. We found no differences in THg concentrations between age groups in the case of muscles only (average ~0.780 mg/kg). There were significant correlations between THg concentrations in all tissues and between body weight and THg levels in the liver and kidneys. We found fifteen reports in literature (1980-2017) on THg liver concentrations in North American raccoons, where in 6 of the total 24 collection sites (25%) the THg concentrations were higher than in western Poland; at 3 of the sites raccoons showed similar THg levels to Poland, and at the remaining 15 sites the levels were clearly lower (62%). This comparison suggests that the raccoons inhabiting the riparian ecosystem of the middle Odra River are probably exposed to elevated Hg levels. Our results also show, similar to North America, that this invasive alien species can be used as a bioindicator of environmental mercury pollution in Europe.

R.P.2.43

STOPOVER DEPARTURE BEHAVIOR AND FLIGHT ORIEN-
TATIONS OF SPRING-MIGRANT YELLOW-RUMPED
WARBLERS (SETOPHAGA CORONATA) EXPERIMENTALY
EXPOSED TO METHYLMERCURY

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Mercury is a global pollutant that has wide-ranging impacts on the physiologic systems of birds, but almost nothing is known about how this affects migration. We manipulated methylmercury (MeHg) burdens of 24 wild-caught Yellow-rumped Warblers (Setophaga coronata) before releasing them and tracking their spring migration with automated radio-telemetry to study the effect of MeHg on stopover departure behavior and flight orientations. Dosing half the birds for 14 d prior to release resulted in environmentally relevant mean blood total mercury (THg) concentrations of 6.61 (± 0.16) ppm while a group of 12 controls had nearly undetectable blood THg. We observed starkly different departure behavior between groups, with dosed birds leaving the release site significantly sooner than controls. Among birds that were detected beyond the release site, seven (three dosed, four control) initially made a landscape-scale relocation before a longer-distance migratory flight, while two (controls) migrated directly from the release site. All flights were in the seasonally appropriate direction regardless of group. Rapid departures by dosed birds could have been the result of hyperactivity that can be induced by MeHg, or due to decreased social dominance that caused them to seek areas with less resource competition. We found no evidence that MeHg impaired orientation, although sample sizes were small and we had less ability to detect birds flying in incorrect directions than to the north. The dramatic difference in departure decisions between groups indicates a potential effect of MeHg on the neurological and/or physiological mechanisms that control migratory movement behaviors of birds.

R.P.2.44

GEOGRAPHIC VARIATION OF MERCURY IN BREED-
ING TIDAL MARSH SPARROWS OF THE NORTHEAST-
ERN UNITED STATES

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Both the Saltmarsh Sparrow (Ammodramus caudacutus) and Seaside Sparrow (A. maritima), collectively referred to as tidal marsh sparrows, have become species of conservation concern due to anthropogenic stressors including environmental mercury contamination. To assess methylmercury exposure, we sampled blood from adult male tidal marsh sparrows from Maine south to the Delaware in collaboration with the Saltmarsh Habitat and Avian Research Program (SHARP). This is the first study of its kind to provide a comprehensive evaluation of mercury contamination in saltmarshes throughout the majority of northeastern coastline — a geographic scale that encompasses the entire Saltmarsh
VARIATION OF MERCURY CONCENTRATION IN DIFFERENT TISSUES OF SPECTACLED CAIMAN (CAIMAN YACARE) IN THE BENI RIVER BASIN LA PAZ-BOLIVIA

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The organic form of mercury, methylmercury (MeHg), can bioaccumulate in the tissues of the animals and biomagnify at each trophic level to reach a high concentration in the top predators. Consequently, it was expected that the concentration of mercury in the muscle tissue of the Spectacled Caiman (Caiman yacare) would be the highest. However, in a previous study, low concentrations of mercury were reported for muscle tissue of the C. yacare compared to the muscle tissue of carnivorous fish which are part of the C. yacare diet. A plausible explanation was that most mercury in the C. yacare accumulates in other tissue than the muscle. Here we compared the accumulation of mercury among liver, kidney, fat, and muscle. Samples of 1 g of each type of tissue were obtained from seven different individuals, and placed into cryo-tubes and stored in liquid nitrogen until analysis. Total mercury analysis shows a significant difference in mercury concentrations among tissues. Fat had the lowest concentrations (0.025 ± 0.037 μg·g⁻¹) followed by muscle (0.14 ± 0.07 μg·g⁻¹), kidney (0.57 ± 0.32 μg·g⁻¹) and liver (1.81 ± 0.87 μg·g⁻¹). Most tissues of C. yacare have mercury concentrations below the recommended limit for human consumption according to WHO (0.5 and 1.0 μg·g⁻¹ for fresh and marine fish respectively). The liver tissue clearly accumulates a higher concentration of mercury probably due to its high protein content and activity, but there may be a specific mechanism because the accumulation is relatively higher than in other groups of animals. Although such preferential accumulation would make C. yacare harvest for human consumption a better alternative than carnivorous fish, such high concentrations in the liver may cause hepatotoxicity and may endanger C. yacare survival in more polluted areas of the Amazon. Further studies are needed to understand the impact of mercury pollution in C. yacare populations as well as investigating any specific pathway of selective liver bioaccumulation.

ELEVATED MERCURY CONCENTRATIONS IN THE NORTHERN SAW-WHET OWL OF HAIDA GWAI

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The Haida Gwaii subspecies of the Northern Saw-whet owl (Aegolius acadicus brooksi) is a distinctive bird endemic to Haida Gwaii off the northwest coast of British Columbia. Unlike its continental cousin (A. a. acadicus), the Haida Gwaii subspecies is non-migratory. The owl is designated as “threatened” because of its small and rapidly declining total population. The reason for the population decline is not well known, although habitat change and invasive species have been suggested to have contributed to it. As part of a pilot study on geochemical tracers of the bird’s behavior, mercury concentrations in the claw of the Haida Gwaii owl were found as high as 20–40 μg/g (dry weight or dw), more than an order of magnitude higher than those in the owl claw of the nearby Vancouver Island subspecies, and in feather or eggs of other species of owls. As these concentration levels are greater than the potential toxic threshold of 20.0 μg/g (dw) that has been suggested for other avian species, further studies were carried out to investigate the source of mercury to the owl and whether mercury has contributed to its population decline.

Samples of water, sediments and potential prey items to the Haida Gwaii owl were collected in June 2016. Water samples taken in marsh and wetland areas had a total Hg ranging from 0.1 to 9 ppb, and methylmercury of 0.01 to 0.90 ng/L, with higher (7-45%) of methyl mercury (MeHg) to total mercury (THg) ratio compared to coastal areas (1-3%). In terms of prey items, the owls tend to breed in mature, old-forest habitats, often close to wetlands. The habitat requirements during the nonbreeding season are less well known, but dietary analysis suggests that some move towards coastal areas to feed on intertidal invertebrates such as isopods and amphipods. The owl is also known to prey on terrestrial animals such as bird chicks, amphibians (e.g., toads) and small mammals (e.g., mice, moles). Mercury concentrations in mice were found to be very low (6-80 ng/g), whereas higher concentrations were found in the amphipods (50-200 ng/g). Mercury concentrations in other more vital tissues (e.g., muscle, liver) have also been measured but are much lower in mercury (1-7 μg/g) than in the claws and feathers. Further tests are being carried out to better understand why mercury levels are elevated in the Haida Gwaii owl species and its potential implications for the population dynamics.

SPATIAL DISTRIBUTION OF MERCURY AND METHYL MERCURY IN COASTAL SOIL AND SEDIMENTS OF GADANI SHIPBREAKING AREA, PAKISTAN

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During the past century, anthropogenic activities have altered the distribution of mercury (Hg) on the earth's surface. Sea-bound ships are made, owned and used for their trade by developed countries but are often demolished, together with their toxic materials, in developing countries i.e. Pakistan, India and Bangladesh. Pakistan’s Gadani shipbreaking industry is the third largest shipbreaking in the world. Although pollutants have been released from the industry for the last fifty-six years, yet few studies exist where the environmental impacts of the industry have been assessed. Heavy metals, including Hg, are some of the pollutants of concern. A preliminary report from the World Bank (Report No 58275-SAS), on the recycling yards of Gadani, reported mercury concentrations (HgTOT) in a range from 0.078 to 0.158 mg/kg. Transfer of inorganic Hg from abiotic compartments to methylmercury (MeHg) in aquatic food webs and ultimately to humans is a potential risk. Quantitatively measure shipbreaking yards Hg loadings and their distribution in the environment is critical for science-based decision making. To address this knowledge gap, total Hg and MeHg concentrations were determined from 69 surface soil and sediment samples to understand the spatial distribution and overall pollution status of the Gadani Shipbreaking yards and adjacent sea. Total Hg analysis was performed using Direct Mercury Analyzer (DMA-80) in according with U.S. EPA method 7473. MeHg was determined after extraction of MeHg from soil/sediment to dichloromethane with CuSO4/KBr followed by back extraction to DI water and detection using CVAFS.
Mercury (Hg) is recognized as a pollutant of global concern due to its long-range transport in the atmosphere and its persistence in the environment. The combustion of fossil fuels accounts for a significant share of total anthropogenic mercury emissions. Being released in its elemental form (Hg0) or as oxidized Hg-compound (Hg2+), mercury may undergo transformations into organo-metallic compounds with increasing toxicity. Thus, its emission reduction is an important issue from a sustainable point of view and in the context of public acceptance of fossil fuel fired power plants. The paper presents the technical scale demonstration of a novel process for the controlled desorption and reliable immobilization of Mercury (Hg) in waste water treatment (WWT) units, at the example of WWT of wet flue gas desulphurization (FGD). The aim is to create a specific and highly concentrated sink for Hg for further processing. The suggested low-tech process has several advantages and could be easily implemented into existing plants, increasing sustainability and reducing the consumption of chemical additives. Additionally, the findings could be used for the prevention of unnoticed Hg emissions in conventional FGD waste water processing. The design of the experiments and the test-rig parameters are scaled up from previously published results from lab-scale experiments. Synthetic waste water of variable composition is processed in a batch wise operated WWT unit. Neutralization of the waste water is performed by addition of Ca(OH)2 slurry. As a result of redox reactions, dissolved Hg2+ compounds are reduced to Hg0, an element with very low solubility in water. An adjustable air flow is bubbled through the liquid, monitoring its increase in Hg0-concentration as a function of experimental parameters. The Hg-rich air flow is directed to an activated carbon adsorber. Hg-sampling and analysis includes all gaseous and liquid process streams, hence the efficiency of Hg-removal from the waste water and its safe capture is determined. The findings are evaluated in terms of process efficiency optimization as well as for improved safety in existing WWT plants.

