

## Gaseous Mercury Emission from Open Prescribed Grassland Burning in Japan

Irei S<sup>1</sup>, Kameyama S<sup>2</sup>, Shimazaki H<sup>3</sup>, Sakuma A<sup>3</sup>, Yonemura S<sup>4</sup>

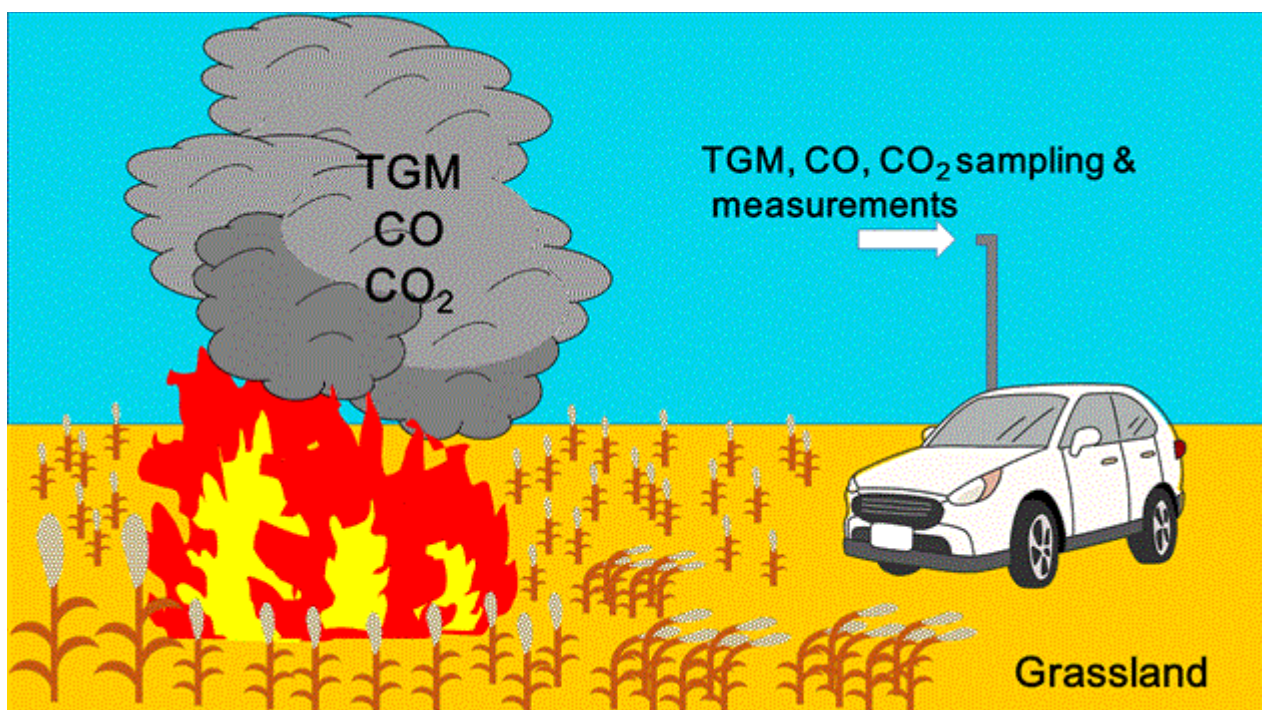
<sup>1</sup>National Institute For Minamata Disease, <sup>2</sup>National Institute for Environmental Studies, <sup>3</sup>National Institute of Technology, Kisarazu College, <sup>4</sup>Prefectural University of Hiroshima

Plants are known to uptake mercury from air and water in soil, then retain it in parts of their body. The retained mercury is released when plants are burned. In some areas of Japan, such as Aso in Kumamoto, there are traditions that grasslands are burned in every early Spring to be conserved. This fire may emit gaseous mercury, which the Ministry of Environment Japan has not counted as the domestic emission source yet.

We conducted emission studies of total gaseous mercury (TGM) from open prescribed burning in Japan. Big gold amalgam traps we developed were used for sampling total gaseous mercury in plumes. For estimation of total emission, we also measured carbon monoxide and carbon dioxide as reference substances. The TGM samples were brought to the laboratory, and their quantities and stable mercury isotope ratios were analyzed. For the estimation of total TGM emission, we also analyzed satellite images and determined the total area burned. Additionally, we sampled the inhabiting plants before the burning so that we gained fuel loads and their mercury and carbon contents.

Measurement results showed four times or more of elevation in atmospheric TGM concentrations during the prescribed burning, indicating the emission of TGM. Their stable isotope ratios resembled those reported for mercury found in plants. Based on the measurement results of fuel loads and burned area, the total emission of TGM from one of the studied areas (Akiyoshidai in Yamaguchi Prefecture) was estimated as 160 g over the 11.4 km<sup>2</sup> area, which accounts for only 0.02% of the annual emission of total domestic TGM in Japan. The estimations in other locations, such as Aso in Kumamoto Prefecture and Hirado in Nagasaki Prefecture, will also be discussed.

### Abstract Graphics



## Application of Volumetric Absorptive Microsampling (VAMS) for Human Biomonitoring of Mercury Species in Blood

Rakete S<sup>1</sup>, Burianova A<sup>1</sup>, Gutknecht C<sup>1</sup>, Bose-O'Reilly S<sup>1,2</sup>

<sup>1</sup>University Hospital, LMU Munich, <sup>2</sup>Department of Public Health, Health Services Research and Health Technology Assessment, UMIT (Private University for Health Sciences, Medical Informatics and Technology)

**Introduction:** Venous blood sampling is the gold standard for mercury analysis in blood. However, microsampling methods such as Dried Blood Spots (DBS) or Volumetric Absorptive Microsampling (VAMS) are increasingly used as an alternative sampling method for mercury biomonitoring. Advantages are less invasive sampling, transport and storage at ambient temperatures and the potential self-sampling, thus significantly reducing costs for exposure assessment. In this study, we investigated the applicability of VAMS for human biomonitoring of mercury species in blood.

**Methods:** A LC-ICP-MS/MS system (Infinity 1260 II HPLC and 8900 ICP-MS/MS, Agilent Technologies) was used for mercury speciation of inorganic mercury and methylmercury. The extraction of mercury species from VAMS was optimized using certified reference material as well as spiked native blood samples. The performance of VAMS for mercury speciation under field conditions was assessed by collecting capillary blood samples (three blood samples, one blank) from 54 adults without occupational exposure to mercury. Matching venous blood samples were collected as a reference.

**Results:** For mercury speciation using VAMS, a good and excellent correlation with venous blood samples was found for inorganic mercury ( $r=0.77$ ) and methylmercury ( $r=0.94$ ), respectively. Limits of detection were  $0.26 \mu\text{g/l}$  for inorganic mercury and  $0.17 \mu\text{g/l}$  for methylmercury, respectively. Blank samples of VAMS showed relative high background levels of inorganic mercury whereas no background was found for methylmercury.

**Conclusions:** We could show that VAMS is a viable alternative for biomonitoring of mercury species in blood. The sensitivity achieved is sufficient to detect mercury species in the majority of the general population. Thus, this method may be used for cohort studies or in regions with limited infrastructure such as ASGM areas. However, background levels of inorganic mercury impede lower limits of detection that would be necessary for biomonitoring of populations exposed to very low levels of inorganic or elemental mercury.

## Mercury dynamics at the base of the pelagic food web of the southern Baltic Sea

Jedruch A<sup>1</sup>, Bełdowski J<sup>1</sup>, Bełdowska M<sup>2</sup>

<sup>1</sup>Polish Academy of Sciences, Institute of Oceanology, <sup>2</sup>University of Gdańsk, Faculty of Oceanography and Geography

Planktonic organisms, which have direct contact with water, serve as the entry point for mercury (Hg), into the marine food web, impacting its levels in higher organisms, including fish, mammals, and humans who consume seafood. This study provides insights into the distribution and behavior of Hg within the Baltic Sea, specifically the Gulf of Gdańsk, focusing on pelagic primary producers and consumers. Phytoplankton Hg levels were primarily influenced by its concentrations in water, while Hg concentrations in zooplankton resulted from dietary exposure through suspended particulate matter and phytoplankton consumption. Hg uptake by planktonic organisms, particularly phytoplankton, was highly efficient, with Hg concentrations on average 10,000 times higher than in the surrounding water. However, unlike biomagnification of Hg between SPM and zooplankton, biomagnification between zooplankton and phytoplankton was not apparent, likely due to the low trophic position and small size of primary consumers, high Hg elimination rates, and limited tissue absorption.

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## Mercury in the Arctic and Antarctica: The Role of Benthic Organisms

Korejwo E<sup>1</sup>, Sniewska D<sup>2</sup>, Jarzynowska M<sup>2</sup>, Cichecka A<sup>2</sup>, Wilman B<sup>2,3</sup>, Bełdowski J<sup>1</sup>

<sup>1</sup>Institute Of Oceanology Polish Academy Of Sciences, <sup>2</sup>Univeristy of Gdańsk, <sup>3</sup>Institute of Meteorology and Water Management - National Research Institute

Mercury (Hg) is one of the most toxic trace metals. It is mainly emitted into the atmosphere in the form of elemental mercury (Hg<sup>0</sup>). It is a stable form of Hg, which is volatile and insoluble in water under normal conditions. Therefore, the time of residence of Hg<sup>0</sup> in the atmosphere is several months, making mercury a globally distributed pollutant. This results in the presence of mercury in regions far away from anthropogenic sources.

The polar regions are interesting areas of research due to the various possible sources of this metal in the environment. A complete understanding of the mercury transformation processes in the Arctic and Antarctica is challenging because these areas are undergoing intense changes. It is estimated that more than 90% of the 4,000 species living in the Arctic live on the seabed. Benthic organisms play a crucial role in the food chain - they are the food of fish, birds and humans. The objective was therefore to identify the concentration of mercury and its forms in organisms such as starfish, sea urchins, brittle stars and snails, and to determine factors that influence Hg accumulation and biomagnification in the marine trophic network.

In the years 2019-2022, in the Spitzbergen fjords and the Admiralty Bay area, dominant benthic organisms were collected. The samples were analyzed for the concentration of total mercury and methylmercury, as well as the contribution of five fractions of mercury.

The research revealed that in both regions, starfish were the most contaminated with total mercury. Hg concentrations in these organisms were at least 10 times higher than in other organisms. However, the starfish effectively dealt with this metal, transferring about 60% of it to their hard tissues. The situation was different for snails, which only transported 5% of mercury to their shells.

## Mercury Sources in the Antarctic Sea and Their Potential for Accumulation in the Marine Tropic Chain

Korejwo E<sup>1</sup>, Saniewska D<sup>2</sup>, Jędruch A<sup>1</sup>, Saniewski M<sup>3</sup>, Balazy P<sup>1</sup>, Bełdowski J<sup>1</sup>

<sup>1</sup>Institute Of Oceanology Polish Academy Of Sciences, <sup>2</sup>University of Gdansk, <sup>3</sup>Institute of Meteorology and Water Management - National Research Institute

Recent research has shown that the Antarctic region acts as a mercury sink (Hg), with unique atmospheric mercury depletion events that accumulate Hg and integrate it into the ocean's food web. In addition, this metal can be stored in the snow pack throughout the continent, making the region a massive cold trap for mercury. However, the western Antarctic ice sheet is currently in a dynamic imbalance, with ice loss five times greater than previously estimated. As a result, ice sheets and melting glaciers have become an important secondary source of mercury in Antarctica, resulting in an increase in the concentration of Hg in marine organisms.

The aim of the study was to identify mercury sources in Antarctica and determine their potential for accumulation in the marine trophic chain. In December 2018, samples were collected at Admiralty Bay, where sea samples including water, suspended particulated matter, phytoplankton and zooplankton were collected. The total concentrations of mercury, methylmercury and fractions of Hg were analyzed in the collected samples.

The highest Hg values were measured near glaciers. Although most of the mercury in water was suspended, it was discovered that the most toxic form of Hg, methylmercury, was dissolved, facilitating its accumulation in plankton.

This study has been performed within the framework of a National Science Center projects No. 2019/33/B/ST10/00290 and No. 2017/27/N/ST10/02230.

## Labile and stable fractions of mercury in marine sediments from the Spitsbergen region

Narwojsz D<sup>1</sup>, Bełdowski J<sup>1</sup>, Bełdowska M<sup>2</sup>, Zaborska A<sup>1</sup>, Jedruch A<sup>1</sup>

<sup>1</sup>Polish Academy of Sciences, Institute of Oceanology, <sup>2</sup>University of Gdańsk, Faculty of Oceanography and Geography

Mercury (Hg) is one of the most toxic metals in the environment, lacking positive biological functions and accumulating in living organisms and soil. This highly reactive element persists in the environment, biomagnifying in trophic chains. Anthropogenic mercury emissions impact the Arctic, where volatile mercury, with a tropospheric half-life of several months, persists in the atmosphere, facilitating long-distance transport. This study aims to assess the contributions of mercury fractions, processes, and transformations in sediment cores from Spitsbergen fjords.

The study examined eleven sediment cores from Kongsfjorden and Hornsund fjords, utilizing a thermodesorption technique via a DMA-80 analyzer (Milestone) with a 5-step Hg fractionation method, during which three labile and two stable mercury fractions are released. This facilitated the assessment of mercury's fate in the Arctic environment.

An important feature of mercury speciation profiles at all stations studied is the dominance of stable fractions. Both diagenesis processes occurring in the sediments involving the transformation of labile fractions into stable fractions and the direct delivery of these fractions to the bottom sediments are responsible for this. The location of the station, including its distance from the glaciers, as well as its depth, was an important factor determining the concentration and proportion of mercury fractions in bottom sediments in the study area. Understanding the fate of mercury in the Arctic environment helps identify its sources and predict further changes, which are strongly influenced by the changing climate. The study indicates that the process of melting glaciers, as a secondary source of pollutants, is increasing its importance in supplying them to the marine environment. Increased erosion caused by melting ice cover provides an additional load of Hg to the marine environment.

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## Navigating Mercury Emission Reduction in Coal-Powered Economies

Nelson P<sup>1</sup>, Archer E<sup>1</sup>

<sup>1</sup>Macquarie University

Stationary combustion of fossil fuels for energy generation is not only known as the primary anthropogenic driver of climate change through greenhouse gas emissions but also a major contributor to atmospheric mercury emissions, estimated at around 290 and 126 tons each year coming from the coal-fired power plant (CFPP) and coal-fired industrial boiler (CFIB) sectors respectively. Although the complete transition to renewable energy will be pivotal to reducing emissions significantly within these sectors, it is crucial to recognize that emerging economies may face challenges in such a transition without support from a variety of financial mechanisms.

The reality is thus to find a balance in accelerating the retirement/cancellation of existing/future CFPPs and promoting the installation of multi-pollutant air pollution control devices for plants that still need to operate until they can successfully be replaced with renewable energy. The benefits and challenges to both these strategies will be presented in the context of providing a co-benefit towards reducing mercury emissions for coal-dependent countries.

The global mercury emissions outlook for the CFPP sector suggests a polarized future at this stage, with emissions experiencing a decline in some countries but increasing in others, and dependent on different scenarios that may play out in countries predicted to have a continuing reliance on coal-fired energy generation for the decades until 2050. This presentation aims to shed light on the intricate dynamics, challenges, and opportunities to produce the highest global environmental benefit in reducing emissions from the coal sector in times of a renewable energy revolution. The strategies for implementing the best available technologies and adhering to best environmental practice guidelines (BAT/BEP) will vary considerably between countries based on their socio-economic conditions and should be carefully considered to foster a sustainable future in the global energy sector.