R.P.3.2

TECHNICAL SCALE INVESTIGATIONS ON THE CONTROLLED STRIPPING OF MERCURY IN WASTE WATER TREATMENT

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The high temperatures formed by flue gas after the combustion of coal in a power plant boiler can be used to calcine the precursor material prepared by the chemical coprecipitation method, and a modified biochar adsorbent can be obtained during the pyrolysis of biomass. Hg0 is then efficiently adsorbed by modified biochar in a suitable low-temperature region. This technology uses biomass as a raw material, integrates the conventional chemical coprecipitation method with the biomass pyrolysis coking process and uses the high temperature after combustion in the boiler to modify the adsorbent and achieve continuous mercury removal from the flue gas flow. It has great potential for development and has not been widely reported. To provide a theoretical basis for the development of future mercury removal methods, two types of biochars modified by the coprecipitation method were investigated: undoped iron-based biochars modified with FeCl3 and iron-based biochars doped with Cu and Mn from CuSO4, Mn(CH3COO)2, and KMnO4. The crystal phase compositions, pyrolysis characteristics, pore structures, microscopic morphologies, elemental speciations and functional groups of the modified biochars were characterized. The adsorption mechanism was further explored by temperature-programmed desorption (TPD). The results showed that the mercury adsorption of the modified biochars was significantly enhanced. The
mercury adsorption performances first increased and then weakened with increased loading. The modification decreased the graphitization degree. Spinel structure solid solutions of MnFe2O4 (galaxite) and CuFe2O4 (copper iron oxide) were formed in the modified biochars, generating many cation vacancies on the biochar surface. After biochar modification, the pore structures and the contents of carbonyl, carboxyl, and metal hydroxyl functional groups were significantly increased. The removal of Hg0 by modified biochar is the result of a combination of adsorption and oxidation. The modification process significantly promotes the chemical adsorption of Hg0. Functional groups, lattice oxygen, chemisorbed oxygen, halogen components, and metal oxides or ions on the sorbent surface all play roles in the oxidation of the adsorbed Hg0. Fe2O3 and CuO (MnO2 and Fe2O3) double metal oxides or ions have a synergistic effect on the removal of Hg0. However, the strong oxidative ability of Mn7+ and Mn6+ allows them to oxidize Hg0 competitively with Fe3+.

R.P.3.5

MERCURY REMOVAL FROM NATURAL WATERS USING EUCALYPTUS GLOBULUS BARK AS AN EFFICIENT BIOSORBENT: MODELLING AND OPTIMIZATION BY RESPONSE SURFACE METHODOLOGY

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Mercury is one of the most toxic metals responsible for the contamination of the aquatic systems due to its ability to bioaccumulation in the living organisms and biomagnification along the food chain. The concerns about its dangerousness and impacts on environment and human healthy led the ratification of the Minamata convention emphasizing the importance of phasing-out this pollutant. Additionally, the 2030 Agenda for Sustainable Development of United Nations promotes the improving of water quality minimizing release of hazardous chemicals and materials, and foments an enhance in wastewater treatment and their recycling and safe reuse globally.

Sorption systems have been pointed as good alternatives for the removal of contaminants in water treatment, mainly due to their high efficacy and low operating costs. Agricultural or industrial by-products are excellent sorbent options since they are largely available and do not require any pre-treatments. The efficiency of the sorption is highly dependent of the operation conditions and hence the optimization of the process variables must be. In this line, the Response Surface Methodology (RSM) is a set of techniques that describe the relation between the variables or factors and can predicts and optimize the process behavior.

In this work, a by-product from a paper pulp industry, Eucalyptus globulus bark, was used as biosorbent for mercury removal from contaminated natural waters containing realistic mercury concentrations. Three different variables, namely pH (4, 6.5 and 9), sorbent dosage (0.2, 0.5 and 0.8 g L-1) and salinity (0, 15 and 30 g L-1) were studied under batch conditions and the response evaluated was the % of element elimination. A design of the experiments was accomplished using a Box-Behnken matrix and the experimental results showed removal percentages between 23 % and 77 %. The model obtained presented a good fit to the experimental data (R2=0.945) and allowed to determine the optimized conditions, which were 0.55 g L-1 of biosorbent, no salinity (0 g L-1) and pH of 6.0 with the expected metal removal of 81 %. The high affinity between the biosorbent and mercury allows the use of small dosages of solid and the generation of few amounts of wastes. Taking into account the environmental efforts to develop sustainable and eco-friendly solutions, this study afforded an innovative application of the RSM for sorption processes considering realistic variables and matrices and provides knowledge for an effective implementation of this biosorbent in wastewater remediation.

R.P.3.6

TREATMENT/RECOVERY OF MERCURY GUARDS AND ACTIVATED CARBON IN THE OIL & GAS INDUSTRY AS WELL AS STABILISATION OF MERCURY AS HGS

CHIFFFLIER, Gabriel

Batrec is a company based in Switzerland specialised on the treatment/recovery of hazardous waste containing mercury. Having several treatment units, including for the reactivation of activated carbon and the decontamination of mercury guards coming from the Oil & Gas industry around the world. Such absorbents are widely use within so-called Mercury Removal Units (MRU). Following a number of well documented industrial accidents caused by corrosion related to the presence of mercury, the Industry has invested extensively in MRUs. The Batrec treatment process can decontaminate absorbents, removing the Mercury, and facilitating their further recovery. Activated carbon is reactivated allowing direct reuse for Water or Air treatment. The decontaminated mercury guards (also described as metal oxides absorbents) are sent to smelters for Copper and/or Zinc recovery.

In this way Batrec’s treatment process supports the circular economy, recycling activated carbon instead of sending it to landfill and enabling the further recovery of metals present in the absorbent which due to the presence of mercury would normally be impossible to send to smelters for recycling.

Following the treatment/recovery of mercury absorbents, by removal and recovery of liquid mercury is followed at Batrec by a proprietary stabilisation process which transforms the recovered mercury into mercury sulphide (HgS). The global evolution of environmental legislations (e.g. Minamata Convention on Mercury) has established in law the requirement for a safe disposal of metallic mercury. All industrial sectors are concerned but especially the Chlor Alkali industry, the Oil & Gas, nonferrous mining and nonferrous metallurgy which have responded with increased controls on the fate of mercury produced or used in their processes.

The Batrec wet chemical process to transform mercury into mercury sulphide sets new milestones in terms of safety, conversion rate and process efficiency. The process employs a stabilisation reagent, which is mixed with pure liquid mercury. Active sulphur within the stabilisation mixture reacts with the metallic mercury to form HgS (cinnabar), resulting in a mercury-sulphide cake with less than 5 % water. A conversion rate of 99.999% of the mercury to mercury-sulphide is guaranteed. Being a wet process, there are no gaseous mercury emissions. The process has been operational since 2016 and has a capacity of approx. 1.200-1.500 t/year. A complete traceability chain has been implemented around the stabilisation process – including external inspections, sampling, analysis and mass balancing.

R.P.3.7

STUDY OF THE ENVIRONMENTAL AVAILABILITY OF MERCURY IN SOILS FROM A CONTAMINATED AREA IN MINAS GERAIS, BRAZIL

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Mercury is one of the most toxic metals responsible for the contamination of the aquatic systems due to its ability to bioaccumulation in the living organisms and biomagnification along the food chain. The concerns about its dangerousness and impacts on environment and human healthy led the ratification of the Minamata convention emphasizing the importance of phasing-out this pollutant. Additionally, the 2030 Agenda for Sustainable Development of United Nations promotes the improving of water quality minimizing release of hazardous chemicals and materials, and foments an enhance in wastewater treatment and their recycling and safe reuse globally.

Sorption systems have been pointed as good alternatives for the removal of contaminants in water treatment, mainly due to their high efficacy and low operating costs. Agricultural or industrial by-products are excellent sorbent options since they are largely available and do not require any pre-treatments. The efficiency of the sorption is highly dependent of the operation conditions and hence the optimization of the process variables must be. In this line, the Response Surface Methodology (RSM) is a set of techniques that describe the relation between the variables or factors and can predicts and optimize the process behavior.

In this work, a by-product from a paper pulp industry, Eucalyptus globulus bark, was used as biosorbent for mercury removal from contaminated natural waters containing realistic mercury concentrations. Three different variables, namely pH (4, 6.5 and 9), sorbent dosage (0.2, 0.5 and 0.8 g L-1) and salinity (0, 15 and 30 g L-1) were studied under batch conditions and the response evaluated was the % of element elimination. A design of the experiments was accomplished using a Box-Behnken matrix and the experimental results showed removal percentages between 23 % and 77 %. The model obtained presented a good fit to the experimental data (R2=0.945) and allowed to determine the optimized conditions, which were 0.55 g L-1 of biosorbent, no salinity (0 g L-1) and pH of 6.0 with the expected metal removal of 81 %. The high affinity between the biosorbent and mercury allows the use of small dosages of solid and the generation of few amounts of wastes. Taking into account the environmental efforts to develop sustainable and eco-friendly solutions, this study afforded an innovative application of the RSM for sorption processes considering realistic variables and matrices and provides knowledge for an effective implementation of this biosorbent in wastewater remediation.
The emergence of metallic Hg was observed on the surface of the soil from an area of the city of Descoberto. This metal came from gold mining activities from 1824 to mid-twentieth century. Studies of soil superficial layer of this area indicated Hg concentrations above the level in which there is potential risk of damage to human health. The aim of this work is to study the behavior of Hg in this soil performing quantitative analysis using the HGAAS technique, speciation analysis of Hg by thermodesorption system coupled to atomic absorption spectrometer and chemical fractionation using the following: deionized water, CH3COOH 0.1 mol.L-1 + HCl 0.001 mol.L-1, KOH 1 mol.L-1, HNO3 12 mol.L-1, HCl 6 mol.L-1 and aqua regia. The statistical interpretation of the physical and chemical characterization of the samples along with chemical fractionation showed that the Hg is not in a mobile form. This indicates that this metal is oxidized and bound mainly to oxy-hydroxides of Fe, Mn and Al. Part of it is also linked to the humic fraction, reaching 30%. The study on the use of the heating treatment as a procedure to determine Hg0 showed that part of the Hg2+ is reduced and volatilized at 180 °C for 48 hours. It shows that the methodology applied by many authors may be overestimating the quantification of Hg0. It was also concluded that it is possible to decontaminate the soil from this and probably other contaminated areas avoiding using high temperatures.

R.P.3.9

**EFFECTS OF Cl AND O SURFACE GROUPS OF BIO-CHAR ON MERCURY REMOVAL FROM FLUE GAS**

Luo, Jingjing

Oxygen containing groups and chlorinated sites on biochar was studied their effects on mercury removal from flue gas. Hydrogen chloride (HCl) non-thermal plasma was applied to introduce Cl active sites on biochar and both chemical impregnation and plasma activation methods were applied to introduce more O surface groups on carbon. Mercury removal efficiency in typical flue gas components was investigated. To elucidate the adsorption mechanisms & binding properties, samples were characterized by N2 adsorption, scanning electron microscopy with energy dispersive spectrometer (SEM-EDS) and X-ray absorption near edge structure (XANES) analysis of Hg and Cl edges. Results showed that non-thermal plasma treatment could successfully increase Cl and O active sites on biochar and greatly increased its mercury removal efficiency. HCl treatments re-organized biochar’s surface structure and layered structure generated on the surface. The chemical species estimated by linear combination fitting (LCF) from XANES spectra revealed that HCl-treated biochar captured Hg0 and mainly formed as the chemical species of Hg+. While, on carbon rich in O active-sites, mercury was bound on surface mainly in HgO. In the presence of NO and SO2, adsorbed mercury existed mainly as Hg+. SO2 competed with Hg0 and inhibited the adsorption of Hg0; while NO promoted Hg0 removal capacity due to both increased the active sites and enhanced the adsorption kinetics of adjacent Cl-containing sites.

R.P.3.8

**IMPACT OF ENRICHED CO2 AND H2O ON MERCURY REMOVAL OVER MAGNETIC BIOCHAR IN OXYFUEL COMBUSTION ATMOSPHERE**

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High concentration mercury in oxyfuel combustion flue gas could destroy processing CO2 processing devices through metal embrittlement and aluminum corrosion. In this study, mercury adsorption and oxidation efficiencies over biochar (BC) and magnetic biochar (MBC) in air and oxyfuel combustion atmospheres were investigated. Mercury programmed temperature desorption (Hg-TPD) was applied to demonstrate the mercury species on spent BC and MBC samples after mercury removal experiments. In air combustion atmosphere, mercury adsorption efficiency over BC was higher compared to oxyfuel combustion atmosphere. However, mercury oxidation efficiency was improved in oxyfuel combustion atmosphere. MBC was capable to adsorb both Hg0 and Hg2+, but enriched H2O in oxyfuel combustion atmosphere significantly prohibited mercury adsorption. Hg-OM and physical adsorption Hg0 were predominant mercury species on spent BC, and the Hg-OM consisted of mercury combined with various kinds of organic group. And HgO was minor on spent BC. While, HgCl2 accounted for most of mercury captured on MBC in the both atmospheres. High concentration CO2 in oxyfuel combustion atmosphere promoted the formation of organic groups, especially C=O groups, which combined with mercury and resulted in Hg-OM. However, enriched CO2 could lower the content of chemisorbed oxygen on MBC and subsequently inhibited the formation of HgO. Thus, as the CO2 concentration in atmosphere increased, the proportion of HgO decreased. Chlorinated group is the most significant active site for mercury removal. Spent MBC samples after mercury removal experiments with different time were applied to Hg-TPD. The results showed that, Hg0 was firstly captured through physical adsorption and then oxidized and transformed to mercury compounds.

R.P.3.10

**IMPACTS OF EMISSION CONTROL MEASURES ON THE ENVIRONMENTAL MERCURY BURDEN OF INDIA AND TRANSBOUNDARY FLUXES OUT OF INDIA VIA AIR AND WATER**

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(1) IIT Hyderabad

India is a major emitter of mercury to the atmosphere. Material flow of mercury within the Indian technosphere is also very high; even though the contents of mercury in many consumer products is low the amount of consumer products being produced is very high. Most previous studies have tried to compute only the atmosphere deposition of mercury under emission scenarios derived from IPCC or equivalent reports. Here, we use a ‘unit-world’ multimedia model for India (based on a previously developed global multimedia model for mercury) to compute mercury inventory in the Indian environment, and the trans-boundary fluxes of mercury out of India through air and river run-off to oceans, using a number of emission scenarios from present to the year 2050. While a couple of emission scenarios are similar to the IPCC driven scenarios (for example, which assume all coal-fired power plants to install flue gas desulfurization (FGD) with 70% removal efficiency, or start using washed coal) other scenarios are new. These include some aggressive measures such as selective sourcing of ‘cleaner’ coal for energy generation, >90% recovery of mercury from zinc smelters (identified in previous papers as an important industry), complete recycling of mercury in consumer products, or a complete ban of mercury in consumer products, and some new policy driven scenarios not evaluated before in any study. These new scenarios are based on the latest energy outlook for India and the recent governmental policies. They include: reduction of the contribution of coal to total power generation in India to 50% from 75% (50% contribution by renewables such as solar power). However, use of coal in iron and steel is expected to increase because of a positive push in the manufacturing sector. After running computer simulations to the year 2050, we find that measures such as coal washing and FGD reduce inventories in Indian air and
Mercury pollution has gained global attention. Mercury is released from many industrial processes (coal-fired power generation, cement, non-ferrous metal smelting, waste incineration, etc.) and is used in the production of numerous manufactured products (PVC, medical devices, compact fluorescent lights, batteries, dental fillings, etc.). Its control thus requires complex and widespread measures. This paper provides an overview of the global patent landscape in the area of mercury disposal technology by analyzing relative patents based on Derwent Innovations Index, selected from 1949 to 2018, covering patenting activity related to technologies in removal or recycle mercury from the process in the above-mentioned areas. The most common technologies for each area were identified and their developments were analyzed over time. The 8164 patent families for mercury disposal technology in this study included in total 20,267 individual patent applications, covering 75 priority countries. Information related to the main countries, important applicants, key technologies and development trend were identified. The patent development on mercury disposal technology has been divided into 3 steps: germination period (1949-1968), slow development period (1969-2000) and rapid growth period (2001-2018). Among the geographical distribution of relevant patenting activities, US, Japan, and Germany are the main technique exporting countries while China is the country with the largest number of patent filings; China, US, JP and Canada are the leading countries very active in mercury disposal; the global ranking of TOP10 patent applicants are from Japan (60%), China (20%), US(10%) and Germany (10%), whose patenting activities increased significantly after 2001. The relevant patent families were separated into five major categories: atmosphere mercury removal technology, mercury wastewater treatment technology, Mercury-containing waste disposal technology, mercury recovery technology and mercury-containing soil remediation technology. According to the International Patent Classification based on the technology disclosed in the patent documents, key

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**R.P.3.11**

**INFLUENCE OF OPERATING CONDITIONS ON MERCURY REMOVAL BY ACTIVATED CARBON INJECTION IN A PILOT-SCALE COAL-FIRED BOILER**

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Mercury in coal-fired flue gas which has three forms: element mercury (Hg0), divalent mercury (Hg2+) and particle-bound mercury (Hgpp) has aroused widespread concern around the world due to its high toxicity, migration, bioaccumulation. In this work, the experiments to explore the effect of real coal-fired flue gas under different conditions on the mercury removal efficiency by activated carbon injection (ACI) with air pollution control devices (APCDs) were carried out on a pilot-scale 0.3 MWth circulating fluidized bed (CFB) experimental system which was a simulation system for coal-fired boiler power plants. The results showed that the mercury removal efficiency of SCR+ACI+FF system (SAFs) and the proportion of Hgpp after ACI increased with the increase of temperature in a certain extent due to the promotion of Hg0 oxidation in SCR and chemical absorption in ACI. SO2 not only suppressed the combination between mercury and halogen in ACI but also had competitive adsorption with mercury which result in the mercury removal efficiency reduction. It was noteworthy that high concentration of NO cannot improve the removal efficiency of flue gas mercury result from the promotion of oxidation on Hg0 by NO2 which could completely counteract the adverse effect on mercury oxidation in SCR. The FF device could not only capture all HgP, but also had considerable adsorption with mercury which result in the mercury removal efficiency completely counteract adverse effect on mercury oxidation in SCR. The results showed that the mercury removal efficiency of SCR+ACI+FF system was more than 97.4%. The results in this study have great value to provide optimization of the operational parameters of the ACI system for mercury removal technology and highly synergistic effect on mercury removal by conventional APCDs.

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**R.P.3.12**

**MERCURY CONCENTRATION AND MOBILITY IN SOILS FROM THE VICINITY OF AN INFORMAL E-WASTE RECYCLING SITE, LAGOS, NIGERIA**

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Informal e-waste recycling sites can be a source of mercury (Hg) exposure due to the unregulated processes such as open burning that take place. This study investigated the concentration and the mobility of Hg in soil samples from the vicinity of an informal e-waste recycling site in Lagos, Nigeria. Samples were collected from five locations during both the wet and dry seasons. Total Hg concentrations were determined using cold vapour atomic absorption spectrometry (CV-AAS) following sample digestion with nitric acid. Operationally defined mobile and semi mobile forms of Hg were determined by CV-AAS following sequential extraction with increasing strengths of nitric acid (EPA, 2014). Total Hg concentration in soil from the main recycling site during the dry season was 624 ± 84 mg kg⁻¹, of which 4% was in mobile forms and 7% in semi-mobile forms. During the wet season, total Hg concentration was lower at 443 ± 53 mg kg⁻¹, possibly due to run off, of which 3% was in mobile forms and 10% in semi-mobile forms of Hg. At the second site, that was used previously for recycling activities, total Hg concentration was lower at 15.2 ± 3.8 mg kg⁻¹ during the dry season and 13.1 ± 1.7 mg kg⁻¹ during the wet season. The dominant forms were non-mobile (>74%). It is possible that Hg concentrations were higher at this site in the past when recycling was routinely carried out but have fallen with Hg run off during the wet season. At the remaining three sites where recycling activities have not been carried out, total Hg concentrations were below 2 mg kg⁻¹. Despite the predominance of non-mobile forms of Hg, further investigation is necessary to determine the exposure of workers, many of whom are children and wear no protective equipment, to Hg. Measures for personal protection and site regulation, and an assessment of environmental transfer of Hg to nearby water courses and uptake by plants should also be considered.