## Decreased plasma thiol antioxidant capacity precedes neurological signs in a rat methylmercury intoxication model

Fujimura M<sup>1</sup>, Usuki F<sup>2</sup>, Unoki T<sup>1</sup>

<sup>1</sup>National Institute for Minamata Disease, <sup>2</sup>Joint Research Center for Human Retrovirus Infection

The main target organ for MeHg is the nervous system, and its neurological dysfunction remains irreversible. Therefore, predictive biomarkers associated with individual susceptibility to MeHg and future clinical severity are needed to protect against the progression of MeHg toxicity. In this study, we demonstrated that plasma thiol antioxidant capacity (-SHp) is a useful predictive biomarker associated with future clinical severity using MeHg-intoxicated rats administered 1 mg/kg/day for 4 weeks. Blood samples were collected from the subclavian vein of each rat once a week to examine total blood mercury concentrations and the levels of plasma oxidative stress markers. Time course analyses of the correlation between these weekly blood examination values and hind limb crossing signs score after 4 weeks of MeHg exposure were performed, and plasma -SHp levels after 2 weeks of MeHg exposure showed strong correlations with future hind limb crossing sign scores. Neuropathological changes also developed in parallel with hind limb crossing sign scores. Quantitative analysis of vacuolar areas in the spinal cord showed a strong correlation with hind limb crossing sign scores. In conclusion, evaluation of plasma -SHp levels allowed us to detect individuals at risk for health damage and could protect the sensitive population against MeHg toxicity.

## Stoichiometric relationship between mercury and selenium in the nutrition of populations in the Northwest Territories (Canada), with special emphasis on remote indigenous communities

Wallschläger D<sup>1</sup>, Branton A

<sup>1</sup>Wilfrid Laurier University

For this presentation, we compiled an inventory of the human diet in the Northwest Territories (NWT), Canada, with respect to the mercury (Hg) and selenium (Se) content in individual food items. For the 64 different food items contained in the revised Northern food basket (RNFB), which is assumed to represent the average diet of urban Northern Canadian populations, representative Hg and Se concentrations were gathered from the published literature. Mercury was only elevated in fish products, while Se was elevated in fish, meat, flour and milk products. Daily average uptake doses of 142  $\mu\text{g}$  Se and 2.4  $\mu\text{g}$  Hg were calculated, which appear to suggest no immediate health risk for the average NWT population. Furthermore, molar Se/Hg ratios were calculated for each food item, and ranged between 14 (in fish) to over 3,000 (in milk products), with an overall Se/Hg ratio for the RNFB of 151. This suggests that the average diet in the NWT contains sufficient Se to prevent toxic Hg effects.

Since rural, mainly indigenous, populations in the NWT consume more country foods (especially fish and caribou), an attempt was made to estimate the changed Hg and Se uptake of members of such rural communities. For this purpose, Se and Hg concentrations in fish from water bodies impacted by industrial operations and Hg concentrations in fish from lakes impacted by long-range atmospheric Hg transport were considered, and substituted into the “urban” NWT diet. While the Hg and Se uptake doses increased in the estimate for the rural populations in the NWT, they still remain within ranges considered safe, and the continued large molecular Se excess should provide additional protection against Hg-based effects. Therefore, aside from extreme individual cases, it is unlikely that the NWT population is at risk of negative health effects from either Hg or Se exposure.

## Effect of sediment resuspension on near-bottom mercury dynamics: Insights from a Baltic sea Experiment

Jędruch A<sup>1</sup>, Korejwo E<sup>1</sup>, Siedlewicz G<sup>1</sup>, Cichecka A<sup>2</sup>, Bełdowski J<sup>1</sup>

<sup>1</sup>Institute of Oceanology PAS, <sup>2</sup>Faculty of Oceanography and Geography, University of Gdańsk

Sediment resuspension can mobilize mercury (Hg), significantly impacting its biogeochemical cycling in aquatic ecosystems. The released Hg can elevate water concentrations, potentially causing bioaccumulation and biomagnification in aquatic organisms. Understanding these processes is crucial for predicting and mitigating the potential impacts on aquatic ecosystems. A laboratory experiment using sediment cores from the southern Baltic Sea was conducted to assess the effect of sediment resuspension on Hg release into water.

Sediment cores from the southern Baltic Sea, collected in 2022, underwent a controlled laboratory experiment simulating resuspension events. Water Hg concentration was analyzed using cold vapor generation with atomic absorption spectrometry (CV-AAS) on a Tekran 2600 analyzer. Hg in suspended matter was determined via thermal desorption and atomic absorption spectrometry (TD-AAS) on a DMA-80 direct mercury analyzer.

Analysis revealed that the remobilization of Hg from sediment is complex, influenced by factors like sediment and water column properties. In the identified Hg hot spot, Mecklenburg Bay, disruption led to a more than 100-fold increase in water mercury concentration. In the Gdańsk Basin, a site of final sediment deposition, surface sediment resuspension resulted in a 60-fold increase. Temporarily deposited basins, Arkoński and Bornholmski, experienced a 30-fold rise. In erosion-prone Słupsk Furrow, the increase was minimal, not exceeding five times the water mercury concentration induced by resuspension. These findings offer insights applicable to understanding the repercussions of natural phenomena, like currents or inflows from the North Sea, as well as human activities such as offshore investments and dredging.

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## Development of a remote-controlled system for bioremediation and phytoextraction experiments for research and teaching purposes

Heidel B<sup>1</sup>, Schmidtke S<sup>1</sup>

<sup>1</sup>Esslingen University

Despite intensive research and educational efforts in the chemical analysis and monitoring of Hg concentrations in the biosphere and in agriculture, our understanding and awareness of the overall levels and dynamics of phytoextraction and accumulation processes still falls short of what is desired. Therefore, the University of Esslingen is addressing this issue as an integral part of its research and curriculum. Hg awareness is greatly enhanced by the integration of application-oriented laboratory experiments. Due to dense curricula, such courses can usually only be offered in the form of short units. Long-term processes, such as phytoextraction of Hg by plants, are often excluded from individual practical assessment. This paper presents a concept to overcome these limitations by using digital hybrid laboratory didactics. The concept allows for real experiments that can be remotely controlled. This opens up new possibilities for the long-term observation of the accumulation of Hg from substrates by plants as a function of growth conditions. On the one hand, conditions and stabilisers of soil amendments will be investigated under which food plants accumulate as little Hg as possible, and on the other hand, parameters for accelerated extraction of Hg for bioremediation of contaminated soils by hyperaccumulators will be researched. The development of the plants will be monitored remotely using smartphones. Conditions such as temperature, pH, lighting, irrigation and nutrient supply will be continuously monitored and evaluated by the responsible group using webcams, specific sensors and actuators for each plant. The conference paper will outline the didactic concept and present the current state of hardware and software development of the "Remote Controlled System" for phytoextraction and bioremediation applications. The idea of open science is an integral part of the concept; all hardware and software developments will be published openly and made available to science, education and the general public.

35

## Scientific Challenges in the Update of an Assessment of Methylmercury Neurotoxicity

Kopylev L<sup>1</sup>, Segal D, Dzierlenga M, Lin Y, Nachman R, Radke E

<sup>1</sup>Us Epa

The US EPA is currently updating the reference dose (RfD) for Methylmercury developmental neurotoxicity (DNT; assessment plan and systematic review protocols were publicly released in 2019-20). Multiple health agencies (Health Canada, 2007; UNEP, 2002; US EPA, 2001, 1997; ATSDR, 1999) and the US National Academy of Sciences (NRC, 2000) have established that prenatal oral exposure to methylmercury in humans causes DNT. The existing US EPA quantitative risk assessment of methylmercury was finalized by the IRIS (Integrated Risk Information System) program in 2001. That assessment established RfD based on DNT effects in children following prenatal exposure using information from 3 epidemiological cohorts (Faroe Islands, Seychelles, New Zealand). The RfD of 0.1  $\mu\text{g}/\text{kg}\text{-day}$  was derived from multiple DNT outcomes related to cord blood concentrations of 46–79  $\mu\text{g}/\text{L}$ , which the assessment estimated corresponded to maternal daily intakes of methylmercury during pregnancy of 0.86–1.47  $\mu\text{g}/\text{kg}\text{-day}$ . Since 1998, more than 200 epidemiological studies have been published with dose-response information on DNT of methylmercury exposure pre- and/or postnatally, based on dozens of cohorts, including the 3 original cohorts considered in the 2001 IRIS assessment. Updating the risk assessment with this collection of new studies presents several scientific issues that must be considered, including what biomarkers of exposure are most appropriate for deriving the RfD and how different studies account for potential confounding, including such factors as selenium and fish consumption.

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.

## Mercury sources, accumulation and biomagnification in the Antarctic coastal zone: Insights from isotopic fingerprints

Saniewska D<sup>1</sup>, Božič D<sup>2</sup>, Živković I<sup>2</sup>, Bełdowska M<sup>1</sup>, Horvat M<sup>2</sup>

<sup>1</sup>Department of Chemical Oceanography and Marine Geology, University of Gdansk, <sup>2</sup>Department of Environmental Sciences, Jožef Stefan Institute; Jožef Stefan International Postgraduate School  
The Antarctic, renowned for its pristine nature, is now under scrutiny due to potential contamination by anthropogenic pollutants, including mercury (Hg). This research aims to identify mercury sources in the Antarctic coastal zone and assess their potential for accumulation and biomagnification in the marine trophic chain.

Conducted during scientific expedition in Admiralty Bay (December 2018-January 2019), our sampling included terrestrial samples (mosses, lichens, animal fur, feathers, and excrements) and marine samples (fish and zoobenthos). Total mercury and methylmercury concentrations as well as stable isotopic ratios of Hg were determined in the samples. In addition, selenium concentration, as well as stable isotope of carbon and nitrogen were analysed.

Our findings indicate that atmospheric sources contribute significantly to terrestrial flora Hg content. Among benthic organisms, accumulation and biomagnification of Hg was observed. However, the highest Hg concentration among all studied organisms was found in the fur of elephant seal (average 2711 ng/g). Ranges of -1.21 to 1.64‰ of  $\delta^{202}\text{Hg}$  and -0.85 to 1.85‰ of  $\Delta^{199}\text{Hg}$  in terrestrial flora and 0.12 to 2.46‰ of  $\delta^{202}\text{Hg}$  and 0.26 to 2.21‰ of  $\Delta^{199}\text{Hg}$  in marine fauna were observed. This research is one the first of its kind in Antarctic, therefore the wider context is hard to establish. It seems to be clear that the isotopic fingerprint is heterogeneous which might be a result of different factors. One of them seems to be the bioaccumulation within the zoobenthos-fish-penguins-elephant seals food chain. This is confirmed by an increase of  $\Delta^{199}\text{Hg}$  along the trophic chain and correlation between  $\Delta^{199}\text{Hg}$  and  $\delta^{15}\text{N}$ . Further research is necessary to understand Hg cycling in the Antarctic.

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37

## The determination of inorganic mercury by solid phase extraction and laser induced breakdown spectroscopy

Nam S<sup>1</sup>, Lee Y<sup>1</sup>, Park J<sup>1</sup>

<sup>1</sup>Mokpo National University

The toxicity of mercury compounds is influenced by both their chemical structure and concentration. Accurate determination of these chemical species and their concentrations in diverse samples is crucial for assessing mercury toxicity. A novel approach for quantifying Hg(II) has been developed using an ion exchange membrane coupled with laser-induced breakdown spectroscopy (LIBS). Hg(II) present in water was captured by a cation-exchange membrane, and the membrane loaded with Hg(II) was directly subjected to LIBS analysis. The detection limit for Hg(II) was found to be 2.53 mg/kg. The recovery efficiency for 80 mg/kg mercury standard solutions was excellent, reaching 104%. This method was successfully applied to analyze a certified reference material of Hg-spike water. Overall, this innovative method offers a more cost-effective, simpler, and less labor-intensive approach for quantifying inorganic mercury compared to traditional chromatography-coupled elemental analysis techniques.

## The development and application of methylmercury-to-total mercury ratios for exposure assessment of methylmercury from the consumption of traditional foods

Eccles K<sup>1</sup>, Chan L<sup>2</sup>

<sup>1</sup>Health Canada, <sup>2</sup>University of Ottawa

Mercury is often detected in traditional foods consumed by Indigenous Peoples. Therefore, it is important to understand the proportion of methylmercury (MeHg) comprising the total mercury (THg) measurement in wildlife and fish tissues that are commonly consumed. We identified key traditional foods and developed a database reporting MeHg and THg concentrations from the literature. The literature review found 31 relevant papers and two private databases, reporting, total, and MeHg concentration. We developed a database that contained 298 entries from 184 species-tissue combinations or food items. We then used a meta-analysis approach to calculate the mean and the upper confidence interval of the mean (UCLM) of the MeHg:THg ratio; we developed a set of 65 species and tissue-specific ratios (with  $n > 19$ ) based on the UCLM with an additional uncertainty factor for ratios with large variability. Forty-six species-tissue combinations (71%) had a MeHg:THg ratio less than 100%. We also aggregated the MeHg:THg ratios into 27 general species types (i.e., the whole body of bird, crustacean, fish, fungi/plant, land mammal, freshwater mammal, and marine mammal) and tissue groupings (i.e., egg, liver, kidney, brain, skin, and fat). Fifteen species tissue groupings (56%) had a MeHg:THg ratio less than 100%. We applied these conversion factors to data from the IHS and the FNFNES to demonstrate the utility of using our conversion factors to estimate MeHg intake. The results suggest that using the conversion factors can still potentially over or underestimate the risk at a local scale. Further work is needed to quantify the influence of co-variates (e.g., age, sex, location) on the MeHg:THg ratios in tissues. Therefore, the approach will be useful for hazard identification purposes and can be used to screen for when a more detailed investigation, such as measuring the MeHg concentrations in the local foods, is required to characterize the risk.

## Insights from the analysis of artisanal and small-scale gold mining Minamata Convention National Action Plans

Davis K<sup>1</sup>, Stylo M, Dossou Etui I, Bernaudat L

<sup>1</sup>UN Environment Programme

National Action Plans (NAPs) are the cornerstone of the Minamata Convention's approach to reducing and where feasible eliminating mercury use in artisanal and small-scale gold mining (ASGM). NAPs contain baseline information on the state of the ASGM sector in the country, as well as national strategies and targets for mercury elimination and other policy actions. As such, the NAPs are a valuable source of data and indication of policy goals. 30 NAPs published on the Minamata Convention web site were analyzed and quantitative and qualitative information extracted. NAP estimates for mercury use ranged from 345.5 to 0 tonnes Hg. Comparisons of NAP data on mercury use were compared with estimates from the 2018 Global Mercury Assessment, with notable differences observed in some countries, which may result from actual change in mercury use or differences in methodologies of estimation. ASGM gold production estimates ranged from 53.8 tonnes to 0.02 tonnes. Based on the submitted NAPs, nearly 400 tonnes of ASGM gold are produced in 30 countries. Countries also reported mercury reduction targets in the NAPs. If these were achieved, mercury use would fall by about 80% from 777 to 157 tonnes by 2030 in the 30 countries. The NAP strategies reveal a range of approaches for eliminating worst practices, formalizing the sector, and protecting vulnerable populations. Given the significant need for capacity and resources to carry out these strategies, implementation will be a challenge in the years ahead.

## Measuring Results of Mercury Reduction Strategies under Minamata NAPs: the case of planetGOLD

Keane S<sup>1</sup>, Bernaudat L

<sup>1</sup>Natural Resources Defense Council

Artisanal and small-scale miners are responsible for producing 20 percent of the world's gold each year. Many of these small-scale mining operations use mercury to extract their gold, making this sector the largest source of mercury pollution in the world. The Minamata Convention on Mercury requires countries with "more than insignificant ASGM" to reduce and where feasible eliminate the use of mercury in the sector. The planetGOLD programme, funded by the Global Environment Facility, aims to assist Parties to meet this obligation by supporting their National Action Plan (NAP) strategies for ASGM mercury reduction, including introducing mercury-free technologies, supporting formalization, and increasing access to finance and formal markets. Resulting mercury reductions can contribute to a Party's progress on its overall mercury reduction targets, as stated in their NAPs. However, quantifying the mercury reductions attributable to program activities is a complex exercise that requires consideration of reductions resulting from technical interventions and from educational and other program activities. An overview of the method development and proposed indicators for reporting mercury reductions resulting from planetGOLD programme activities will be presented.

41

## Time course variations of seawater characteristics by environmental incubation experiments using Minamata Bay sediment and seawater.

Matsuyama A<sup>1</sup>, Tada Y<sup>2</sup>, Yano S<sup>3</sup>

<sup>1</sup>Department of International Affairs and Research, <sup>2</sup>Department of Environment and Public Health, <sup>3</sup>Department of Marine Engineering

Time course variation of seawater characteristics by environmental incubation experiments using Minamata Bay sediment and seawater.

Akito Matsuyama<sup>1</sup>, Yuya Tada<sup>2</sup>, Shinichirou Yano<sup>3</sup>

1) Department of International Affairs and Research, National Institute for Minamata Disease (NIMD), 4058-18 Hama, Minamata, Kumamoto 867-0008, Japan.

Email address: correspondence author AKITO\_MATSUYAMA@env.go.jp

2) Department of Environment and Public Health, National Institute for Minamata Disease (NIMD), 4058-18 Hama, Minamata, Kumamoto 867-0008, Japan.

3) Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.

Aim of our study is showing that how affects to seawater characteristics by mercury in Minamata Bay sediments by variation of environmental condition in seawater chronologically. Accumulated sediments in the Minamata Bay and seawater were utilized as experimental samples in our study, then batch model of cylinder type and environmental incubator for incubation experiment. Incubation factors are seawater temperature, dissolved oxygen concentration (DO) and Addition of glucose. Seawater temperature was set 25 degrees centigrade that is average value between Summer and Autumn then DO (mg/L) were set between 0.1 to 7.5. Also, oxidation-reduction potential (ORP) was measured as an indicator for time course change of seawater quality. Mercury measurements are dissolved total mercury concentration (diss-THg) and methylmercury concentration(diss-MeHg) in seawater and pore water in the sediments then total mercury and methylmercury concentration in sediments and suspended solid (SS). Furthermore, time course change of micro-organisms characteristics in seawater is verified. As a result, the diss-THg and the diss-MeHg in time course were drastically change by addition of the glucose and variation of DO level in seawater. Then, ORP is good indicator as for time course change of dissolve mercury concentration(diss-Hg) in seawater.

## Combating air pollution significantly reduced air mercury concentrations in China

Feng X<sup>1</sup>, Fu X, Zhang H, Wang X, Lin J

<sup>1</sup>Institute Of Geochemistry, Chinese Academy Of Sciences

Long-term observations of atmospheric mercury are important for the evaluation of the effectiveness of the Minamata Convention on Mercury. We continuously measured gaseous elemental mercury (GEM) concentrations at four remote sites in China for more than ten years, i.e., Mt. Waliguan (100.90° E, 36.29° N) during 2008-2022, Mt. Changbai (128.11° E, 42.40° N) during 2008-2022, Mt. Ailao (101.02° E, 2453° N) during 2011-2022, and Mt. Damei (121.57° E, 29.63° N) during 2011-2022. Our observations showed that GEM concentrations in China increased slightly during 2008-2013, and then the GEM concentrations decreased significantly after 2013. The mean GEM concentrations at the four Chinese sites during 2022 were  $1.51 \pm 0.35$  ng m<sup>-3</sup>, which is close to mean concentrations observed in Europe, North America, the Arctic, and the free troposphere in Pacific Ocean during 2021 (Individual means: 1.14 to 1.51 ng m<sup>-3</sup>, overall mean:  $1.34 \pm 0.11$  ng m<sup>-3</sup>, n = 13). During 2013-2022, GEM concentrations in China decreased by 35%, which was much higher than the decreasing rates observed in Europe (9%), North America (10%), the Arctic (6%), and the free troposphere in Pacific Ocean (9%) during 2013-2021. The declines in GEM concentrations in China since 2013 matches well with the decreasing anthropogenic Hg emission in China estimated by Chinese anthropogenic Hg emission inventory, indicating the reduction in anthropogenic Hg emissions in China was the major driver for the GEM declines.

## Air-sea exchange of elemental Hg and dimethylmercury in the South Pacific and Southern Ocean

He Y<sup>1,2</sup>, Inman H<sup>2</sup>, Mason R<sup>2</sup>, Despins M<sup>3</sup>, Lamborg C<sup>3</sup>

<sup>1</sup>Florida International University, <sup>2</sup>University of Connecticut, <sup>3</sup>University of California, Santa Cruz

Air-sea exchange of mercury (Hg) is an important part of the global Hg cycle, affecting the input and output of Hg from the surface ocean, and prolonging the residence time of Hg in the biosphere. It could also impact the fate of methylated Hg (i.e. monomethyl- (MMHg; CH<sub>3</sub>Hg) and dimethylmercury (DMHg; (CH<sub>3</sub>)<sub>2</sub>Hg)). Previous studies have provided new insights into the factors controlling the deposition of ionic Hg (Hg<sup>II</sup>) and the evasion of elemental Hg (Hg<sup>0</sup>), but not of methylated Hg. The U.S. GEOTRACES GP17-OCE Cruise aboard the R/V Roger Revelle, which sailed from San Diego to Tahiti to Punta Arenas, Chile (Nov 2022 – Jan 2023), was designed to understand the distribution and air-sea gas exchange Hg<sup>0</sup> and DMHg and the deposition, of Hg<sup>II</sup> and MMHg in the equatorial Pacific and oligotrophic South Pacific subtropical gyre, across the sub-Antarctic front, and at sites of new water mass formation and upwelling, as well as along the Antarctic and Chilean continental shelves. We used the Tekran 1130/1135/2537X instruments for high-resolution measurements of the atmospheric Hg speciation (Hg<sup>0</sup>, reactive gaseous Hg (RGHg) and particulate Hg (HgP) and automated high resolution continuous equilibrium systems were used for measuring dissolved Hg<sup>0</sup> and DMHg in surface water. Additionally, MeHg and total Hg concentrations were quantified in atmospheric aerosols and in precipitation. Results of these measurements will be discussed in terms of the overall air-sea exchange of inorganic Hg and methylated Hg in the South Pacific and Southern Ocean, and the importance of gas exchange as an oceanic sink for Hg<sup>0</sup> and methylated Hg compared to other processes, and the potential role of DMHg evasion in contributing to the deposition of MMHg to remote environments. Overall, the potential role of the ocean and air-sea exchange of methylated Hg, and the impact of climate change will be highlighted.

## Speciation, Partitioning, and Transport of Hg from the Penobscot River to the Gulf of Maine

Smith S<sup>1</sup>, Mason R<sup>1</sup>, Taylor V<sup>2</sup>, Inman H<sup>1</sup>

<sup>1</sup>University Of Connecticut, <sup>2</sup>Dartmouth College

Mercury (Hg), in the form of methylmercury (MeHg), is a neurotoxin that bioaccumulates in marine organisms and biomagnifies up the food chain. Thus, understanding its behavior in coastal ecosystems is important, especially in major fishing grounds such as the Gulf of Maine (GoM). Due to climate change, watershed runoff to the GoM has increased, resulting in an increase in the inputs of terrestrial organic matter (OM). This change is important because Hg can be co-transported with terrestrial OM, and OM character and concentration influences Hg methylation and the bioavailability of MeHg. To evaluate the impact of increased watershed inputs to the GoM, the relationship between MeHg, Hg, and OM quality and quantity was assessed by collecting samples at multiple stations on four cruises in the GoM and a major tributary, the Penobscot River, between April 2023 to April 2024. Dissolved and particulate MeHg and total Hg concentrations, and dissolved gaseous Hg, were measured throughout the water column, as well as the concentration of DOC and particulate organic carbon, the character of DOM and particulate OM, and other ancillary variables. Additionally, two trips were made to sample the Penobscot River further inland. The aim of this work is to examine the relationships between Hg speciation and other variables, both seasonally and spatially along a transect from a historically contaminated river to the Gulf, with a focus on the role of OM in influencing Hg fate, transport and transformation. Ultimately, this study expands upon the limited pool of Hg measurements in the GoM, provides for a better understanding of Hg cycling, and will help clarify the relationships between Hg, MeHg, and DOM.

## Isolation and identification of mercury and dissolved organic matter complexes

Qasim G<sup>1</sup>, Mangal V<sup>2</sup>, Montesdeoca M<sup>1</sup>, Harris L<sup>2</sup>, Todorova S<sup>1</sup>

<sup>1</sup>Syracuse University, <sup>2</sup>Brock University

The complexation of mercury (Hg) with dissolved organic matter (DOM) is a critical factor influencing mercury transformation, transportation, and bioavailability in aquatic environments. Nevertheless, the identification of these complexes poses a challenge due to their exceedingly low concentrations and the presence of coexisting ions. This study focuses on the isolation of Hg-DOM complexes through solid phase extraction (SPE) and their identification using ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS). The SPE was performed using cartridges with silica structure bonded with hydrocarbon chains (C18) and hydrophobic styrene divinylbenzene copolymer (PPL). DOC and total Hg analysis before and after SPE showed an increase in DOC:Hg after extraction, suggesting that not all Hg measured in the initial samples was complexed with DOM and most of Hg in the extracts was complexed with DOM. The DOC:Hg was lower in extracts from C18 than PPL at circumneutral pH, indicating that C18 was more effective in collecting complexed Hg. These results were confirmed with FTICR-MS analysis as nine Hg-DOM complexes were confidently identified through a combination of isotope simulation software. Two Hg-DOM complexes were identified from PPL extracts, while seven Hg:DOM complexes were identified from C18 extracts (Winnow score >75%). C<sub>8</sub>H<sub>13</sub>HgN<sub>2</sub>O<sub>2</sub>S molecule with a m/z ratio of 403.04042 was identified across three separate extractions with a C18 cartridge, suggesting that preferential identified complexes were preserved during extraction and, presumably, electrospray ionization. These results highlight the effectiveness of SPE coupled with FTICR-MS in isolating and identifying Hg-DOM complexes and present an opportunity to explore their molecular composition in understanding the effect of mercury speciation and bioavailability in aquatic environments.

## Impact of Anthropogenic Nutrient Inputs on Mercury (Hg) Methylation and Demethylation in Sediments of a Nutrient-Enriched Lake

Li J<sup>1</sup>, Wang Y, Wang D

<sup>1</sup>西南大学

The impact of anthropogenic nutrient inputs on mercury (Hg) methylation, demethylation, and their potential accumulation within aquatic food chains was investigated using sediments from a lake characterized by significant anthropogenic nutrient influx in this study. Sediment samples were gathered from two distinct zones: aquaculture and non-aquaculture areas. These samples underwent treatment involving exogenous additives, such as algae powder, livestock manure, and fish food. A mesocosm study was conducted, complemented by the application of stable isotope tracing techniques.

Preliminary findings indicate a decrease in both total Hg and MeHg concentrations in surface water across all treatments, contrasting with an initial increase succeeded by a decline observed in interstitial water. Substantial increases in Cl<sup>-</sup> concentrations in both surface and interstitial waters were noted following the addition of exogenous nutrients, suggesting an enrichment of Cl<sup>-</sup> due to the introduction of organic matter. Conversely, the absence of exogenous nutrient additives resulted in notably higher SO<sub>4</sub><sup>2-</sup> concentrations compared to the treated group, possibly indicating the reduction of SO<sub>4</sub><sup>2-</sup> leading to dissolved sulfides. Among all treatments, SO<sub>4</sub><sup>2-</sup> concentrations in interstitial water consistently increased initially, peaking at 7 days, and then stabilized. S<sup>2-</sup> concentrations in interstitial water among various treatment groups displayed an initial rise, reaching a peak around 15 days, followed by a gradual decline. The analysis of microbial community diversity and the abundance of potential microbial methylators in sediments (i.e., copies of the *hgcA* gene) is currently ongoing. The outcomes of this study will provide valuable insights into how anthropogenic nutrient input influences the migration and transformation of Hg within aquatic ecosystems.

47

## Assessing sources and bioaccumulation of mercury in two contrasting Arctic ecosystems using stable mercury isotopes

Li M<sup>1</sup>, Havron I<sup>1</sup>, Loseto L<sup>2</sup>, Kwon S<sup>3</sup>, Lim S<sup>3</sup>

<sup>1</sup>University of Delaware, <sup>2</sup>Fisheries and Oceans Canada, <sup>3</sup>Pohang University of Science and Technology

The Arctic, with minimal local anthropogenic pollution, serves as a global mercury (Hg) sink from distant sources. Significant knowledge gaps persist on Hg sources, transport, and fate in the Arctic marine food webs. This study aims to improve our understanding of present-day environmental sources and bioaccumulation mechanisms of Hg in two distinct arctic ecosystems – Bering Sea vs. Beaufort Sea, representing the marginal sea of the Northern Pacific Ocean and the Arctic Ocean, respectively. We examined 12 fish species from four habitats in Bering and Beaufort Seas (nearshore vs. offshore, pelagic vs. benthic) and conducted total Hg and Hg isotope analysis of their muscle tissues. Results from Bering Sea samples revealed a characteristic Hg isotopic pattern typical of marine offshore ecosystems, indicating a relatively homogenous environmental MeHg source and photodegradation in the water column before MeHg uptake into the Bering food web. In contrast, a very different Hg isotope pattern is observed in Beaufort Sea fish samples, with a much narrower range in  $\delta^{202}\text{Hg}$  values and a wider range in  $\Delta^{199}\text{Hg}$ . The  $\Delta^{200}\text{Hg}$  data suggest that Hg in Bering Sea might be more influenced by river input whereas air and snow could play an important role in contributing Hg to Beaufort Sea. The Eastern Beaufort Sea beluga is a highly migratory Arctic whale known to spend its year between the Bering and Beaufort Sea. Their Hg isotopic composition indicates their MeHg burden primarily comes from Beaufort Sea offshore deep-sea fish. This study underscores the effectiveness of Hg stable isotopes in tracing foraging habitats in the Arctic, including highly migratory species such as beluga whales. The comparison between the Bering Sea and the Beaufort Sea provides insights into the factors driving variations in MeHg burdens in marine organisms across these two distinct Arctic ecosystems.