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**R.P.3.13**

**A PATENT LANDSCAPE OF MERCURY DISPOSAL TECHNOLOGY BASED ON BIBLIOMETRIC**

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Mercury pollution has gained global attention. Mercury is released from many industrial processes (coal-fired power generation, cement, non-ferrous metal smelting, waste incineration, etc.) and is used in the production of numerous manufactured products (PVC, medical devices, compact fluorescent lights, batteries, dental fillings, etc.). Its control thus requires complex and widespread measures. This paper provides an overview of the global patent landscape in the area of mercury disposal technology by analyzing relative patents based on Derwent Innovations Index, selected from 1949 to 2018, covering patenting activity related to technologies in removal or recycle mercury from the process in the above-mentioned areas. The most common technologies for each area were identified and their developments were analyzed over time. The 8164 patent families for mercury disposal technology in this study included in total 20,267 individual patent applications, covering 75 priority countries. Information related to the main countries, important applicants, key technologies and development trend were identified. The patent development on mercury disposal technology has been divided into 3 steps: germination period (1949-1968), slow development period (1969-2000) and rapid growth period (2001-2018). Among the geographical distribution of relevant patenting activities, US, Japan, and Germany are the main technique exporting countries while China is the country with the largest number of patent filings; China, US, JP and Canada are the leading countries very active in mercury disposal; the global ranking of TOP10 patent applicants are from Japan (60%), China (20%), US(10%) and Germany (10%), whose patenting activities increased significantly after 2001. The relevant patent families were separated into five major categories: atmosphere mercury removal technology, mercury wastewater treatment technology, Mercury-containing waste disposal technology, mercury recovery technology and mercury-containing soil remediation technology. According to the International Patent Classification based on the technology disclosed in the patent documents, key
technologies are predominantly in (1) Exhaust gas purification technology (B01D53, 63.3%); (2) Mercury extraction technology (C22B43); (3) Solid adsorption separation technology (B01D15). The main technology in B01D53 is mostly activated carbon adsorption.

R.P.3.14

BENEFIT OF ULTRA-LOW TECHNICAL TRANSFORMATION TO THE REDUCTION OF MERCURY EMISSION IN CHINA’S COAL-FIRED POWER PLANT: EVIDENCE FROM FIELD EXPERIMENT

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Ultra-low technical transformation has been carried out in the coal-fired power plants of China to reduce the emission of fine particles, sulfur dioxide and nitrogen oxide. Field measurement, sampling the flue gas at the inlet and outlet of air pollution control devices (APCDs) and the combustion byproducts, are conducted to evaluate the synergetic mercury removal effect of ultra-low technologies. More than 99% mercury in feed coal are released as elemental mercury from furnace. However, approximately 17.0%-81.3% of gaseous elemental mercury are oxidized by chlorine homogeneously or adsorbed by fly ash with decreasing flue gas temperature at the outlet of furnace, where both mercury concentration and speciation are impacted by coal property. Selective catalytic reduction (SCR) catalyst helps to oxidize elemental mercury heterogeneously, leading to elemental mercury accounting for 3.8%-53.0% at the outlet of SCR. Approximately 42.1%-88.4% of total mercury, adsorbed on fly ash, are removed by low-low temperature electrostatic precipitator (LLET-ESP), where the absorbability of fly ash increases in the cooler flue gas. Flue gas desulfurization system removes most of oxidized mercury and particle-bound mercury. The total mercury concentrations in emission flue gas are at the range of 0.56-1.38 μg/m³, which are significantly lower than the emission limits in China. In addition, the mercury removal efficiencies of APCDs are in the range of 89.9%-99.3%, which are comparable with the efficiency of specific mercury removal technologies. Thus, ultra-low emission power plants are proven to show significant benefit in mercury emission reduction, which aids to the implementation of Minamata Convention on Mercury.

R.P.3.15

IMPLEMENTATION OF THE MINAMATA CONVENTION WITH RESPECT TO VINYL CHLORIDE MANUFACTURE IN CHINA: GOVERNMENT STRATEGY AND UNIDO PROJECT STATUS

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China ratified the Minamata Convention on 3st August, 2016. Compliance by China involves specific challenges not faced by other countries, particularly due to one chemical manufacturing process. In most of the world, vinyl chloride monomer (VCM), from which polyvinyl chloride (PVC) plastic is made, is derived from ethylene and chlorine. In China, however, VCM is made by reacting HCl with acetylene derived from coal, catalyzed by mercury chloride (HgCl2). This process was superseded virtually everywhere else in the world by about 1970 as petroleum and natural gas became the dominant feed-stocks for industrial organic chemistry. China, however, continued to require coal as its primary raw material. Today, 59 companies capable of making 15.25 million tons VCM (ca. 40% of global capacity) utilizing the acetylene process are still in operation. The VCM sector has been identified as the most prioritized sector by China to meet the obligation of the Minamata Convention. In 2010, approximately 837 tons of mercury were used in this process, with most becoming waste. Under Minamata, the industry must comply on a number of fronts, most importantly, to reduce the use of mercury by 50% by 2020 vs. the 2010 usage.

To aid with treaty implementation, the United Nations Industrial Development Organization (UNIDO) and Foreign Economic Cooperation Office, Ministry of Ecology and Environment of China (FECO/MEE) jointly developed a project, which was finally funded by the Global Environment Facility (GEF) in 2017. The objective of the project is to reduce risks of mercury on human health and the environment from industrial production of Vinyl Chloride Monomers (VCM) in China, through enhancing the policy and regulatory framework for mercury management in the VCM sector, identifying and replicating Best Available Techniques and Best Environment Practices (BAT/BEPs) to reduce mercury release and emission to the environment from the use of low-concentration mercury catalyst, demonstrating full-scale non-mercury catalysts and processes, creating a Pollution Release and Transfer Registry (PRTR) and greatly increasing recovery of mercury waste including both spent catalyst and process waste, developing strategies for identifying and assessing mercury-contaminated sites associated with VCM production, leading to reduced mercury use by 360 tons. Significant public outreach and awareness-raising with respect to mercury is included as well. This presentation reviews progress to date, including new regulations on the industry in China, status of the substitution of low-mercury catalyst as well as progress made in pilot projects and selection of non-mercury catalysts and processes.

R.P.3.16

MIGRATION AND TRANSFORMATION CHARACTERISTICS OF MERCURY IN A 600MW COAL-FIRED POWER PLANT WITH ULTRA LOW EMISSION AIR POLLUTION CONTROL DEVICES

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Coal-fired power plants (CFPPs) is an important source of atmospheric mercury in China. Understanding the emission and transformation of Hg across different air pollution control devices (APCDs) is significant to improve the ability of different devices in mercury removal. In this study, the form and amount of mercury at the inlet and outlet of different devices (SCR, ESP, WFGD) in an ultra-low emission coal-fired power plant was investigated. SEM, XPS and TPDD were used to analyze the mercury species. As measured by the Ontario Hydro method (OHM), mass balance rate of Hg for each device is acceptable, ranging from 76% to 122%. Total mercury was found to be 10.47 μg/m³ at the inlet of SCR, with elemental mercury, oxidized mercury and particle-bound mercury accounting for 64.2%, 24.8% and 11.0%, respectively. 43.9% of elemental mercury was converted to valence state mercury in the utilization of solid by-products.

Poster abstracts
R.P.3.18

EFFECTS OF LOW TEMPERATURE ECONOMIZER AND AIR POLLUTION CONTROL DEVICES ON MERCURY REMOVAL IN COAL-FIRED POWER PLANTS

ZHOU, Zijian; LIU, Xiaowei; XU, Minghou (1)Huazhong University of Science & Technology

Coal-fired power plants are the main sources of anthropogenic mercury emission. In the coal-fired flue gas, elemental mercury (Hg0) is difficult to be controlled due to its high volatility and low solubility. It has been reported that transforming the Hg0 to the soluble oxidized mercury (Hg2+) or/and particulate-bound mercury (HgP) is an effective way to remove the mercury in the coal-fired flue gas, because the Hg2+ and HgP could be easily removed by the wet flue gas desulfurization (WFGD) and the dust removal devices. Therefore, the understanding of mercury transformation process is crucial. In the present study, the impacts of a low temperature economizer (LTE) on the mercury removal across an electrostatic precipitator (ESP) and influence of load variation on mercury conversion over selective catalytic reduction (SCR) catalysts were determined for two coal-fired boilers. Mercury concentrations and speciation in the flue gas were measured by the continuous emission monitoring (CEM) method. When the LTE was on, the removal efficiency of the total and elemental mercury increased by 45% and 20%, respectively, due to the improvement of adsorption and oxidation capacity of the fly ash at lower temperatures. The Hg speciation in the flue gas at the inlet and outlet of the SCR system were analyzed, and the impacts of load variation and catalyst aging on the Hg0 conversion were discussed. The variable loads resulted in simultaneous changes of the gas hourly space velocity, the ambient temperature, and the oxygen content. The results showed that the load rate was a significant factor for Hg0 conversion by the SCR catalysts in the actual condition. In particular, load reduction benefitted the Hg0 conversion. When the load rates were 100%, 75% and 60%, the Hg0 conversion efficiency were 52%, 66% and 72%, respectively. Another finding was that Hg0 conversion was more significantly affected by the catalyst aging than NOx reduction. The efficiency of Hg0 conversion by the SCR catalysts decreased to 4% after 35000 h when tested at the 100% load rate. Among the three discussed factors, the most important one influencing mercy conversion across the SCR catalysts is the flue gas temperature based on the grey relational analysis. In the realistic power plant, the variable range of the factors should be considered as well.