48

## Tracing atmospheric Hg levels around active volcanoes in southern Chile through tree rings records.

Valenzuela N<sup>1</sup>, Chiang G<sup>2</sup>, Stotz G<sup>2</sup>, McLagan D<sup>1</sup>

<sup>1</sup>Queen's University, <sup>2</sup>Universidad Andres Bello

The continuous volcanic activity in southern Chile (37°-39°S) makes it an interesting area to study geogenic activities and associated (natural) contaminant emissions. Mercury is one such contaminant emitted from geogenic sources (predominantly as elemental Hg). In addition, the natural Hg biogeochemical cycle has been heavily perturbed by anthropogenic emissions (i.e., combustion of fossil fuels, mining, and other industrial activities) since industrialization. Our knowledge of mercury cycling in the southern hemisphere is typically more limited than in the north, particularly when studying biogeochemical archives to review past records. We use dendrochronological records of two long-lived, high-altitude tree species to assess historical emissions from volcanoes in Chile's "La Araucanía" region and pre-industrial mercury levels throughout the Southern Hemisphere. "La Araucanía" is characterized by the presence of five active volcanoes and approximately 160 volcanic events since 1500 CE. Unique to this region are the *Araucaria araucana* trees that grow between ≈600 and ≈2000m asl. We sampled ≈30x *Araucaria araucana* trees and ≈20x *Nothofagus dombeyi* (also endemic to Southern Chile and Argentina) across three sites: two near active Andean volcanoes, and a third control site upwind of volcanic activity in the coastal mountain range. We will examine total Hg concentrations in the tree rings across the temporal range of their growth. Sampling resolution will vary between 1 and 10 rings per sample depending on the volcanic activity of the period corresponding to each tree ring sample. Ring widths of trees within each site will be measured and used (1) for cross-dating with dendrochronological archives for the southern South America region and (2) to determine if the volcanic activities themselves impacted tree growth. Data will provide information on the impact volcanic emissions have on local forests and provide critical information on atmospheric Hg levels in the Southern Hemisphere both pre- and post-industrialization.

## Research on mercury pollution control and resource utilization technology of industrial flue gas

Qu Z<sup>1</sup>

<sup>1</sup>Shanghai Jiao Tong University

Coal-fired flue gas and non-ferrous metal smelting flue gas are the two major sources of anthropogenic atmospheric mercury emission in China. Meanwhile, they are also two important mercury emission industries that are clearly required to take mercury pollution control measures under the Minamata Convention on Mercury. Therefore, research on mercury pollution control technology for flue gas of these two industries is significant to achieve mercury pollution reduction in these two industries. However, there are obvious differences in mercury emission characteristics between coal-fired flue gas and non-ferrous smelting flue gas. Generally, the volume of coal-fired flue gas is relatively large and the mercury concentration of flue gas is low, so it is advisable to adopt the mercury pollution control technology of abandonment. However, the volume of non-ferrous smelting flue gas is relatively small, the concentration of mercury in flue gas is very high, and the concentration of coexisting sulfur oxides is also very high. Thus, it is necessary to adopt recycling mercury pollution control technology to adapt to high concentration of sulfur dioxide interference for non-ferrous smelting flue gas. This study is aimed at the characteristics of coal-fired and non-ferrous smelting flue gas, and introduces some research progress of our team in recent years.

## Identifying the role of native versus non-native wetland vegetation to influence methylmercury production

Johnson M<sup>1</sup>, Eckely C<sup>2</sup>, Luxton T<sup>3</sup>, Bollman M<sup>1</sup>, Wilkin R<sup>4</sup>, Eagles-Smtih C<sup>5</sup>, Goetz J<sup>3</sup>, Crawford J<sup>2</sup>

<sup>1</sup>U.S. Environmental Protection Agency, <sup>2</sup>U.S. Environmental Protection Agency, <sup>3</sup>U.S. Environmental Protection Agency, <sup>4</sup>U.S. Environmental Protection Agency, <sup>5</sup>U.S. Geological Survey

Wetlands are often associated with elevated concentrations of methylmercury (MeHg) because the conditions are favorable to methylating microbes, such as stagnant/low oxygen water and higher nutrient and organic carbon concentrations compared to other aquatic systems (i.e., rivers, lakes). Wetlands can become dominated by exotic/invasive species. A common invasive wetland species is reed canarygrass (*Phalaris arundinacea*), which is distributed globally and can out-compete native vegetation. It is a fast-growing and high-density plant species that can produce large quantities of organic matter. The objective of this study was to determine if wetland plants influence MeHg production and if removing reed canarygrass and replacement with native species can decrease MeHg production. Controlled experiments were performed in mesocosms containing different wetland plant species. In addition to reed canarygrass, common/soft rush (*Juncus effusus*), Sitka willow (*Salix sitchensis*), daggerleaf rush (*Juncus ensifolius*), and Baltic rush (*Juncus balticus*) were all planted in triplicate mesocosms containing mercury-contaminated sediments. The plants were selected to identify if variables such carbon storage and nitrogen fixation influence sediment redox conditions and microbial methylation. In addition, field measurements from wetlands that are dominated by reed canarygrass were compared to areas that have been restored to native vegetation. Measurements of sediment and porewater were analyzed for total-Hg (THg) and MeHg concentrations as well as common ancillary parameters associated with methylation (i.e., major anions, sulfide, reduced iron, oxidation-reduction potential, dissolved oxygen). The project results show that wetland plant community composition can have a significant impact on MeHg production, and that wetlands that have had reed canarygrass removed and restored to lower density native species have significantly lower THg and MeHg in the porewater as well as lower dissolved organic carbon and higher a higher oxidation-reduction potential. Overall, these results highlight the potential to utilize wetland vegetation management as a strategy to decrease MeHg production.

## Characteristics of Brain Tissue Damage and Neurological Symptoms Caused by Methylmercury

Takaoka S<sup>2</sup>, Fujino T<sup>2</sup>

<sup>1</sup>Minamata Kyoritsu Hospital, <sup>2</sup>Minamata Kyoritsu Hospital

Although it is well known that methylmercury damages nerve cells, there are few areas where such severe neurological damage has been observed as in Iraq and Japan. In Minamata disease in Japan, there was a wide range of patients, from those with all the symptoms of Hunter-Russell syndrome to those with almost none.

While the severity of the syndrome tends to be more pronounced in patients with more severe disease, the presentation and course of the syndrome vary widely. This may be due to the amount of exposure, the nature of exposure, and individual differences. The mechanism of methylmercury-induced nerve tissue injury is discussed by examining the nature of these symptoms together with cellular and animal experimental data and pathological data.

The syndromes and findings we focused on were characteristics of early severe Minamata disease cases, characteristics of long-term chronic Minamata disease cases, single massive exposure accident case at Dartmouth University, human pathological findings, animal experiments, and cell experiments.

Based on these findings, the following characteristics of methylmercury-induced neurological syndromes may exist: 1. the neurotoxic effects of methylmercury vary depending on the dose, duration of exposure, and age of the individual; 2. the central nervous system is composed of a large number of cells and is plastic, and a significant number of neurons must be injured for symptoms to appear; and 3. At the same time, there can be a time lag of weeks, months, or years between elevated methylmercury blood levels and the onset of neurological symptoms. 4. Neurological damage due to methylmercury toxicosis can present as a complex syndrome, involving negative factors of exposure and aging and positive factors of brain plasticity.

In order to analyze the pathogenesis of methylmercury toxicosis, statistical estimation should be made with these factors in consideration.

53

## Mercury stable isotopes link deep-diving behavior to twilight-zone foraging in pelagic sharks from the eastern Pacific.

Le Croizier G<sup>1</sup>

<sup>1</sup>Ird

Many marine predators that primarily use surface waters make frequent forays into the twilight zone of the deep ocean, between 200 and 1000 meters. Although foraging on mesopelagic prey is one of the most plausible functions of deep-diving behavior, robust evidence supporting this hypothesis remains surprisingly limited. Here, we used stable mercury isotopes to characterize the proportion of mesopelagic prey in the diet of eight species of pelagic sharks from the eastern Pacific. By comparing these dietary estimates with telemetry data from the literature, we showed that mesopelagic prey consumption increased with shark maximum diving depth (median, mean, absolute) at the species level, confirming twilight-zone foraging as primary functional role for deep diving. Performing reversed vertical diel migrations as well as spending time in surface waters decreased the proportion of mesopelagic prey in the shark diet, likely explained by a vertical spatiotemporal mismatch between prey and predators. Our study provides strong evidence for the feeding motivation of deep ocean use by pelagic sharks, suggesting that future mesopelagic fisheries may significantly alter the trophic linkages between surface-oriented predators and twilight zone fauna.

54

## Tuning compliance strategies to regional needs

Sloss L<sup>1</sup>

<sup>1</sup>Unep Coal Partnership

Under Article 8 of the UN Minamata Convention, signatory nations must evaluate and then “control and, where feasible” reduce emissions of mercury from named sources. For developed nations, monitoring and control of emissions has been going on for years, sometimes decades. For emerging economies, which are often heavily reliant on coal for their growing economies, the evaluation and control of emissions requires a knowledge and technology leap. Whilst Western economies turn their backs on coal, this is not an option for many developing nations that have no affordable alternatives.

Countries such as India and Indonesia are adopting emission standards for coal plants which are as stringent as those in Europe and the USA. This requires them to achieve, in 5 years or less, what richer countries have taken decades to achieve. And, whilst it may be assumed that strategies and technologies for emission reduction can be cut and pasted to all coal plants – this is not the case. Different fuel characteristics, plant configurations, grid strategies and energy policies mean that many emerging regions will take very different approaches to emissions reduction, with more focus on plant efficiency and fuel switching as well as a demand for more flexibility from coal plants to maintain grid stability as the proportion of renewable energy increases. All this poses a challenge for emission reduction and will require a broad and considered strategy to ensure that emissions of species such as mercury are still adequately addressed.

55

## Results of the workshop- Measurement of Atmospheric Mercury: Assessment of new measurement and calibration methods and development of a path forward

Gustin M<sup>1</sup>

<sup>1</sup>University Of Nevada

Mercury (Hg) researchers have made progress in understanding atmospheric Hg, for example, we now know that ambient HgII concentrations can be 2 to 20% of atmospheric Hg. This is in contrast to earlier work that stated that Hg<sup>0</sup> was 99% of that in the air. Knowledge developed over the past ~10 years has pointed to existing challenges in current methods for measuring atmospheric Hg concentrations and the chemistry composition of HgII compounds. In October 2023, a group of 26 atmospheric Hg experts convened on the campus of the University of Nevada-Reno, USA, to attend a US National Science Foundation supported workshop. The workshop focused on bringing together scientists that measure atmospheric mercury to discuss the benefits and limitations of current measurement and calibration methods, as well as suggest needs for new measurement systems. Atmospheric Hg measurements are critical to addressing questions regarding mitigation of impacts to humans, wildlife, and ecosystems, since the atmosphere is the primary pathway for Hg input into ecosystems. Workshop participants identified specific gaps in data and instrumentation, suggested development of new air sampling systems and improvements to existing methods, and discussed how method results fit within our understanding of atmospheric chemistry and monitoring network needs. Major conclusions include: [1] new methods need to be adopted to measure gaseous elemental Hg versus total gaseous Hg; [2] current methods to measure gaseous oxidized (GOM) and particulate bound Hg (PBM) are inadequate and new methods need to be developed to make these measurements accurately; [3] it is important to determine the chemical composition of GOM compounds, and our current capabilities are limited; [4] field deployable GOM calibrators are needed and must be traceable to NIST standards; and [5] current mercury monitoring networks need to reassess methods being used.

## Speciation and Distribution of Mercury in the Water Column and Sediments of the Bering and Chukchi Seas

Inman H<sup>1</sup>, Mason R<sup>1</sup>, He Y<sup>3</sup>, Hammond D<sup>2</sup>

<sup>1</sup>Department of Marine Sciences, University Of Connecticut, <sup>2</sup>Department of Earth Sciences, University of Southern California, <sup>3</sup>Florida International University

The Arctic is a sink of atmospheric and terrestrial mercury (Hg) and source of monomethylmercury (MMHg). The bioaccumulation of MMHg into seafood and marine mammals consumed by people is an important regional human health concern. The atmospheric deposition and evasion of Hg in the Arctic is not well constrained due to ice cover and other factors, which are changing rapidly due to climate change. Additionally, sediment and riverine inputs of Hg and MMHg to the water column are poorly constrained. Estimating the net external inorganic Hg and MMHg inputs to the Arctic is complicated by the lack of information on the distribution of mercury species in the polar mixed layer and sediments, and of the internal conversion between Hg forms in these environments. Here we report the results of studies completed in May/June 2021 aboard the RV Sikuliaq in the Bering and Chukchi Seas. Waters were mostly shallow (<100 m) and water and sediment samples were collected and analyzed for elemental Hg (Hg<sup>0</sup>), dimethylmercury, total Hg and total methylated mercury, to assess the distribution of mercury species through the water column, sediments, and potential fluxes. The sources and sinks for Hg and MMHg will be discussed, and the relative role of sedimentary inputs evaluated. Our data has further resolved the distribution of mercury species in the water column and sediments in this area and the exchange of Hg at the sediment-water and ocean-atmosphere interfaces.

## Factors influencing the air-sea exchange of mercury in the Gulf of Maine

Mason R<sup>1</sup>, Inman H<sup>1</sup>, Smith S<sup>1</sup>, Taylor V<sup>2</sup>

<sup>1</sup>Department of Marine Sciences, University Of Connecticut, <sup>2</sup>Department of Earth Sciences, Dartmouth College

Mercury (Hg), primarily as methylmercury (MeHg), is a neurotoxin that biomagnifies up the marine food chain and is a health concern for humans and wildlife. Anthropogenic inputs have enhanced atmospheric Hg concentration and its deposition to ocean waters as well as increased terrestrial inputs. The net conversion of ionic Hg (HgII) to elemental Hg (Hg<sup>0</sup>) in surface waters results in its loss to the atmosphere via gas exchange, thus mitigating the increase in ocean Hg. Previous studies have suggested that the efficiency of conversion to Hg<sup>0</sup> is less for coastal waters compared to offshore. Therefore, understanding the factors controlling Hg<sup>0</sup> concentration and evasion in coastal ecosystems is important, especially as these are often major fishing grounds, and because of additional point source Hg contamination inputs. Additionally, climate change has impacted terrestrial inputs of Hg and other constituents that can alter the net formation of Hg<sup>0</sup>. To examine these factors in detail we collected high resolution measurements of dissolved gaseous Hg, primarily Hg<sup>0</sup>, in the Gulf of Maine (GoM) and the Penobscot River, its largest freshwater source and a historically Hg contaminated watershed, during cruises between April 2023 and April 2024. The surface concentrations of Hg<sup>0</sup> showed distinct seasonal trends and Hg<sup>0</sup> concentrations were higher in the GoM compared to the Penobscot even though total Hg concentrations were higher in the estuary. We will compare surface Hg<sup>0</sup> data to total Hg concentration, and other ancillary variables such as DOC, and its chemical characteristics, and chlorophyll concentration, as well as physical variables, to determine the primary factors influencing its concentration and evasion flux. Finally, data will be compared to studies in the GoM of 15 years ago to understand how the dynamics of the air-sea exchange of Hg has been affected by climate change and changes in global Hg emissions.