R.P.3.20

EXPERIMENTAL STUDY ON MERCURY REMOVAL AND REGENERATION OF SO2 MODIFIED ACTIVATED CARBON

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Gas-phase elemental mercury removal by activated carbon impregnated with SO2 was studied under simulated flue gas conditions. Brunauer-Emmett-Teller (BET) measurements and X-ray photoelectron spectroscopy (XPS) were used to compare the physicochemical characteristics of original activated carbon with the modified samples. Despite the fact that activated carbon was impacted by the modified temperature, its specific surface area declined, and the pore structure of the carbonyl groups improved mercury removal by 46.16%. In addition, the easier group increased by 59.85% in the oxygen-containing functional group. The formation of sulfur-containing functional group was beneficial to the improvement of mercury removal ability. The effects of different sulfur-containing compounds on the performance of mercury removal were further studied. The results showed that the mercury removal performance of activated carbon with sodium sulfide, elemental sulfur and sodium thiosulfate is better than that of sodium sulfite and sodium sulfate. The inactivated sample was impregnated with SO2 for sulfur-carrying thermal regeneration, and its mercury removal performance was compared before and after regeneration. The average efficiencies of the three regeneration cycles were 89.71%, 85.48% and 79.92%. It is feasible to regenerate modified activated carbon by sulfur-loading thermal regeneration, and this study demonstrates has great potential for industrial application prospect.

R.P.3.19

DENSITY FUNCTION THEORY STUDIES OF MODELING MN-V2O5-WO3/TIO2 SCR CATALYST IN LOW-TEMPERATURE FLUE GAS UNDER HGOXIDATION

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Fundamentally, due to significantly reduce sulfur dioxide poisoning and fly ash mechanical wear, low-temperature selective catalytic reduction (SCR) denitration technology has attracted much attention worldwide which can regulate NOx emissions and facilitate Hg0 conversion to Hg2+. In our group previous experimental study, Mn-V2O5-WO3/TiO2 catalyst yielded nearly 100% Hg0 oxidation to Hg2+ in the low-temperature windows 1203 - 2803. Density function theory (DFT) calculation was performed to modeling Mn-V2O5-WO3/TiO2 SCR catalyst. electron wave function was based on plane-wave super soft pseudopotential method using the Vienna ab initio simulation package (VAPW) code. The Perdew-Burke-Emzerhof functional (PBE) within generalized gradient approximation plus Hubbard model (GGA+U, U = 4.2eV for Ti, 3.0 eV for V and 4.5eV for Mn) was used to calculated exchange-correlation functional. A four-layer (001) TiO2-anatase (4×4) was modeled as support, dimer V2O5 and WO3 were loaded on the surface respectively and Mn was doped in the TiO2 structure. The Monkhorst-pack k points mesh which was used for the Brillouin zone sampling were set as 2×2×1 for (001) TiO2 surface slabs. A specified plane–wave cutoff energy of 500eV was used in all cases. After calculation, the bond distance of V=O (single coordinated oxygen), V-O-V (bridge oxygen), V-O-Ti (anchor oxygen) were 1.62Å, 1.81Å, 1.79Å and 1.94Å respectively, which has been a reasonable agreement with previous DFT studies. The adsorption energy order on V=O active site is HgCl > Hg > HCl. In addition, the adsorption energy and projected density of states (PDOS) shows that W and Mn promoted adsorption energy of Hg and HgCl in the nearby V=O sites.

R.P.3.21

CAN CO-FIRING OF BIOMASS TO COAL-FIRED POWER STATIONS REDUCE GLOBAL HGO EMISSIONS?

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Globally, 24% of annual mercury (Hg) emissions stem from coal, where the metal is present in sub-ppm concentrations. During coal combustion, all coal Hg is reduced to elemental Hg0, independent of its previous speciation. In the post-combustion environment, flue gas chemistry may lead to the oxidation of Hg0 and the formation of particulate Hgp through sorption onto reactive surfaces such as fly ash. Both HgL and Hgp have been shown to have higher retention rates in conventional flue gas clean-up systems, thus a lower chance of being emitted through the stack. The main influences on Hg speciation within coal-fired power plants (CFPP) have been suggested to be flue gas temperature, presence and speciation of chloride, sulfur and unburnt fly ash carbon. The co-firing of certain biomass to CFPPs has been suggested as a low-capital investment option of reducing CO2, NOx and SOx emissions, while utilizing types of biomass or biomass residues that may be regionally abundant. Some research has also shown that there may be an additional co-benefit to this technique: The forma-
Coal consumption is one of the main anthropogenic atmospheric mercury (AM) emissions sources. In 2017, China’s coal consumption accounted for 50.7% of the world’s total coal consumption, with half was used for power generation. The control of the AM emissions from coal-fired China’s power plants is therefore of great significance for China and the world. As one of the signatories of the Minamata Convention on Mercury, China promulgated the “emission standard of air pollutants for thermal power plants” in 2011. This is the first time, in China, that the emission of mercury and its compounds (MC) in the flue gas of coal-fired power plants is limited to be less than 0.03 mg/m³. Besides, in order to promote the utilization of clean coal usage, the “ultra-low emission” policy of coal-fired power plants has been implemented since December 2015. It requires that, under the condition of 6% of reference oxygen content, the emission concentrations of PM, SO2 and NOx should be less than 10, 35, and 50 mg/m³, respectively. This tightened the previous standards in 2011, by 67%, 65%, and 50%, respectively. It is reported that, by the end of 2018, 80% of the total coal power capacity of China (equals to 0.81 billion kilowatts coal-fired power units) has achieved “ultra-low emission” standards.

The results indicated that, on one hand, CeO2 significantly improved NO conversion at low temperature and slightly increased N2 selectivity at high reaction temperature. On the other hand, CeO2 modification apparently enhanced Hg0 oxidation. The optimal reaction temperatures for SCR and Hg0 oxidation are well matched (250 ~400 °C). Hg-TPD results suggest that Hg0 can be oxidized to Hg(NO3)2 but that it was hard to desorb from the catalyst, leading to the blockage of active sites. The result of HCl transient experiment confirmed that HCl facilitated the desorption of adsorbed Hg(NO3)2, which enabled the recovery of active sites. The aforementioned result provide a new sight into the promotional effect of HCl on Hg0 oxidation, which has not been reported before. An innovative nitrate pathway for Hg0 oxidation was proposed in this work. In situ FTIR experiments indicated that NO can strongly adsorb and generate more nitrite species on a V1CeTi catalyst, with bidentate nitrate species playing an important role in Hg0 oxidation. The proposed nitrate pathway in this work provided a new design and modification strategy for catalysts used for simultaneous removal of NO and Hg0.
DUAL ROLES OF NANO-SULFIDE IN EFFICIENT REMOVAL OF ELEMENTAL MERCURY FROM COAL COMBUSTION FLUE GAS WITHIN A WIDE TEMPERATURE RANGE

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Nanostructured zinc sulfide (Nano-ZnS) has been demonstrated to be an efficient adsorbent for removal of elemental mercury (Hg0). However, the Hg0 removal performance deteriorates once the flue gas temperature deviates from the optimal temperature of 180 °C. In this study, ultraviolet (UV) light, which is generally generated through corona discharge in electrostatic precipitators (ESP), was adopted to enhance Hg0 removal by Nano-ZnS. With the UV irradiation, Nano-ZnS exhibited excellent performance in Hg0 removal within a much wider temperature range from room temperature to 240 °C. A Hg0 removal efficiency of 99% was achieved at 60 °C even under extremely adverse conditions, i.e. gas flow with an extremely high gas hourly space velocity but without hydrogen chloride. At low temperatures, Hg0 was mainly oxidized by superoxide radicals (O2-) and hydroxyl radicals (OH) generated by UV photostimulation to form mercuric oxide (HgO). At high temperatures, most Hg0 was immobilized as mercuric sulfide (HgS), as both the enhanced chemisorption and the accelerated transformation of HgO to HgS facilitated the formation of HgS. Compared with commercial activated carbon, injection of Nano-ZnS can utilize the UV in ESPs to warrant a higher Hg0 removal efficiency within a much wider temperature range.

EFFECT OF SELENIUM ON MERCURY ADSORPTION OVER ACTIVATED CARBONS IN COAL COMBUSTION FLUE GAS

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Mercury pollution is one of the greatest environmental threats besetting human beings. Considering that coal combustion has become the largest anthropogenic source of mercury, it is imminent to control mercury emission from the coal combustion. Activated carbons (AC) have been widely used for the mercury uptake from coal combustion flue gas. The mercury adsorption capacity of active carbon is highly influenced by the flue gas components. The effect of normal flue gas components such as SO2, NOx, HCl have been widely studied. However, as one of the most volatile trace elements of environmental concern present in coal, there is little study on the effect of selenium on mercury adsorption over AC. In this work, Density functional theory calculations were performed to investigate the interaction between mercury and selenium over AC. Firstly, the adsorption energies, Mulliken bond population and total atomic charges of Se atoms on AC was calculated. Se was found to be strongly adsorbed on the AC surfaces. The adsorption of Se atoms would decrease the mercury adsorption capacity since they compete for the active sites on the AC surface. Secondly, the electrostatic potential of Se-loaded AC and AC was compared, and the results provided further evidence that the reactive sites for mercury adsorption were occupied by Se atoms. More importantly, the adsorbed Se on AC surface decreased the activity of its neighbor sites for Hg0 adsorption. The results of this study would cause the researchers pay more attention on the negative effects of selenium, and find more economic and effective method for mercury control in coal combustion flue gas.
Mercury species potentially present in crude oil will be described including the effect of mercury speciation on mercury removal technology selection.

Processes to remove mercury from crude oil and condensate will be described. The successful application of the MERCAYWAY process in the Oil and Gas industry will be described. MERCAYWAY is a process that uses a chemical addition to convert mercury into filterable species. In one application, >98% of the mercury was removed to produce a condensate with <5 ppb Hg. MERCAYWAY process technology is a straightforward and commercially proven process for reducing mercury (Hg) content in crude oil and condensate using easily understood chemistry and well-proven unit operations.