58

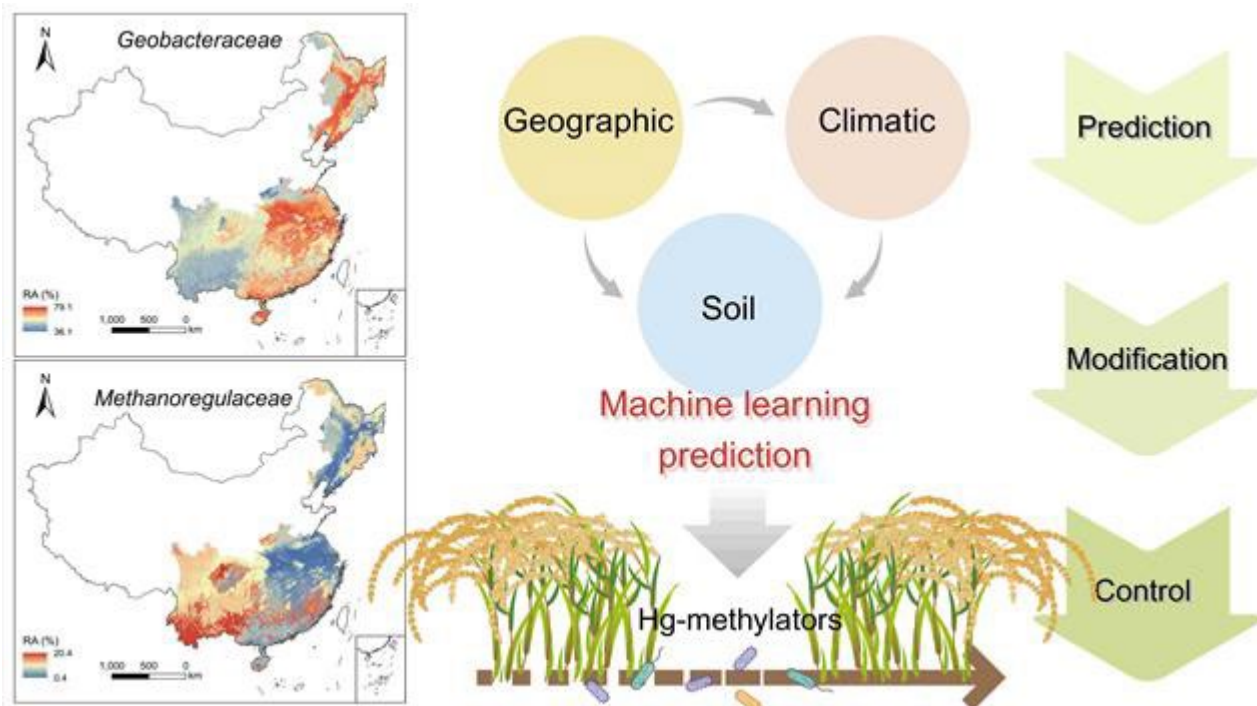
## Prevalence and environmental preference of putative mercury methylating microorganisms in paddy soils across China

Hao Y<sup>1</sup>

<sup>1</sup>Huazhong Agricultural University

Potent neurotoxin methylmercury (MeHg) in soils is mainly produced from the transformation of inorganic mercury (Hg) by microorganisms carrying the *hgcAB* gene pair. Paddy soils are known to harbor a highly diverse microbial community exhibiting contrasting capacity for Hg methylation; however, their distribution and environmental drivers remain unknown at a large spatial scale. In the present study, we analyzed soil Hg-methylating communities from main rice producing areas of China across ~3,600 km transects and a ~1300 m altitudinal gradient. Through amplifying and sequencing a portion of *hgcA* genes, we found a total of 8430 phylotypes of Hg-methylators living in the paddy soils of China, exhibiting similar phylotype richness of Hg methylators despite their distinct relative abundance among locations. *HgcA*<sup>+</sup> Geobacteraceae, Smithellaceae and Methanoregulaceae were identified as the most dominant families with significant associations with MeHg production, collectively accounting for up to 77% of total Hg methylators. Hierarchical partitioning analyses revealed that pH was the main driver of *hgcA* genes from Geobacteraceae (17%) and Methanoregulaceae (16.6%), while it was altitude for *hgcA* genes from Smithellaceae (21.4%). We then used a machine-learning algorithm to predict the distribution of these three dominant *hgcA*<sup>+</sup> families in paddy soils of China. Our work provides novel insights into the prevalence and environmental preference of Hg-methylators in paddy soils and could contribute essential microbial parameters for the development of future models predicting Hg methylation.

### Abstract Graphics



## Seasonal variations in mercury species and selenium in plankton from Kagoshima Bay, southern Kyushu, Japan: The impact of active submarine volcanoes on ecosystems

Tomiyasu T<sup>1</sup>, Nozoe C<sup>1</sup>, Uwashitomi H<sup>1</sup>, Wakimaru T<sup>1</sup>, Kodamatani H<sup>1</sup>, Kanzaki R<sup>1</sup>

<sup>1</sup>Kagoshima University

The seawater and plankton sampling were conducted every 2 months from 2019 to 2022 at inner and central parts of Kagoshima Bay; submarine volcanic activity continues at a bottom of 200 m depth in the inner part. Water samples were collected with a CTD-Rosette sampling system, and were used for reactive gaseous Hg, Hg(II), particulate Hg and filtered total Hg analysis. The plankton samples were collected with plankton net by vertical halting at 0 - 140 m and 140 – 200 m at just above the submarine volcano and at 0 – 200 m at the central part of the Bay. The collected plankton samples were separated to phytoplankton (< 100 µm) and zooplankton (> 100 µm), and were used for analysis of organic Hg, inorganic Hg and total Se. The inorganic Hg concentrations in phyto- and zooplankton collected at 140 - 200 m depth at just above the submarine volcano were  $1.42 \pm 0.83$  mg/kg and  $0.37 \pm 0.33$  mg/kg, respectively. The organic Hg concentrations in phyto- and zooplankton were  $0.15 \pm 0.16$  mg/kg and  $0.14 \pm 0.09$  mg/kg, respectively. These values were one order of magnitude higher than the values in plankton collected in the central part of the bay. The values in plankton collected in the inner part of the bay increased in summer and decreased in winter, which was consistent with changes in mercury concentrations in seawater affected by volcanic activity. On the other hand, the Se concentrations in phyto- and zooplankton for the inner part of the bay were  $1.45 \pm 0.86$  mg/kg and  $1.75 \pm 0.82$  mg/kg, respectively, and for the central part  $0.98 \pm 0.61$  mg/kg and  $1.62 \pm 0.77$  mg/kg, respectively. No significant differences were observed among them.

## Mercury Management - First temporary mercury storage unit and institutional protocol in Colombia

Rodriguez A<sup>1</sup>

<sup>1</sup>Pure Earth

Although the use of mercury in mining activities has been prohibited in Colombia since June 2018, there is no clear procedure for miners, environmental authorities, and government agencies on the proper management of mercury for its final disposal.

Under the project “Promoting Responsible Recovery and Handling of Mercury from Contaminated Artisanal Gold Mining Tailings in Colombia”, funded by the US Department of State (DoS), the NGO Pure Earth developed a Technical Protocol for the handling, reception, transportation, and temporary storage of mercury in order to provide for the adequate final disposal of the toxic heavy metal in a safe manner.

The Protocol provides the necessary tools to help resolve existing regulatory, administrative, and technical gaps in the responsibility for mercury management, from specifications on the necessary forms for the chain of custody, storage containers, and required personal protection equipment to the methodology for monitoring mercury vapors in the facilities where the storage unit was installed, among other considerations.

The involvement of various government agencies in the process, such as the Office of the Attorney General of Colombia, the Ministry of the Environment, the Ministry of Mines, and regional environmental authorities, made possible the generation of a robust Protocol, easy to implement and capable of being replicated in other countries.

As part of the process, a mercury storage unit was installed, which is considered the first temporary mercury storage unit in Latin America. Although it is a small pilot, its scaling and replicability in other locations is very feasible.

The technical specifications are:

Temperature range of 2 to 12 degrees Celsius.

Data logger - Electronic recording system of temperatures.

External structure in hot-dip galvanized steel, anti-corrosion treated.

Stainless steel internal structure.

Completely sealed, silent and highly efficient compressor.

Total capacity of 240 kilos of Hg.

Monitoring of mercury vapors.

61

## Advances in permeation tube-based mercury calibration

Lyman S<sup>1</sup>

<sup>1</sup>Utah State University

Permeation tubes have been used as standards for elemental and oxidized mercury (Hg) compounds for decades, but no established method exists for traceable, certified permeation tube-based calibration of Hg instrumentation. We have developed several automated calibrators for elemental and oxidized Hg and have recently demonstrated that two of our elemental Hg and HgBr<sub>2</sub> permeation tubes maintained a stable permeation rate in three locations across two continents over a period of one year. We have validated these permeation tubes against several alternative methods, including two that are directly traceable to NIST standards. Our permeation tube-based calibrations of atmospheric Hg measurements at Storm Peak, Colorado, U.S.A., are the first NIST-traceable oxidized Hg calibrations ever conducted in a field setting.

This presentation will discuss some of the key features and challenges of permeation tube-based Hg calibration, including (1) permeation tube design, characterization, and stability over time, (2) NIST-traceability of permeation tube output via gravimetric and other methods, (3) progress and challenges with transporting Hg compounds through valves and tubing and into the device to be calibrated, (4) progress with non-halide Hg compounds, (5) dynamic dilution calibration with permeation tube-based systems, and (6) uncertainty budgets.

62

## GEOS-Chem is unable to reproduce high oxidized mercury episodes in western U.S.A.

Lyman S<sup>1</sup>, Elgiar T

<sup>1</sup>Utah State University

We measured elemental (Hg<sup>0</sup>) and oxidized (Hg<sup>II</sup>) mercury, along with a suite of ancillary chemical and meteorological parameters, at Storm Peak Laboratory, a high-altitude station in the Rocky Mountains of Colorado, in 2021 and 2022. We used a cation exchange membrane-based dual channel method to measure Hg, and we used NIST-traceable permeation tubes in a field-deployable calibrator to verify measurement accuracy. Calibrations showed that the dual channel instrument accurately quantified Hg<sup>0</sup> and HgBr<sub>2</sub> in ambient air ( $92 \pm 9.6\%$  and  $100 \pm 4.1\%$  of expected recovery, respectively).

We used the GEOS-Chem 3D photochemical model with the recent Shah et al. (2021) chemical mechanism to simulate a measurement period in June 2021 with sustained high Hg<sup>II</sup>. Our Hg<sup>0</sup> measurements were similar to those simulated by GEOS-Chem, but Hg<sup>II</sup> in the model was less than 20% of measured values. The model captured temporal trends in Hg<sup>0</sup> and Hg<sup>II</sup> well ( $r^2$  values for the relationship between measurements and model output ranged from 0.53 to 0.79), and the measurements and model output both showed a strong negative relationship between Hg<sup>0</sup> and Hg<sup>II</sup>. We increased the reaction rate of Hg<sup>0</sup> + Br, decreased the rate of decomposition of HgOH, and increased the reaction rate of HgBr + O<sub>3</sub> and HgOH + O<sub>3</sub>, in three separate GEOS-Chem sensitivity tests. All of the tests resulted in increased Hg<sup>II</sup>, but average Hg<sup>II</sup> was still only 22-25% of measured values, and the additional oxidation increased Hg deposition, leading to unrealistically low Hg<sup>0</sup>. This provides evidence that not just Hg<sup>0</sup> oxidation, but also Hg emissions and deposition, are inadequately represented in the model.

## Exploring the concept of climate penalty in the context of mercury contamination

Angot H<sup>1</sup>, Mattio D<sup>1</sup>, Bertrand Y<sup>1</sup>, Bonfanti N<sup>2,3</sup>, Bourgeois I<sup>3</sup>, Gateuille D<sup>2</sup>, Gautier E<sup>1</sup>, Guédron S<sup>4</sup>, Sabatier P<sup>2</sup>

<sup>1</sup>Univ. Grenoble Alpes, CNRS, INRAE, IRD, Grenoble INP, IGE, Grenoble, France., <sup>2</sup>EDYTEM, CNRS, Université Savoie Mont Blanc, Le Bourget du Lac, France., <sup>3</sup>Univ. Savoie Mont Blanc, INRAE, CARTEL, Thonon-Les-Bains, France., <sup>4</sup>ISTerre, Univ. Grenoble Alpes, Université Savoie Mont Blanc, CNRS, IRD, IFSTTAR, Grenoble, France.

Mercury (Hg) global emissions peaked in the 1970s but have since declined due to environmental policies, resulting in reduced atmospheric deposition to ecosystems and biota. This impact is well-documented in environmental archives and the majority of biomonitoring studies dating back to the 1970s or 1980s. However, regional disparities arise as climate change can counteract these policy efforts by remobilizing legacy reservoirs, presenting a challenge for research and policy communities in understanding its influence on environmental trends and ecosystem recovery. Our primary goal is to differentiate between anthropogenic and climate-driven contributions to observed environmental trends and quantify the climate penalty —i.e., the impact of climate change on ecosystem recovery time. Despite its environmental and societal implications, quantifying the climate penalty has, to the best of our knowledge, not been achieved before. By presenting results from sedimentary archives in two neighboring alpine lakes —one characterized as a rain gauge type lake reflecting changes in atmospheric Hg deposition, and the other as a proglacial lake reflecting changes in both atmospheric deposition and glacial melt input— we aim to shed light on the potential significant difference in recovery rates expected as a result of ongoing glacial melt. Although region dependent, our objective is to emphasize the necessity of studies addressing climate change impacts on the Hg cycle, especially in evaluating the effectiveness of the Minamata Convention.

## Migration and methylation of mercury in legacy contaminated sites driven by climate change

Liang X<sup>1</sup>, Zhao J<sup>2</sup>, Liu Y<sup>3</sup>

<sup>1</sup>Northwest A&F University, <sup>2</sup>Zhejiang University, <sup>3</sup>Huazhong Agricultural University

Legacy-contaminated sites act as significant sources of mercury (Hg) to their surrounding environments. While Hg pollution characteristics in industrially contaminated sites have been extensively documented, little is known about vertical migration and methylation of Hg in these sites, particularly in response to extreme precipitation events. Here, we conducted column leaching assays with soils collected near a contaminated site under different extreme precipitation patterns. We observed that elevated frequency of simulated precipitation profoundly increased the vertical migration of Hg through the soil profile, whereas precipitation intensity showed minimal impacts. The majority of leached Hg was prone to migrate vertically within the top 10 cm of the soil profile. Furthermore, rainfall stimulated microbial Hg methylation, as demonstrated by enhanced production of methylmercury in both simulated and field contaminated soils. We identified specific microbial taxa including Geobacteraceae, Desulfuromonadaceae, Syntrophaceae, Oscillospiraceae, and Methanomicrobiaceae as key predictors of methylmercury production, which differed from those typically observed in agricultural soils. Particularly, the relative abundance of these dominant Hg methylators significantly increased during rainfall-induced leaching compared to that of the control, suggesting the crucial yet previously overlooked impacts of increased precipitations on the process of microbial Hg methylation in contaminated sites. Given the rising incidence of extreme precipitation events worldwide due to climate change, this study highlights the significance of assessing Hg mobility and microbial transformation in legacy contaminated sites.

## Potential human exposures to Hg in staple crops from agricultural areas impacted by Artisanal Small-scale Gold Mining (ASGM) activities.