Research and development of new additives to enhance mercury removal will also be presented. New research is allowing us to develop MERCAYWAY additives that may increase removal with faster kinetics.

**R.P.3.29**

**SUBCELLULAR DISTRIBUTION OF MERCURY IN THE MACROPHYTE ELEOCHARIS INTERSTINCTA PLANTED IN A VERTICAL WETLAND: A MICROOSM EXPERIMENT**

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Artisanal gold mining operations in Colombia have been generated severe impacts on several ecosystems where significant amounts of mercury (Hg) were released. The aquatic Eleocharis interstincta macrophyte can be found in different areas impacted by gold mining activities. The aim of the present work was to evaluate the accumulation and subcellular distribution of Hg in the root and aerial parts of the macrophyte planted in vertical wetlands. The system was supplied with river water enriched with nutrients and Hg at a concentration of 0.1 mg/L (Hg-1) and 1.0 mg/L (Hg-10). Experiments were conducted in a mesh house located in the central campus of the University of Córdoba – Colombia. The constructed wetlands operated at a time of residence of 5 days, during 2 months. Subcellular fractionation (cell wall, fraction I; cytoplasmic organelles, fraction II and cytosol, fraction III) was performed according to the differential centrifugation technique in the fresh tissues of the roots and aerial biomass of the macrophyte E. interstincta in a mixture of 0.5 mM of sucrose, 50 mM of Tris-Maleate, 1 mM of magnesium chloride and 10 mM of L-cysteine. The removal achieved by the constructed wetland systems in all treatments were over 99%. In order to calculate the accumulation of metals in different plant tissues, translocation (TF) and bioconcentration (BCF) factors were calculated. The BCF results were much higher than 1 in all cases while the TF were less than 1 regardless of the concentration in the medium. With respect the subcellular fractionation, a large proportion (78%) of Hg-I accumulated in fraction II of the leaf was found, whereas a large accumulation (77%) in fraction I in the root was found. For Hg-10, the highest accumulation (57%) occurred in the fraction II of the leaf, while the highest proportion (70%) occurred in the fraction I in the root. Finally, it should be highlighted that decrease values in the chlorophyll content as well as an inhibition in the growth of aerial and radicular tissue of the plant suggest that Hg exposure impact negatively in the normal development of the macrophyte.

**R.P.3.30**

**REHABILITATING MERCURY CONTAMINATED MINING LANDS IN COLOMBIA USING BIOCHAR**

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Increasing extraction of natural resources such as gold in Colombia is driving economic growth, while at the same time causing pollution of soil, water and increased risks to human health. Artisanal mining accounts for 70% of the gold mined in Colombia. Two affected areas in Colombia, Segovia and Tado, were selected to develop this project. The principal objective of this study was to develop a strategy to reuse contaminated sites with mercury based on the use of biochar as low input “gentle remediation” option in a lab scale. UK based lab scale testing of mercury immobilisation was carried out on superficial soil samples. Each of the samples were assessed for total and leachable mercury concentrations using UK standard procedures. Subsequently samples with highest concentrations of mercury were extracted using a sequential extraction procedure to determine if the mercury was (a) water soluble, (b) stomach acid soluble (c) bound to organic matter, (d) in an elementary form or (e) present as mercury sulphide. Finally, each sample was treated using different amendment of biochar in order to find the most effective immobilization of contaminants present. A Segovia sample used to test treatment with biochar (provided by C-Cure-CCA), showed elevated concentrations of mercury (361 mg/kg) and highest leachable Hg concentration (383 µg/kg). Sequential analyses showed that Segovia sample contained no organic-matter bound mercury or methyl mercury, but did contain 812 µg/kg of water soluble and 2755 µg/kg of human stomach acid soluble mercury. Treatment with biochar at an amendment rate of 5% (w/w) resulted in all of the water soluble and human stomach acid soluble mercury being stabilised in the soil. A further test aimed at quantifying the minimum amount of biochar that was needed to bind all the water soluble and stomach acid soluble mercury showed that an amendment rate of 0.5% (w/w) reduced the concentration of water soluble mercury by 80%, while a 1% amendment rate resulted in the complete elimination of water soluble mercury. To remove all stomach acid soluble mercury an amendment rate of 5% was needed while an amendment rate of 3% (w/w) eliminated 95% of all the stomach acid soluble mercury from the soil. The results indicated that the use of biochar as a low impact remediation technique was very effective in the immobilization of mercury. Providing stable risk mitigation in the sites we can facilitate re-use of the affected land for multiple purposes.

**R.P.3.31**

**EFFECT OF SORBENTS ON MERCURY METHYLATION AND METHYLMERCURY REMOVAL FROM WATER**

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We measured methylmercury (MeHg) production by Desulfovibrio desulfuricans ND132 when presented with inorganic Hg (Hgl) or a Hg-disolved organic matter (DOM) complex that had been pre-equilibrated with one of four commercially available sorbents (BioChar (BC), ThiolsAMMS™ (TS), SediMits (SM), and OrganoclayTM PM-199 (OC-199)). The sorbents provided little, if any, inhibition of total MeHg production, but decreased MeHg passing a 0.2 µm filter. Total MeHg produced was substantially greater than the initial equilibrium aqueous Hgl implying sorbed Hgl was bioaccessible over the 24-h methylation timeframe. MeHg production increased when Hgl was introduced as a Hg:DOM complex. Some of the increased MeHg production is attributed to lower Hgi sorption with DOM, but a substantial amount of sorbed Hgl must have been accessible. DOM increased the filter-passing MeHg fraction, stressing the importance of Hg:DOM and MeHg:DOM inter-
actions in experimental investigations. Sulfate concentrations did not affect Hg(II) methylation and could not explain the increased methylation seen with the Hg-DOM complex. Extended equilibration of Hg-sorbent mixtures for up to 1 year before the methylation assays did not affect the amount of MeHg produced for BC or SM treatments, but significantly lowered MeHg production for TS. The inclusion of DOM in these experiments presented the sorbents with a more environmentally relevant form of Hg and lowered sorbent effectiveness to decrease MeHg production and sorb the produced MeHg.

In a second phase of this work, methylmercury (MeHg) sorption isothersms were determined for the same four sorbents in the absence and presence of DOM. In the absence of DOM, MeHg sorption onto BC, TS, and SM was comparable and substantially greater than OC-199. DOM-sorbent interactions controlled MeHg-DOM sorption. DOM decreased MeHg sorption onto BC and SM, slightly increased MeHg sorption onto OC-199, and had no discernible effect for TS. Overall, TS showed the greatest MeHg sorption with no apparent saturation over a very broad concentration range. Using East Fork Poplar Creek in Tennessee, USA, we developed a relationship between MeHg sorption onto OC-199, and had no discernible effect for TS.

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**DIFFUSIVE GRADIENT IN THIN FILM (DGT) SAMPLERS AS A BIOMONITORING TOOL FOR Hg BIOACCUMULATION IN FRESHWATER WETLANDS**

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Mercury (Hg) contamination is an ongoing issue globally and monitoring of contaminated sites is an important and often costly task. Traditional site assessment involving Hg and methylmercury (MeHg) measurements in soil and water samples provides insight into bulk concentrations, but conditions unique to each site render may much of the measured Hg unavailable for bioaccumulation. This greatly changes the impact of sites with similar bulk concentrations on human and environmental health. Diffusive gradient in thin film (DGT) have previously been shown to be a promising tool for estimating the bioavailable fraction of Hg, but have not been used previously as a means to quantitatively predict bioaccumulation. Here, we assess the viability of using samplers deployed in the water column to predict bioavailable Hg in the water column and subsequent accumulation in freshwater wetland biota. Mesocosm wetlands were dosed with four isotopically labeled Hg endmembers designed to span a gradient of MeHg production (dissolved Hg2+, nanoparticulate Hg, humic-acid bound Hg, and Hg bound to iron sulfide particulate). DGTs were then deployed in the water column at regular time intervals for a three-month period and accumulation of MeHg and TotHg over a one-week period were measured. During this time period plants, biofilms, snails, and mosquito fish were retrieved from the mesocosms and assessed for MeHg accumulation. Linear regressions were utilized to assess the correlation between endmember accumulation on DGTs and bioaccumulation in the biota previously listed. MeHg and TotHg accumulation on DGTs were both found to be good predictors of variance in MeHg concentrations in biota. Bioaccumulation factors were then calculated based on these data and used to predict bioaccumulation of Hg in the organisms based on DGT accumulation one year after dosing. The results of this research indicate that DGTs deployed in the water column may be a useful biomonitoring tool for mercury bioaccumulation in freshwater wetlands.

**NOVEL FE-ZSM-5 CATALYST FOR CATALYTIC OXIDATION OF ELEMENTAL MERCURY IN THE PRESENCE OF NH3**

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Catalytic oxidation of elemental mercury (Hg0) by SCR catalysts has received considerable attention over the past decade. However, ammonia (NH3) sprayed in NH3-SCR process has a significant inhibitory effect on the oxidation of Hg0. Therefore, the NH3 resistance was very important for SCR catalysts. In this work, iron-based Fe-ZSM-5 catalysts were synthesized by liquid ion exchange method with an alkaline treatment and prepared at pH value of 2 and 4 (denoted as Fe-2, Fe-4). Reaction conditions for Hg0 oxidation was as follows: 50 mg samples, 10 ppm HCl, 50 ppm NH3 (when used), Hg0 112 μg/m3. 5% O2, N2 as balance, total flow rate 500 ml/min, GHSV 640000 h-1. The results showed that excellent Hg0 oxidation activity was obtained over the Fe-4 and Fe-2 catalysts. The Hg0 removal efficiency reached nearly 100% over both Fe-2 and Fe-4 at 100 cC-400 cC. Meanwhile, the Hg0 removal efficiency in the presence of NH3 over Fe-4 could reach almost 100% at 150-400 cC. However, the Hg0 removal efficiency in the presence of NH3 over Fe-2 increased to 93.8% at 200 cC, and decreased above 300 cC. It indicated that Fe-4 showed much better NH3 resistance than that of Fe-2.
To elucidate the mechanism, NH3-TPD of catalysts was performed. The desorption peak at 100-300 °C could be ascribed to weak acid desorption. Fe-2 and Fe-4 exhibited weak acid desorption peak at 195 °C with 217 ppm and 180 °C with 285 ppm, respectively. Previous studies found the competitive adsorption of HgO and NH3 on weak acid sites was slight. Hence, we predicted that the large amount of weak acid sites of Fe-4 benefited Hg0 removal and further promoted Hg0 removal in the presence of NH3.