Eboigbe E<sup>1</sup>, Odukoya A, Veerasamy N, Anene N, McLagan D

<sup>1</sup>Queen's University

Artisanal small-scale gold mining (ASGM) is a rapidly expanding sector that manifests complex political, social, and environmental issues. Chief among these problems is the emissions (air) and releases (terrestrial/aquatic) of mercury (Hg) that is employed as the primary method of recovering gold from mined ores and sediments (Hg-gold amalgam burning). Recent work with stable Hg isotopes has demonstrated stomatal uptake of elemental Hg by higher plants to dominate Hg deposition in vegetated systems. ASGM activities are indiscriminate in where they occur and often impact highly productive forest, wetlands and agricultural areas. Considering the importance of the latter for sustaining human populations and the extensive atmospheric emissions of Hg from ASGM activities, the stomatal uptake pathway of Hg by staple crops in agricultural areas impacted by ASGM is worthy of scientific investigation. In this study, we examine potential human exposure pathways in ASGM impacted agricultural areas in Nigeria using a total systems approach. The study works collaboratively with a local mining community in Nigeria to facilitate knowledge dissemination with impacted individuals and to ensure a more holistic study design. Samples of tubers/grains, leaves, roots, stems of maize, cassava, and peanuts were collected from three farms along a transect away from an active ASGM site (Farm 1 closest; Farm 3 furthest). Air (passive samplers) and soils were sampled at the ASGM site and the three farms. Preliminary data from soils (ASGM site: 8.5mg/kg; Farm 3: 0.015mg/kg) and plant leaves (Farm 1: 0.4mg/kg; Farm 3: 0.013mg/kg) confirm Hg exposure gradient away from the mine. Samples of ASGM miner's hair, (qualitative) dietary surveys, and cooked tuber/grain samples were collected and will be analysed in on-going work to more effectively evaluate human exposures. We also intend to analyze samples for Hg stable isotopes to assess the processes controlling Hg cycling through this potential exposure pathway.

### Abstract Graphics



## Experimental exposure of a model fish species to methylmercury and food restriction reveals interactive effects of stressors and complex responses at multiple reproductive endpoints

Zabala J<sup>1</sup>, Portugal-Baranda T<sup>1</sup>, Ortiz-Zarragoitia M<sup>1</sup>

<sup>1</sup>University of the Basque Country UPV/EHU

Effects of methylmercury (MeHg) in animal reproductive success have been well studied in laboratory conditions and exposure/response curves developed for several taxonomic groups. However, results of observational studies with wildlife species often depart from expectations derived from laboratory results. Interactions between contaminants and other natural stressors are commonly invoked to explain these divergences. Food restriction is, arguably, the most common natural stressor. Yet, its interactive effects with contaminants remain largely unassessed. We exposed 228 adult zebrafish to MeHg (5 ppm in food) and food restriction (75% of the recommended daily food intake) in four groups: control; MeHg; food restriction; and MeHg and food restriction. We predicted the combined exposure to be interactive and more deleterious, differing from the sum of individual effects. The experiment lasted 41 days and included three consecutive reproductive occasions. We assessed reproductive success using 8 endpoints: laying probability; clutch size; average successful clutch size; egg fertility; probability of fertile eggs producing live larvae at 120 hours post fecundation (hpf); probability of a not abnormal larva at 120 hpf; number of viable larvae at 120 hpf per reproductive occasion; and probability of an egg resulting in a larva viable at 120 hpf.

We found interactive effects between MeHg and food restriction in seven out of eight endpoints. However, combined effects were not always deleterious. Fish exposed to combined stressors laid smallest clutches, but their eggs were most fertile and showed the highest number of viable larvae per reproductive attempt of all groups. While hormetic effects could be invoked to explain some of the results, life history plasticity seems more plausible. Combined stressors might have triggered reproduction/survival trade-offs with consequences beyond the duration of the experiment. Studies assessing lifelong performance of exposed animals and transgenerational effects might elucidate the net cost of combined exposure.

Funding: IT-1571-22 and IT-1743-22.

## Climate-induced changes in mercury deposition in South-Eastern Australia, a study from the last glacial maximum to the mid-Holocene (6,500 to 20,000 years BP)

Schneider M<sup>1</sup>, Schneider L<sup>1</sup>, Cadd H<sup>2</sup>, Thomas Z<sup>3</sup>, Stannard G<sup>4</sup>, Haberle S<sup>1</sup>

<sup>1</sup>Australian National University, <sup>2</sup>University of Wollongong, <sup>3</sup>University of Southampton, <sup>4</sup>La Trobe University

Mercury (Hg) is a volatile metal with a large atmospheric emission and transport capacity of international concern. The biogeochemical cycle of Hg can be influenced by a changing climate, yet our understanding of the specific impact of climate factors on the Hg cycle in the Southeast Asian region remains limited. Here we use a multi-proxy framework supported by AMS 14C dating, to interpret climatic events in South-Eastern Australia for the past 20,000 years from the sediments of Blue Lake in Australia's Alpine region. By combining Hg analysis with pre-existing Antarctic temperature records and modelled outputs, carbon-to-nitrogen ratios (C:N), charcoal, and pollen analysis, we find Hg records within Blue Lake sediments reflecting variations in temperature records. Mercury deposition fluxes in Blue Lake were predominantly associated with atmospheric fallout rather catchment inputs. The Hg and C:N results indicate high wind activity in the Pleistocene, and provide evidence of the influence of the Antarctic Cold Reversal in Australia's Alpine Region, a period of lower temperature and rainfall between 14,400 and 13,900 years BP. Mercury increases substantially during a period of warming in the Holocene, while charcoal presents a minor relationship to the Hg flux variation. Our findings suggest that alteration in environmental temperature is the predominant driver of increases in Hg concentration and deposition fluxes in Blue Lake. A primary challenge in Hg research and climate change is disentangling changes in Hg attributable to anthropogenic activities from those caused by climate change. Our results indicate a discernible climate influence on Hg deposition fluxes in the Australian Alpine region, driven mainly by increases in temperature. This research forms part of a larger study aimed at understanding the influence of climate on the Hg cycle in southeast Australia and the Southern Ocean Islands.

## Long-term trends and patterns in mercury in atmospheric deposition, a lake-watershed mass balance and fish tissue analysis in the Adirondack region of New York

Driscoll C<sup>1</sup>, Olson C<sup>1</sup>, Montesdeoca M<sup>1</sup>, McIntyre P<sup>2</sup>, Jane S<sup>2</sup>, Beier C<sup>3</sup>, McHale P<sup>3</sup>

<sup>1</sup>Syracuse University, <sup>2</sup>Cornell University, <sup>3</sup>SUNY College of Environmental Science and Forestry

Mercury emissions have decreased markedly in the U.S. following shifts in energy sources and federal regulations. We report on long-term changes in mercury in atmospheric deposition and stream and lake water at Arbutus Lake in Huntington Wildlife Forest and more broadly on fish tissue in lakes in the Adirondack region of New York, USA. The Adirondacks is a remote forested region characterized as a biological mercury hotspot due to sensitivity to atmospheric mercury deposition. Long-term estimates of dry deposition of gaseous elemental mercury, gaseous oxidized mercury and litter mercury and wet mercury deposition have decreased consistent with decreases in emissions, while dry deposition of particulate bound mercury increased. Long-term measurements of tributary inflow and Arbutus Lake outflow show no significant changes in fluxes of total or methylmercury. These measurements were coupled with modeled soil evasion to develop a mercury budget for Arbutus lake-watershed. This analysis showed dry deposition to be the largest mercury source with evasion losses the largest mercury sink for the watershed. While components of the budget significantly changed over the monitoring interval (2005-2018), the watershed was a net sink for mercury inputs with no change in net mercury flux (mean value  $25.5 \pm 2.5 \mu\text{g}/\text{m}^2\text{-yr}$ ). Long-term mass balances showed Arbutus Lake was a net sink for total mercury and methylmercury with deposition to the lake surface the major input, and considerable year to year variability. Long-term measurements of length-adjusted mercury concentrations in brook trout since 2007 in five Adirondack lakes showed considerable year-to-year variability and no significant trends. Despite aggressive emission control measures and clear decreases in components of atmospheric mercury deposition, intensive monitoring of a lake-watershed and fish mercury has not revealed evidence of recovery suggesting the importance of ecosystem legacy mercury and climatic variability.

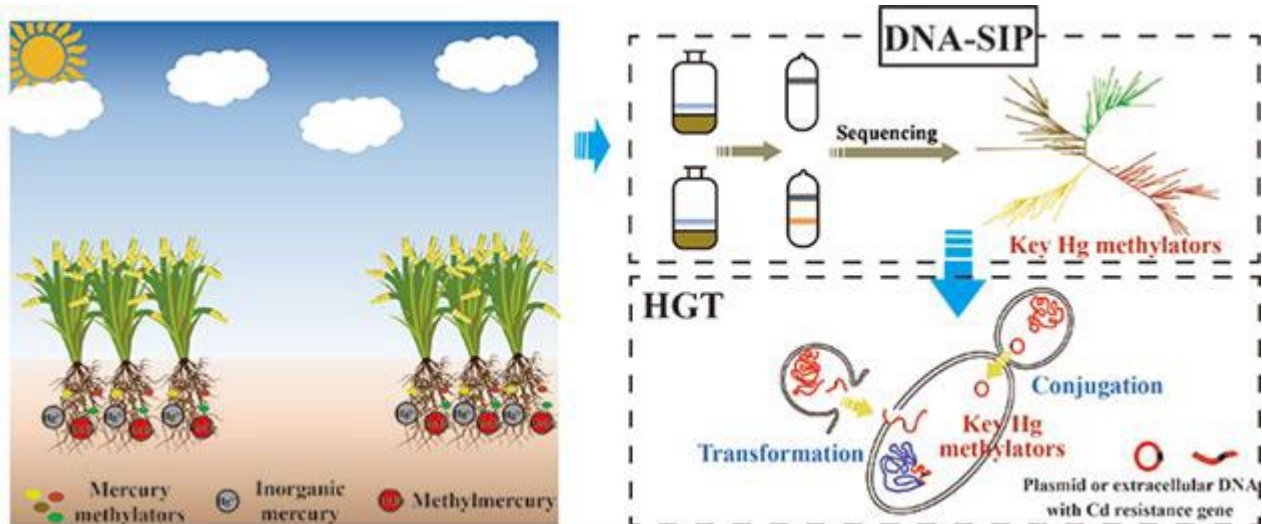
## Horizontal gene transfer mitigates the effect of cadmium on key mercury-methylating microorganisms in paddy soils

Pu Q<sup>1</sup>, Meng B<sup>1</sup>, Zhang K<sup>1</sup>, Liu J<sup>2</sup>, Abdelhafiz M<sup>1</sup>, Feng X<sup>1</sup>

<sup>1</sup>Institute of Geochemistry, Chinese Academy of Sciences, <sup>2</sup>Sichuan Agricultural University

The formation of neurotoxic methylmercury (MeHg) in paddy soil is primarily a microbially mediated process. However, the key Hg-methylating microorganisms and their adaptation strategy are not well understood. In this study, we combined, for the first trial, DNA-stable isotope probing (SIP), Hg isotope labeling technique and *hgcA* gene sequencing to identify *Geobacter* and *Anaerolinea* spp. as key Hg methylators in paddy soils. Metagenome-resolved genomes of key Hg-methylating microorganisms show coexistence of cadmium (Cd) resistance gene (*actR* gene) and mobile genetic element (*tnpA* gene, responsible for horizontal gene transfer, HGT), suggesting the potential for adaptation of key Hg-methylating microorganisms to Cd contamination through HGT. Cd at environmentally relevant concentrations significantly promoted *actR* gene transfer to a key Hg methylator (*Geobacter sulfurreducens* PCA) through conjugation and transformation, together with an increase in MeHg content produced by Cd-sensitive *G. sulfurreducens* PCA, showing evidence of adaptation of key Hg-methylating microorganisms to Cd contamination through HGT. We revealed that exposure to Hg and Cd contamination increases cell membrane permeability and results in enhanced rates of genetic exchange through HGT. Our findings offer insights for adaptation of key Hg-methylating microorganisms and highlight the need to evaluate Cd contamination for its potential role in increasing Hg methylation in Hg-sensitive areas.

### Abstract Graphics



## Towards a gas chromatography mass spectrometry method for quantification and characterization of ambient gaseous oxidized mercury compounds

Dunham-cheatham S<sup>1</sup>, Lown L, Gacnik J, Lyman S, O'Neil T, Gustin M

<sup>1</sup>University Of Nevada, Reno

Current methodologies for ambient gaseous oxidized mercury (HgII) compounds are limited and suffer from biases and interferences. Such limitations include the need to pre-concentrate HgII compounds onto surfaces prior to analysis and the inability to identify the chemistry of individual HgII compounds. Because different HgII compounds have different deposition velocities and effects on ecosystems, it is important to be able to determine not only the concentration of total HgII compounds, but also the chemistry of HgII compounds present. Previous work demonstrated that a custom-designed gas chromatography mass spectrometer (GC-MS) may be capable of quantifying and speciating HgII compounds from ambient samples using cryofocusing to pre-concentrate the samples (Jones et al., 2016). The GC-MS method was successful for Hg halides (e.g., HgBr<sub>2</sub>, HgCl<sub>2</sub>), but not for Hg(NO<sub>3</sub>)<sub>2</sub> nor HgO. Current efforts are aimed to improve upon the previous method and optimize the GC-MS method for other ambient HgII compounds. Having the ability to quantify and characterize the chemistry of ambient HgII compounds will improve global mercury biogeochemical models to better predict global cycling of these compounds and their impacts on human health and ecosystems.

## Assessing and Mitigating Human Health Risks in Mercury Mining Communities: A Case Study in the Kyrgyz Republic

Bartrem C<sup>1</sup>, Spearman S<sup>1</sup>, Sharshenova A<sup>2</sup>, Madmarova G<sup>1</sup>, Isirailov M<sup>3</sup>, von Lindern I<sup>1</sup>, von Braun M<sup>1</sup>  
<sup>1</sup>TerraGraphics International Foundation (TIFO), <sup>2</sup>International Higher School of Medicine, <sup>3</sup>Sanitary Hygienic Laboratory, Kadamjay District State Sanitary and Epidemiological Station

Batken Province, Kyrgyz Republic is home to dozens of active and abandoned Soviet-era mining operations. Since 2016, Kyrgyz authorities and international organizations have collaborated to identify and address environmental health risks in two mercury mining communities: Aidarken town, home to one of the world's last operational mercury mines and smelters, and Chauvay village, home to an abandoned mercury mine and smelter. TerraGraphics International Foundation (TIFO), the Kyrgyz Ministry of Health, and Doctors Without Borders partnered to determine key sources of exposure to heavy metals in these communities and implement interventions to improve health outcomes. Environmental sampling and human biomonitoring undertaken as part of a human health risk assessment revealed exceptionally high levels of antimony and arsenic, but modest amounts of mercury. Heavy metal exposures from direct soil ingestion and from consumption of vegetables grown in contaminated soil are likely contributors to elevated rates of noncommunicable disease in the region, including cardiovascular disease, kidney disease, and cancer. An integrated intervention that combines public health practice, environmental remediation, and medical treatment is being implemented to reduce adverse health outcomes. The case study provides an opportunity to highlight the critical importance of environmental exposures as a leading cause of disease and death globally. Exposure reduction is widely considered to be the most effective tool in reducing environmental disease; comprehensive risk assessments are required to identify exposure pathways of greatest concern and then develop feasible and sustainable interventions tailored to reduce those exposures. This presentation will explore assessment methodologies, review different types of interventions available, acknowledge current challenges in the field, review opportunities for monitoring, policy, and regulation, and highlight the importance of collaborative environmental health programs for communities and countries.

### Abstract Graphics



## A Decade of Environmental Health Response to Catastrophic Heavy Metal Poisoning in Artisanal Small Scale Mining (ASM) Communities in Zamfara, Northern Nigeria

von Lindern I<sup>1</sup>, Tirima S<sup>2</sup>, Mohammed Anka S<sup>2</sup>, Bartrem C<sup>1</sup>

<sup>1</sup>TerraGraphics International Foundation, <sup>2</sup>Doctors Without Borders

ASM extends across 80 countries, providing employment opportunities for nearly 13 million people, equivalent to the workforce in the formal mining sector. ASM produces 20% of the gold supply, 80% of sapphires, 20% of diamonds, 30% of cobalt, plays a pivotal role in supplying critical minerals for energy transition, and is a vital income source for rural communities. However, these notable benefits are juxtaposed against the associated environmental, health, and human rights injustices that present complex stories of opportunity and exploitation. In 2010 in Zamfara, Nigeria, Médecins Sans Frontières (Doctors without Borders/MSF) identified the worst childhood lead poisoning event ever documented. More than 17,000 people were acutely poisoned, >500 children died in six months, and mortality rates among children exceeded 30% in some villages. TerraGraphics International Foundation (TIFO) worked with local and state authorities to identify the origin of the outbreak: grinding, sluicing, and mercury amalgamation of lead-rich gold ores processed in residential areas. A multi-partner, 3-year emergency response of medical treatment, remediation, and safer mining practices successfully reduced mean blood lead levels from 170 ug/dl to <15 ug/dl, remediated >1000 homes, and treated >8500 children. Soil exposures were reduced by 87% and children's mortality rates decreased to <2%. Safer mining practices were developed and ASM was legalized. However, this positive narrative did not insulate the communities from the ravages of climate change, malnutrition, endemic disease, ethnic violence, terrorism, and kidnapping. ASM became the economic hope to address the loss of livelihood and security, but was also the target of those who would exploit the population. More than 30,000 people from 10 villages now largely live in Internally Displaced Peoples (IDP) camps. This presentation will summarize the 15-year project and environmental humanitarian response at the nexus of poverty, violence, and climate change in the Sahel.

### **Abstract Graphics**



## Receptor Modeling of Atmospheric Total Gaseous Mercury in Windsor, Canada

Xu X<sup>1</sup>, Wang X<sup>1</sup>

<sup>1</sup>University of Windsor

Hourly atmospheric Total Gaseous Mercury (TGM) concentrations were measured in Windsor, Ontario, Canada. Weather conditions and concentrations of other pollutants were also monitored. They are hourly temperature, relative humidity, wind speed, atmospheric pressure, and ambient concentrations of CO, SO<sub>2</sub>, NO, NO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>, and PM<sub>2.5</sub>. Principal component analysis (PCA) with varimax rotation was conducted to identify the factors influencing TGM concentrations using the above mentioned 12 parameters. When considering the five-year dataset, it was found that Fossil Fuel Combustion (large loadings of CO, NO, and NO<sub>x</sub>) is the dominant factor, followed by Diurnal Trend (large loading of temperature), Photochemistry (large loadings of O<sub>3</sub> and relative humidity with opposite signs) and PM<sub>2.5</sub>, Synoptic Systems (large loading of pressure), and Industrial Sulfur. The PCA results for each of the five years are largely consistent with each other and with the results obtained with the full dataset. When analyzed by season, Fossil Fuel Combustion and Diurnal Trend are the two common factors influencing TGM variability in all four seasons. Compared with three or four factors in other seasons, TGM was associated with only two factors in summer. One of them is Synoptic Systems (loading of pressure = 0.70) as a lead factor for TGM, indicating stagnant air during high-pressure systems resulted in TGM build-up, while low-pressure systems favored dispersion of TGM. In winter, the Transport factor (large loading of wind speed) suggests the transport of TGM by strong winds. Photochemistry was only significant in spring due to a comparatively stronger correlation between TGM and O<sub>3</sub> than in other seasons. Overall, the results of our PCA analyses indicate that the temporal variability of TGM in Windsor was affected by anthropogenic and surface emissions, and atmospheric transport, mixing, and reactions

## Predicting global impact of climate change on mercury dynamics in diverse ecosystems

Kawai T<sup>1</sup>

<sup>1</sup>National Institute For Environmental Studies

Future mercury levels in the environment and biota could fluctuate not only due to emission reductions but also due to environmental factors such as climate change. To systematically evaluate the effectiveness of emission reductions mandated by the Minamata Convention on Mercury, it is crucial to first assess and isolate the impacts of such environmental factors. This study aims to assess the impact of climate change on future mercury cycling in terrestrial and marine ecosystems using the in-house developed global mercury model named as FATE-Hg. Based on the climate, ecosystem, and reactant concentration data predicted using Earth System Models for various climate scenarios, FATE-Hg was used for past and future long-term simulations. Our analyses focused on the year 2100 for terrestrial elemental mercury (Hg<sup>0</sup>) evasion, divalent mercury (Hg(II)) export from land to coastal oceans, and methylated mercury (MeHg) content in particulate organic matter (POM), which is a base of marine food webs. Globally, both Hg<sup>0</sup> evasion and Hg(II) export showed a marked increase with warming, most remarkable under the fossil fueled-development scenario. However, MeHg content in marine POM demonstrated a minor decline with progressive warming. In contradiction to reported findings, which suggested a positive net Hg<sup>0</sup> evasion (i.e. evasion minus deposition), a negative net Hg<sup>0</sup> evasion was observed throughout the future simulation period, suggesting ongoing mercury accumulation in soil and vegetation. Regionally, the rate of increase in Hg<sup>0</sup> evasion was most significant in polar and subpolar regions, primarily dependent on temperature. MeHg content in marine POM showed a decreasing trend in the North and Central Atlantic and North Pacific, while increasing trend in the Antarctic Ocean as warming progressed. The study results highlight the necessity of considering climate change impacts alongside emission reductions while formulating mercury management policies.

## Assessing the impacts of gold mining to avian communities in the Peruvian Amazon

Sayers C<sup>1</sup>, Pisconte J<sup>2</sup>, Vega C<sup>2</sup>, Huaraca-Charca N<sup>4</sup>, Huamani Valdivia L<sup>2</sup>, Evers D<sup>3</sup>, Fernandez L<sup>2</sup>, Tingley M<sup>1</sup>

<sup>1</sup>University of California, Los Angeles, <sup>2</sup>Centro de Innovación Científica Amazónica, <sup>3</sup>Biodiversity Research Institute, <sup>4</sup>Inkaterra Asociación

The rapid expansion of gold mining in rivers throughout the global tropics presents a myriad of environmental disturbances that threaten the richest biological communities on Earth. Gold mining can lead to habitat degradation, pollution, disease transmission, and overexploitation—all important independent mechanisms of biodiversity loss—but the relative importance of each stressor remains poorly understood because each can interact with and amplify one another within mining landscapes. Birds are accessible and effective indicators of environmental pollution and global change, and thus present a valuable opportunity to understand the conservation externalities of this industry. We introduce a multi-year campaign to isolate and quantify the impacts of gold mining on terrestrial biodiversity in the Peruvian Amazon, in which we monitor how avian populations and communities respond to mercury pollution, deforestation, malaria infection, and hunting pressures along disturbance gradients and across land-use classes. While implementing a simple, cost-effective method for blood sampling in the tropics, we find many taxa occupying high trophic positions with mercury concentrations that exceed known thresholds for biological risk. In addition, we detect strong edge effects on capture rates and species accumulation among artisanal gold mining, large-scale gold mining, and protected sites. Our collective efforts stand to clarify mechanisms of ongoing biodiversity losses in Amazonia and inform future opportunities for sustainable gold mining at local to global scales.

## Novel data on methylmercury bioaccumulation in natural marine plankton from coastal North Atlantic Ocean

Baumann Z<sup>1</sup>, Myer P<sup>1</sup>, Mason R<sup>1</sup>, Mouw C<sup>2</sup>, Ciochetto A<sup>2</sup>, Sonnet V<sup>2</sup>, Sosik H<sup>3</sup>, Peacock E<sup>3</sup>

<sup>1</sup>University of Connecticut, <sup>2</sup>University of Rhode Island, <sup>3</sup>Woods Hole Oceanographic Institution

We investigated patterns in cellular quota (CQ), volume concentration factors (VCF) and biomass-based concentrations (CMeHg) of methylmercury (MeHg) in natural phytoplanktonic assemblages from subsurface estuarine and shelf waters of the North Atlantic Ocean. To gain insights into MeHg bioaccumulation in natural assemblages we used the Imaging FlowCytobot (IFCB) and flow cytometry to characterize the plankton community. We also cultured the heterotrophic dinoflagellate *Oxhyrris marina* with MeHg-spiked seawater in presence or absence of prey *Isochrysis galbana* to investigate if heterotrophy could significantly elevate cellular MeHg. Shelf seawater was sampled in fall 2019 during the NOAA EcoMon cruise across latitudinal (43-35°N) and cross-shelf gradients (e.g., salinity range: 31.6-36.3; temperature range: 12.3-26.7°C, and chromophoric dissolved organic matter range: 0.027-0.24 per m), and bi-weekly from a shore-based site in southern Narragansett Bay, Rhode Island to study temporal patterns in planktonic MeHg. Seawater, collected in trace-metal clean manner from IFCB's supply lines, was sequentially filtered to sort plankton cells into pico (<2µm), nano (2-20µm), and microplankton (>20µm). Filters and filtrates were analyzed for MeHg. Concentration ranges for dissolved MeHg in the surface shelf waters were comparable to the estuary (17.9 to 53.8 vs. 2.6 to 68 pg/L). As expected, based on surface area to volume ratios (SA/V), MeHg VCFs for the offshore plankton were highest in picoplankton (up to 5.7×10<sup>7</sup>), but surprisingly they did not decline as expected for nano- and microplankton in offshore waters, instead remaining comparable to nearshore values. Experimental uptake results showed that *O. marina* acquired more MeHg when able to feed, suggesting that MeHg in nano- and microplanktonic communities may be significantly impacted by food assimilation and not solely by uptake from the dissolved phase. We found that CQs were similar for pico- and nanoplankton (0.4-10 zmol/cell) and 3-4 orders of magnitude higher for microplankton (2×10<sup>2</sup>– 6.13×10<sup>3</sup> zmol/cell).

## Distribution in atmospheric gaseous elemental mercury in a region from the equator to sub-Arctic zone of the western North Pacific Ocean

Marumoto K<sup>1</sup>, Kondo F<sup>2</sup>, Tang C<sup>3</sup>, Noborio K<sup>3</sup>

<sup>1</sup>National Institute For Minamata Disease, <sup>2</sup>Japan Coast Guard Academy, <sup>3</sup>Meiji University

Air-sea exchange of Hg is one of the most important processes in the global Hg cycle in natural environments. In this study, we conducted the continuous monitoring of atmospheric gaseous elemental Hg (GEM) in the marine boundary layer along a latitudinal transect (mainly 155°E line) between the equator and 44°N of the western part of the North Pacific Ocean during the research cruise of R/V Hakuhou-maru (KH-22-07) from 30 June to 1 September in 2022. In addition, dissolved gaseous Hg (DGM) from the sea surfaces of the region between 30°N and 44°N were also measured semi-continuously using a gas-liquid equilibrator system, and the Hg evasion fluxes were calculated. The GEM concentrations in the region from the equator to 30°N were around 1.5 ng m<sup>-3</sup>, similar to the background levels of the Northern Hemisphere. In contrast, the GEM concentrations in the region north of 30°N are as high as approximately 2.0 ng/m<sup>3</sup>, suggesting that they are affected by westerly transport of anthropogenic Hg released in East Asia. These GEM concentrations were also higher than those observed at the ground-based station in the northern part of the Japan Islands during the same observation period. The DGM concentrations increased from north to south, and Hg evasion fluxes were greater around 30°N due to higher DGM concentrations and the strong winds. It is possible that both anthropogenic Hg and gaseous Hg released from the ocean contribute to the higher GEM concentrations in the air of the higher latitude zone of the North Pacific Ocean. This work is supported by JSPS KAKENHI Grant Number 21H04935.

## Over 10 years observations in atmospheric mercury at three sites in the Kyushu and Okinawa regions, Japan

Marumoto K<sup>1</sup>, Hattori T<sup>2</sup>, Nagasaka H<sup>2</sup>, Kuroda I<sup>3</sup>

<sup>1</sup>National Institute For Minamata Disease, <sup>2</sup>IDEA Consultants Inc., <sup>3</sup>Ministry of the Environment, Japan

The atmospheric mercury (Hg) concentrations were continuously observed over 10 years at Cape Hedo on the northern tip of Okinawa Island, Minamata, Fukuoka in the Kyushu islands located in the east edge of the East Asian region which is one of the main anthropogenic Hg emission sources in the globe. At sites other than Minamata, the concentrations of gaseous elemental Hg (GEM), gaseous oxidized Hg (GOM), and fine particulate bound Hg (PBM2.5), were monitored separately. In Minamata, the only GEM concentration was monitored. In the ambient air, GEM is the main component, and its concentration is about 100 times higher than that of GOM and PBM2.5. The average GEM concentrations in Cape Hedo, Minamata and Fukuoka during the all period were  $1.78 \pm 0.39$ ,  $1.78 \pm 0.40$  and  $2.05 \pm 0.72$  ng m<sup>-3</sup>, respectively, slightly higher in Fukuoka site, which is located in urban area. The long-term trends in the GEM concentrations at all sites have been gradually decreasing since the start of observations. These downward trends were also observed at other Asian observation sites such as Mt. Lulin in Taiwan, indicating that atmospheric Hg concentrations in the Asian region are on a downward trend over a wide area. The PBM2.5 concentrations in Fukuoka also showed a decreasing trend over time, suggesting that the long-range transport of PBM2.5 from the Asian continent, which is the major source of PBM2.5, was becoming less effect. On the other hand, no such declining phenomenon has been observed in GOM concentrations at Fukuoka. It is believed that sluggish economic activities or the relocation of industrial areas from coastal areas to inland areas in China may be influenced these decreasing trends in GEM and PBM2.5 concentrations.

## Atmospheric mercury emissions from key industries in China: Characteristics, Amounts and Influence

Fu Z<sup>1,2</sup>, Liao X<sup>1,2</sup>, Tian H<sup>1,2</sup>

<sup>1</sup>School of Environment, Beijing Normal University, <sup>2</sup>Center for Atmospheric Environmental Studies, Beijing Normal University

### ABSTRACT

Mercury (Hg) is a globally concerned pollutant for long due to its adverse effects on ecosystems and health. China was taken as the world's largest emitter for Hg, in which cement and thermal power industry accounting for the first two contributors. To support the unprecedented economic development in China, there have been 3200+ cement factories with an annual total output of 2.3+ billion tons cement, and 4300+ thermal power plants with an annual total consumption of 1+ billion tons of standard coal in China, causing a large amount of mercury emitted from these two key industries synchronously. Meanwhile, the two key industries have been undergoing increasingly strict air pollutants controls in the context of the national strategy of “synergizing the reduction of pollution and carbon emissions”, which shall reshape the spatiotemporal characteristics of Hg emissions in the two sectors. Here, we explored the changes of Hg emission characteristics in the two key industries based on field survey and literature reviews. Further, Hg emissions of the two industries, including different chemical species like Hg<sup>0</sup> and Hg<sup>2+</sup>, were estimated with detailed point source information and refined activity data in recent years. The driving forces resulting in collaborative emission reduction on Hg were also analyzed with counterfactual scenarios. This study would provide insights in the evolution, driving factors and environmental impacts of mercury emissions from key industries in China, and would offer scientific basis and important reference significance to make recommendations for further reduction on mercury emissions in the future. Keywords: mercury; emission characteristics; thermal power; cement industry; environmental and health impacts.