According to UV-vis DR spectroscopy, more Fe2O3 nanoparticles appeared might be one of the factors for its stronger NH3 resistance over Fe-4. The O 1s XPS result indicated that Fe-2 and Fe-4 exhibited the same peaks at 532.7 eV which could be assigned to chemisorbed oxygen. Noticeably, Fe-4 showed another obvious peak at 530.3 eV which could be assigned to chemisorbed oxygen. The O 1s XPS result indicated that Fe-2 and Fe-4 exhibited the same peaks at 532.7 eV which could be assigned to chemisorbed oxygen. The O 1s XPS result indicated that Fe-2 and Fe-4 exhibited the same peaks at 532.7 eV which could be assigned to chemisorbed oxygen.

In conclusion, abundant weak acid sites, plenty of Fe2O3 nanoparticles and lattice oxygen might contribute to the superior Hg0 oxidation performance over novel Fe-ZSM-5 catalyst in the presence of NH3.

**R.P.3.35**

**REMOVAL AND REDUCTION OF MERCURY IN GROUNDWATER BY PUMICE-SUPPORTED NANOSCALE ZEROVALENT IRON: EFFECTS OF DISSOLVED OXYGEN, NITRATE AND NATURAL ORGANIC MATTER**

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Pumice-supported nanoscale zerovalent iron (p-nZVI) was synthesized and tested for Hg(II) removal and reduction in aqueous phase with varying concentrations of dissolved oxygen (DO), nitrate, and natural organic matter (NOM). After the Hg(II) removal reaction inoxic solution, p-nZVI core-shell structure was collapsed and thick ferric layer was observed on the surface, while in anoxic solution, magnetite layer was found on the surface and nZVI wasoe present in chaine-like structure. These surface characteristics were related to the Hg(II) sorption capacity of 6.1 mg g-1 and 1.5 mg g-1, and headspace Hg(0) concentration of 18 and 37 nmol m-3 in the anoxic and anoxic suspensions, respectively. The Freundlich isotherm model fits better than Langmuir model to the experimental data, implying that Hg is adsorbed on the p-nZVI surface in a multilayer adsorption manner with irregular energy distributions. The removal of Hg(II) in anoxic suspensions was not affected by nitrate levels ranging from 0.08 to 8 mM. In contrast, Hg(0) concentration in headspace increased with an increase of nitrate, which was related to the enhanced Fe(II) dissolution under high nitrate concentration. In the presence of 100 mg L-1 Suwannee River NOM, Hg(II) removal rate decreased from 89 to 36%, due to surface passivation of nZVI by NOM. On the contrary, addition of 100 μM of glutathione to the mixture of Hg(II) and p-nZVI increased Hg(II) removal efficiency from 85 to 96%, attributable to the formation and removal of Hg(II)-GSH complex by ferric (i.e., lepidocrocite) surface. The experimental results of this study suggest that the presence of DO and bulk NOM could significantly increase and decrease, respectively, the Hg(III) removal efficiency during the remediation process of groundwater using nZVI techniques.

**R.P.3.36**

**EXPERIMENTAL AND THEORETICAL STUDIES OF MERCURY REMOVAL BY ZNIN2S4 SORBENTS FROM FLUE GAS**

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Abstract: Sorbent injection has been regarded as an effective and environment-friendly technology for mercury emission control. The widely practical application of the sorbent injection technology depends upon the development of effective sorbents. In this work, ternary sulfides ZnIn2S4 microspheres were synthesized using a combined solvothermal/hydrothermal method, and for the first time used to capture elemental mercury from coal-fired flue gas because of its extensive active sulfur sites with high affinity to mercury species. The synthesized sorbents were characterized by BET surface area, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The impacts of different flue gas components on mercury removal were investigated. Moreover, quantum chemistry calculations based on density functional theory (DFT) were conducted to investigate the microcosmic adsorption mechanism of Hg0 over ZnIn2S4 surface. Experimental results indicate that ZnIn2S4 performs well in Hg0 capture from flue gas and shows 95% mercury removal efficiency in the temperature window of 50-150 °C. The excellent mercury adsorption performance of ZnIn2S4 is insensitive to water vapor and sulfur dioxide. ZnIn2S4 sorbents exhibit far greater Hg0 adsorption capacity than the commercial brominated activated carbon manufactured specifically for Hg0 removal from power plants. In addition, XPS and temperature programmed decomposition desorption (TPPD) results suggest that the adsorbed mercury mainly exists in the form of HgS on the sorbent surface. The theoretical calculation results indicate that chemisorption mechanism is responsible for Hg0 adsorption on ZnIn2S4 surface. Hg0 is first adsorbed on surface Zn atom and subsequently reacts with S atom to form HgS molecule. This is consistent with the abovementioned XPS and TPPD results. The reaction pathway leading to the formation of HgS is a two-step process: Hg0 → Hg(adls) → HgS(adls). Electron density difference analysis implies that the significant charge accumulation around sulfur atom of adsorbed HgS molecule is closely associated with the strong interaction between HgS and ZnIn2S4 surface.

**R.P.3.37**

**ASSESSING THE IMPACT OF ACTIVATED CARBON AMENDMENT AND TIDAL INUNDATION ON MERCURY AND METHYLMERCURY PARTITIONING IN CONTAMINATED MARSH SOILS: A MESOCOSM STUDY**

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Field trials and laboratory experiments have shown that activated carbon (AC) amendments to contaminated marsh soils/sediments increase the partitioning of mercury (Hg) and (MeHg) to the solid phase, decreasing porewater Hg and MeHg concentrations and bioaccumulation in benthic organisms. However, more data are needed to determine which environmental parameters influence AC efficacy. With this study, we used field mesocosms to investigate the effectiveness of AC as an in situ amendment in Hg and MeHg-contaminated Phragmites marsh soil from the Berry’s Creek wetland in New Jersey, USA. The objectives of this study were to: (1) assess the impact of AC on MeHg and Hg concentrations in porewater; (2) to evaluate the impact of tidal elevation on the efficacy of the AC amendment; and (3) to determine the impact of AC on Hg and MeHg partitioning into the solid phase. The marsh mesocosms were constructed from capped, PVC pipes and set at two different elevations in a tidal creek. Three types of treatments were constructed: Control, 5% dw AC-amended, and 9% dw AC+MnO2-amended. The MnO2 was added to poise redox potential at manganese reduction, with the aim of reducing the population of Hg-methylation bacteria. Mesocosm porewater was monitored over four months. Sediment cores were taken at the conclusion of the experiment. The 9% AC+MnO2 treatment decreased porewater Hg by ~85% and MeHg ~75% relative to controls, while the 5% AC treatment decreased Hg by ~40% and MeHg by ~25%. Mesocosm elevation significantly impacted redox chemistry in porewater and soil, but no significant dif-
ference was seen in Hg and MeHg porewater concentrations. Both the 5% AC and 9% AC+MnO2 treatments significantly increased Hg and MeHg partitioning to marsh soils, and both amendments significantly increased soil MeHg concentration. These results will contribute to an empirical model predicting the effectiveness of AC for Hg and MeHg remediation across different aquatic ecosystems.

R.P.3.38

IN SITU DECORATED COPPER FOAM WITH COPPER SELENIDE AS A 3D MONOLITH MATERIAL FOR EFFICIENT SEQUESTRATION OF MERCURY

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Abatement of elemental mercury (Hg0) emission from coal-fired power plants remains a serious task for public health and environmental societies. In this work, we successfully in situ decorated copper foam with copper selenide (CuSe/Cu) as a 3D monolith material for mercury removal via a simple heating-stirring method. The Hg0 adsorption performance of CuSe/Cu under different conditions were studied. The involved mechanism for Hg0 adsorption were proposed. The results show that nearly 100% of Hg0 adsorption efficiency was obtained over the CuSe/Cu under a high gas hourly space velocity (GHSV) of 7.0×10^5 h⁻¹. The Hg0 adsorption efficiency of CuSe/Cu maintained above 90% in a wide temperature range of 40-140 °C. The CuSe/Cu exhibited an excellent Hg0 adsorption stability under simulated flue gas atmosphere containing SO2, NO, and H2O. This could fully demonstrate the strong adsorption of CuSe/Cu in different operation conditions. The remarkable performance of CuSe/Cu for Hg0 immobilization was primarily attributed to the high affinity towards Hg0 resulted from the intrinsic layered structure of CuSe. This work provides a new insight for efficient Hg0 sequestration from coal-fired power plants.

R.P.3.40

IS IT POSSIBLE TO CULTIVATE ENERGY CROP ON SOIL EXTREMELY CONTAMINATED WITH MERCURY? A PLOT EXPERIMENT PRELIMINARY RESULTS

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Mercury and its compounds in the environment are the existing threat worldwide, due to high toxicity and harmful effect on the living organisms. Soil mercury contamination is estimated to about 90% of the total mercury stored in whole terrestrial ecosystem, while more than 80% of soil Hg contamination results from anthropogenic sources. The deposition of mercury in soil is mostly related to fossil fuel combustion, smelting as well as to operation of chlor-alkali plants on regional scale. Many remediation technologies for Hg contaminated soils were recently developed, however most of them are very cost consuming, due to ex situ remediation and/or application of expensive reagents. Aided phytostabilisation may offer a cheap solution which will at least counteract of spreading this contaminant further.

The goal of the presented study was to assess possibilities of energy grass Miscanthus growth on soil extremely polluted with mercury, combined with aided phytostabilisation. Soil for the experiment was collected from the former chemical plant in Poland, where mercury and its compounds were used in manufacturing processes. Total soil mercury concentration exceed 6000 mg kg⁻¹, while concentration of mercury bioavailable form was about 100 mg kg⁻¹. Fully randomized experiment was conducted in the plastic pots with volume of 7dm³. Half of the pots were amended with 0.5% w/w granular sulphur, watered and left for Hg stabilization for 4 weeks. Pots were planted with novel Miscanthus seed based hybrids. All experimental variants were performed in triplicate, using standard garden soil as a control variant. After 4 months plants were harvested and analyzed among other for biomass production as well as mercury concentration. Soil samples were also collected and analyzed for total and bioavailable mercury form concentration after soil stabilization and at the end of the experiment.

Granular sulphur addition to the soil decreased significantly concentration of mercury bioavailable form, however effect of this practices was not visible in Miscanthus growth parameters, biomass production and Hg concentration in the shoots. Plant biomass production was severely limited, irrespectively from experimental variant and several time lower when compared to the plants cultivated on garden soil. It could be concluded that turning mercury extremely contaminated land into economically valuable seems to be unrealistic approach so far. Activities should be concentrated on decreasing of mercury bioavailability in the soil and creating dense plant cover to avoid its evaporation to the atmosphere.

R.P.3.41

IMMobilization of mercury in contaminated sediMent: an active capping demonstration in hyeOnsan river estuary, south korea

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The effectiveness of in situ sediment capping as a tool for mercury and heavy metal risk mitigation in Hyeongsan River estuary, South Korea was studied. Sites in the estuary were found previously to show moderate to high levels of contamination of different heavy metals and mercury. A 400 m x 50 m plot area was selected for the capping demonstration, where the total area was divided into 4 sections capped with different combinations of capping materials (zeolite, AC/zeolite, AC/sand, zeolite/sand). Pore water concentrations in the different sites were studied in-situ using diffusive gradient in thin film (DGT) probes. All capping amendments showed reduction in the pore water concentration of the mercury with top 5 cm showing ≥90% reduction greater than 90% for some heavy metals. For two-layered cap with AC, order of placement should be considered since AC can easily be displaced due to its relatively low density. Investigation of MeHg in the site showed that MeHg and %MeHg in pore water corresponds well to maxima for pore water sulfide, Fe and Mn suggesting mercury methylation as probably coupled with sulfate, Fe and Mn reduction in sediments. Our results showed that thin-layer capping of active sorbents such as AC and zeolite, in combination with sand caps, can be an effective remediation strategy for sediments contaminated with mercury and heavy metals.

R.P.3.42

MERCURY MOBILIZATION FROM CONTAMINATED CREEK BANK SOILS AND STABILIZATION USING ENGINEERED SORBENTS

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As a global environmental pollutant, mercury (Hg), threatens our water resources and presents a substantial risk to human health. The goal of this research project was to evaluate the immobilization of Hg on sorbents to reduce ambient Hg concentrations in water leaching from con-
taminated East Fork Poplar Creek (EFPC) (Oak Ridge, TN, USA) soils. Using flow-through columns, we determined the potential of different kinds of engineered sorbents (i.e., ThiolSAMMS®, biocar, SedimentTM, OrganoclayTM PM199) to reduce mercury fluxes from contaminated EFPC soils. The effectiveness of the sorbents in this experiment was determined based on the rate of Hg sorbed and the percentage of Hg removed as compared with the amount of Hg applied; i.e., a mass balance. All the sorbents removed Hg to a certain extent, but none of the sorbents was able to remove 100% of the Hg to which they were exposed. From all the evaluated sorbents, ThiolSAMMS® showed the highest percentage of Hg removed (~87%). A non-reactive Br- [bromide] tracer experiment was conducted to determine the hydraulic properties of the sorbent columns and to ensure that no flow along the walls or preferential flow occurred. Br- was also applied to qualitatively determine how quickly Hg breaks through the sorbent columns, most of the sorbents had a Hg breakthrough within the first 3 pore volume (PV). ThiolSAMMS® was the only sorbent to have retardation on the Hg breakthrough (7 and 70 PV). To determine mechanisms for the Hg uptake by the sorbents, we conducted a set of analyses to identify changes in concentrations of chemical constituents entering and exiting the sorbent columns. We noticed no difference in pH, anions (Cli [chloride], SO4 [sulfate], NO3 [nitrates]) or metals (Al [aluminum], Fe [iron], Mn [manganese] and Sl [silica]). We also observed that the concentrations of dissolved organic carbon (DOC) were statistically different for biochar and OrganoclayTM PM199. Specific UV absorbance (SUVA) showed statistically significant differences for biochar. The differences in DOC and SUVA were minimal, overall, suggesting that the mechanism for Hg uptake remains unknown.

R.P.3.43

TECHNICAL ASSESSMENT OF A SMALL Hg-FREE GOLD PROCESSING PLANT IN COLOMBIA.

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In Colombia 23% of the 1,122 municipalities have traditional artisanal gold mining (AGM). In 2016, the country’s gold production reached 61.8 tonnes of which 87% was produced by approximately 200,000 artisanal miners. In 2017, production declined to 41 tonnes thanks to the implementation of Law 1658 (2013) and the resulting measures taken by the Colombian government to prevent mercury use in AGM. However, artisanal mining is still responsible for 50% of Au production. The reported official Hg import of 2014 was 127 tonnes, 133 in 2015, 119 in 2016 and only 4.6 tonnes in 2017. Formal and informal artisanal miners still use amalgamation as the main gold extraction process. Comunica, a project led by Agriteam Canada Consulting Ltd., is currently implementing an Hg-free plant for 100 “chattareras” (women who process gold tailings and waste rocks) in San Roque, Antioquia. The current mercury release in the project region is approximately 115 kg/a. A lab study was conducted with a 33 kg sample of tailings from the area, with 17.7 g Au/t (ppm) and 105.7 g Ag/t and 80% of the mass below 68.27 mm; nearly 97% of the gold was fine, below 200 mesh (74 mm). The high grade of mercury in this sample (246 g Hg/t) is a result of the whole amalgamation in ball mills conducted in rudimentary processing centres. Based on the gravity concentration tests using 3 centrifugal concentration passes, recoveries of 52.44% of gold and 28.23% of silver were obtained; direct flotation of the tailings using PAX (xanthate) 50g/t and frother D250 25g/t, resulted in 97.6% of gold recovery and 93% of silver recovery. Mercury recoveries were consistently around 55%. A different method to extract mercury, e.g. Ag-Cu plates, has been studied. The Comunica project is implementing an educational program for female miners to build and own a small plant using gravity and flotation that allows them to eliminate mercury through a simple and replicable process (the Ministry of Mines and Energy is implementing 17 similar plants). Comunica’s initiative is led by women and will increment their sustainable and legal production possibilities, preventing increased social and environmental risks, including workplace hazards, threats from regional armed actors, resulting in displacement and child labor. The concentrates can be either leached with cyanide or sold to a larger conventional gold plant. Implementation costs of the 0.5 to 1 tpd plant are approximately US$16,000 with payback of less than one year.

R.P.3.44

A GLOBAL DATABASE OF MERCURY EMISSIONS FOR ARTISANAL AND SMALL-SCALE GOLD MINING (ASGM)

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Artisanal and small-scale gold mining provides livelihoods for an estimated 10 million people and their families in at least 80 countries. At the same time, the sector is the world’s number one source of anthropogenic mercury emissions. Prior to 2018, information on the global magnitude of this emission was limited to disparate literature published on various research mandates of academics, governments, NGOs, and the worlds major development agencies. Post-2018, efforts to quantify the magnitude and trend of the issue have been resourced by the Global Environment Fund (GEF) through the Minamata Convention on Mercury and will boost the global repository of ASGM mercury data by August 2020. However, these efforts have been hindered by lack of a standardized method for measuring mercury use in ASGM and a paucity of data. Both pitfalls stem from the sector’s informal and remote nature and have led to high levels of uncertainty around estimates of ASGM mercury use and whether apparent global temporal trends relate to sector growth and popularity of mercury or simply improved techniques for assessment and greater availability of data. We propose a methodology to (1) quantify the amount of mercury used by ASGM annually in a single country; (2) apply the method to produce the first global dataset of ASGM mercury use; (3) establish a classification system of uncertainty to help prioritize improvements to the dataset. Mercury use is difficult to quantify directly. The illegality of its trade and use in many countries leads to secrecy from miners, corruption among governments, and an absence of formal reporting. Thus, the methodology revolves around two key proxy elements: (a) Gold production, which has a clear monetary value and is thus much more easily estimated by miners and other stakeholders in the sector. Sharing information on gold also does not carry the severe criminal penalties or stigmas that mercury does in many countries; (b) An understanding of the technologies used to produce the gold and a rigorous science-based characterization of the mercury-to-gold ratios (Hg:Ag) of technology categories. Before global temporal trends in ASGM mercury emissions can be quantified with a defined level of confidence, the global dataset must be refined. This presentation is a “call-to-efforts” for more intensive, standardized field and ground-truth participation from the research community to quantify and evaluate uncertainty of the two key elements – gold and Hg:Ag – in each of the 80+ countries where ASGM occurs.

R.P.3.45

ENHANCING STABILITY AND ACCURACY IN DIRECT MERCURY ANALYSIS, IN VARIOUS MATRICES, VIA A DOUBLE BEAM SPECTROPHOTOMETER.

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Direct mercury determination is a well-establish approach in various industries and applications, such as environmental, clinical, biological, cement and coal, as it provides fast and accurate results. Samples are placed directly into the system and through a combustion and amalgamation process, mercury is detected independently from the matrix. Every year there is a constant increase in the number of mercury analysis and on the capability to accurately determine traces and ultra-traces of mercury in various matrices. This enhance the need to develop
fast and reliable procedure. The work how a direct mercury analyser that integrates a double beam atomic absorption spectrometer, allows to further improve the signal stability and the detection limit in direct mercury analysis on various matrices. The configuration used on this work provided great reproducibility and accuracy, even working at ppt level for the determination of mercury in waste water samples. In addition, some of the most common issues in the analytical instrument, such as mercury carry over and memory effect has been considered and addressed using both software and hardware features. On this specific work we have tested various matrices, such as environmental, biological and food to show the applicability of this approach in a wide variety of industries and applications.