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\*Corresponding author: hztian@bnu.edu.cn

## Mercury Interaction with S-containing Molecules: Implications for Potential Methylation and Demethylation Regulation in a Sulfate Reducing Bacteria

Bakour I<sup>1,2</sup>, Isaure M<sup>1</sup>, Barrouilhet S<sup>1</sup>, Goñi-Urriza M<sup>1</sup>, Monperrus M<sup>1</sup>

<sup>1</sup>Université de Pau et des Pays de l'Adour IPREM, <sup>2</sup>University of Bern

S-containing molecules, such as thiols and sulfides, have been found to control the speciation of mercury (Hg) in bacterial exposure experiments. However, the species formed and the impact of these ligands on the counterprocess of demethylation are not yet clear. In this study, we used isotopically enriched mercury species (<sup>199</sup>Hg(II), <sup>202</sup>MeHg) to investigate how molecular speciation of mercury affects both methylation and demethylation in the sulfate-reducer *Pseudodesulfovibrio hydrargyri* BerOc1. Experimental assays were carried out as follows: (i) without external addition of S-ligands, (ii) with the addition of increasing cysteine (Cys) concentrations, or (iii) with the addition of exogenous sulfide. We showed that the highest methylation rate (K<sub>meth</sub>) was obtained without the external addition of S-ligands, whereas the addition of Cys or sulfide decreased Hg methylation, regardless of Cys concentration. By quantitatively determining Hg(II) speciation in the extracellular fractions, we demonstrated that Hg(II) was mostly present in the form of Hg(Cys)<sub>2</sub> when Cys was added. However, metabolic sulfide production from Cys degradation shifted the chemical speciation of Hg(II) from Hg(Cys)<sub>2</sub> to a more insoluble fraction (HgS(S)). In the assay without externally added ligands (Cys or sulfide), speciation models were generated by considering the metabolically produced thiols. These models established the predominance of Hg(II) complexes with mixed ligation involving biosynthesized thiols, OH<sup>-</sup>, and Cl<sup>-</sup> ions. Our results suggest that these complexes with lower thermodynamic stability enhance the MeHg formation rate compared to the more stable Hg(Cys)<sub>2</sub> or HgS(s) species. Unlike Hg(II) methylation, the addition of S-ligands did not affect the rates of demethylation (K<sub>demeth</sub>) of MeHg, even though it caused a shift in the chemical speciation of MeHg (from MeHgCl to MeHgCys and MeHgSH). These findings contribute to our understanding of the potential role of specific S-ligands and chemical speciation in governing the environmental fate and transformation of Hg.

## Beyond Bioaccumulation: Probing Mercury's Effects on Phytoplankton Metabolism

Slaveykova V<sup>1</sup>, Santos J<sup>1</sup>, Millet R<sup>1</sup>, Li W<sup>2</sup>, Keller A<sup>2</sup>

<sup>1</sup>University of Geneva, <sup>2</sup>University of California

Mercury, a priority pollutant raises significant environmental concerns. While numerous studies have investigated mercury bioaccumulation and its impact on aquatic organisms, there is a notable gap in understanding its effects on the metabolic pathways of phytoplankton. Metabolomics, as a tool capable of unraveling organism-environment interactions, offers an ideal approach for integrating metabolic information into cellular responses.

This study aims to elucidate the mechanisms governing the cellular responses of phytoplankton to mercury exposure. Key research questions focus on identifying major metabolic pathways influenced by mercury in phytoplankton species and assessing commonalities or differences in metabolic perturbations across species. The green alga *Chlamydomonas reinhardtii* and diatom *Cyclotella meneghiniana* were selected as representatives of major phytoplankton groups. These algae were exposed to 10 and 100 nM inorganic mercury for 2 h, with assessments including mercury uptake, sub-cellular distribution, and physiological effects such as oxidative stress and photosynthetic yield. Simultaneously, over 90 metabolites, spanning antioxidants, amines, organic acids/phenolics, nucleobases/sides/tides, amino acids, sugars/sugar alcohols, and fatty acids, were quantified using liquid chromatography–mass spectrometry.

The results demonstrated that *C. meneghiniana* exhibited higher mercury accumulation than *C. reinhardtii* at both exposure concentrations. The subcellular distribution of mercury differed between the two species, with *C. reinhardtii* concentrating mercury predominantly in organelles, while the diatom exhibited mercury in both organelles and heat-stable peptides. Physiological endpoints aligned with metabolomic findings, revealing substantial alterations in various pathways, including amino acids, nucleotides, fatty acids, the tricarboxylic acid cycle (TCA), and antioxidant metabolism. This species-specific and mercury concentration-dependent response provides novel insights into mercury accumulation and subcellular distribution in freshwater phytoplankton. Overall, grasping how phytoplankton reprogram their metabolisms under mercury stress is crucial for understanding mercury toxicity in aquatic primary producers and its potential transfer in trophic chains, particularly in highly contaminated environments

## Re-assessment of methylmercury photodemethylation pathways and Hg isotopic fractionation in model freshwater

Lotfi-Kalahroodi E<sup>1</sup>, Amouroux D<sup>1</sup>, Tessier E<sup>1</sup>, Le Behec M<sup>1</sup>, Pigot T<sup>1</sup>

<sup>1</sup>CNRS - UPPA / IPREM

Photodegradation of monomethylmercury (MMHg) in surface waters can induce mass-dependent (MDF) and mass-independent fractionation (MIF) of mercury (Hg) isotopes, subsequently providing information on the transformation and fate of Hg in aquatic systems. Factors affecting the mechanisms and extent of the photodemethylation and photoreduction of MMHg have remained unclear. This work aimed to better elucidate the photodemethylation pathway in a model freshwater containing HMW and LMW humic substances. We investigated the simultaneous photodemethylation to Hg(II) and photoreduction to Hg(0) under both anoxic and oxic conditions. MMHg freshwater solution was irradiated through exposure to three wavelength ranges of full light (280-800 nm), without short UVB (305-800 nm), and visible light (400-800 nm). We determined the Hg isotopic composition of the remaining Hg species, the enrichment factor ( $\epsilon\Delta^{199}\text{Hg}$ ) and odd-MIF slope ( $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ) as photochemical MIF signatures. Results showed the lower  $\epsilon\Delta^{199}\text{Hg}$  at  $-8.5\pm 0.8\%$  and  $10.8\pm 1.1\%$  for the solution irradiated under anoxic conditions regardless of UV light wavelength distribution. Significantly higher  $\epsilon\Delta^{199}\text{Hg}$  at  $-17.3\pm 4.9\%$  and  $-33.0\pm 7.7\%$  have been observed under oxic conditions irradiated by full light and without short UVB, respectively. We proved oxygen inhibits and modify the photodemethylation pathways, while it enhances reactive oxygen species (ROS) production and dissolved organic matter (DOM) photobleaching. Moreover, photodemethylation mechanism under anoxic conditions is independent of UVB spectral distribution whereas it is highly affected under oxic conditions. The average of MIF experimental slopes  $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$  raised from  $1.47\pm 0.03$  to  $1.63\pm 0.02$  by the expansion of the UVB radiation light spectra to shorter wavelength. Our study suggests that  $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$  slope generated by photochemical odd-MIF (magnetic isotopic effect) can vary according to specific irradiation and environmental conditions. This study supports that light spectral distribution, redox condition and reactive LMW DOM in surface waters can induce different mechanisms of MMHg photodemethylation with distinct MIF signatures.

## The impact of agricultural sulfur use on mercury methylation in vineyards

Gerson J, Calvin N, Castro D, Lamborg C, Weiss-Penzias P, Hinckley E

<sup>1</sup>Michigan State University

Since mercury (Hg) methylation can occur by sulfate reducing bacteria under anoxic conditions, elevated methylmercury (MeHg) concentrations have often been reported under enhanced sediment sulfate concentrations. Yet few studies have investigated the impacts of elevated sulfur (S) on Hg methylation in upland soils. The use of S as a fungicide in California, U.S.A. vineyards provides an interesting case study for the environmental consequences of S inputs and the interaction with Hg. California winegrowers apply elemental S as a fungicide to vines in the growing season. Since S is the major chemical addition, these areas are ideal for investigating the transport and fate of S in agricultural soils.

We examine the extent to which S inputs stimulate Hg methylation in California vineyards, and ask: How does Hg methylation in vineyards (high S) compare to non-agricultural (woodland and grassland sites; low S) soils? Samples were analyzed for total Hg, MeHg, and sulfate concentrations. We then performed an incubation experiment with inorganic Hg(II)200 and MeHg198 additions to determine the potential for Hg methylation. We found that while during the dry season, vineyard sites had ~1.5 times the amount of sulfate (360 mg S/kg) compared to non-agricultural (woodland and grassland) sites (230 mg S/kg), total Hg and MeHg concentrations, as well as the percent of Hg present as MeHg and Hg methylation rates were greatest in the woodland sites. Preliminary results show that methylation rates for woodlands and grasslands were consistent across seasons (0.15 percent/day). In contrast, vineyard sites had low methylation rates in the dry season (0.04 percent/day) and comparable methylation rates to the other sites in the wet season (0.15 percent/day). These results suggest that despite high sulfate inputs to vineyards during the dry season, Hg methylation remains low in vineyards until the beginning of the rainy season.

## Increasing retort use amongst artisanal and small-scale gold mining through education and equipment distribution

Gerson J<sup>1</sup>, Chen A, Danfakha F, Hausermann H

<sup>1</sup>Michigan State University

Artisanal and small-scale gold mining (ASGM) is the primary source of anthropogenic mercury (Hg) emissions globally and a significant source of local mercury exposure. In this study, we analyzed the effects of education and distribution of retorts (Hg-capture device) through pre- and post-intervention surveys in Senegalese gold mining communities. We find a combination of a graphics-based and community-oriented educational approach and increased access to mercury-capture equipment (retorts) can lead to increased use of this equipment. As a result of the intervention, 94% of individuals surveyed believed mercury use to be dangerous and 64% of individuals surveyed used retorts at least sometimes compared to 3% pre-intervention. We attribute the success of this intervention to our bottom-up approach that relied on trusted community members to lead educational trainings in local languages using simple graphics, construction of retorts by local metalworkers using locally available material, and the incorporation of individuals' ideas for modifications of retort design. In addition to the efficacy of the intervention in the targeted villages, we also found that there was a social spillover effect, whereby control villages that received no interventions also had increased knowledge. These results suggest the importance of physical and social proximity for increasing the impact of ASGM interventions beyond those communities targeted for the intervention. While our study is focused on Senegal, we believe it has implications for other ASGM locations. As part of the international Minamata Convention - the UNEP treaty focused on controlling mercury releases - countries with ASGM activity must create action plans to reduce mercury emissions. Here we show one mechanism by which Hg reductions from ASGM activity can be reduced that can be incorporated into individual countries' action plans.

## Influence of mercury and other persistent pollutants on fish consumption advisories

Wu P<sup>1</sup>, Foley C<sup>2</sup>, Heiger-Bernays W<sup>3</sup>, Chen C<sup>4</sup>

<sup>1</sup>Department of Biological Sciences, Dartmouth College, <sup>2</sup>Boston University School of Public Health, <sup>3</sup>Boston University School of Public Health, <sup>4</sup>Department of Biological Sciences, Dartmouth College

The majority of fish consumption advisories in the US are developed to limit exposure to mercury but there are multiple contaminants in fish tissue. Advisories typically focus on single contaminants, yet multiple persistent contaminants (eg mercury, dioxins, polychlorinated biphenyls, per and polyfluoroalkyl substances) are present in fish tissue from US water bodies. Here we examine spatial differences in multi-chemical co-exposures from freshwater streams and lakes in the US, as well as highlight a need to revisit the approach to establishing fish consumption advisories to reflect exposure to chemical mixtures while addressing the totality of risks and benefits of fish consumption. Using nationwide freshwater fish contaminant data (e.g., USEPA's National Rivers and Streams Assessment (NRSA), National Lake Fish Tissue Study (NLFTS), Great Lakes Environmental Database (GLEND)), mercury was detected ubiquitously across all fish species regardless of time and space since the start of these environmental monitoring programmes in 1990s. Despite the reductions in mercury emissions and deposition in the US over the last 20 years, the mercury concentrations in fish have not declined in these freshwater ecosystems as observed for many of the organic contaminants. Freshwater fish mercury, total PCBs, dioxin-like PCBs, and PFOS analysed exceeded risk-based levels for weekly consumption, indicating that fish consumption may expose consumers to chemicals and chemical mixtures that contribute to health risks. In no cases were the benefits of consumption evaluated. Our findings suggest that approaches to both assessment and interpretation of contaminant concentrations in fish require re-evaluation in order to protect the public's health.

## Tropical peat: a highly vulnerable global mercury sink

Razavi R<sup>1</sup>, Lamit L<sup>2</sup>, Lilleskov E<sup>3</sup>, Basiliko N<sup>18</sup>, Cobb A<sup>4</sup>, del Aguila Pasquel J<sup>5</sup>, Farmer J<sup>6</sup>, Harvey C<sup>7</sup>, Hoyt A<sup>8</sup>, Jauhiainen J<sup>9,10</sup>, Könönen M<sup>9,11</sup>, Thu P<sup>12</sup>, Rutherford J<sup>13</sup>, Spiers G<sup>18</sup>, Warren M<sup>14</sup>, Watmough S<sup>15</sup>, Zahn G<sup>16</sup>, Janssen S<sup>17</sup>, Driscoll C<sup>2</sup>

<sup>1</sup>SUNY Environmental College Science and Forestry, <sup>2</sup>Syracuse University, <sup>3</sup>USDA Forest Service Northern Research Station, <sup>4</sup>Singapore-MIT Alliance for Research and Technology, <sup>5</sup>Instituto de Investigaciones de la Amazonia Peruana, <sup>6</sup>Newcastle University, <sup>7</sup>Massachusetts Institute of Technology and Singapore, <sup>8</sup>Stanford University, <sup>9</sup>University of Helsinki, <sup>10</sup>Natural Resources Institute Finland, <sup>11</sup>University of Eastern Finland, <sup>12</sup>Vietnamese Academy of Forest Sciences, <sup>13</sup>Department of Biodiversity, Conservation and Attractions, <sup>14</sup>Earth Innovation Institute, <sup>15</sup>Trent University, <sup>16</sup>Utah Valley University, <sup>17</sup>U.S. Geological Survey, <sup>18</sup>Laurentian University

Peat is an important mercury (Hg) sink, but concentration measurements are limited and prevent accurate estimations of global storage across tropical peatlands. Tropical peatlands contain ~30% of global peat reserves and are under severe pressures from conversion to agriculture and gold mining. Here we quantify the Hg content of tropical peat forests from a global archive, provide a first estimate of Hg stored for several tropical peatlands, and use Hg stable isotopes to describe sources and patterns with covariates. We found a range of total Hg concentrations (15 – 912 ng/g dry weight (dw), mean = 200 ng/g dw, n = 295). The highest concentrations occurred at sites proximate to a volcanic point source (204 – 912 ng/g dw, mean = 547 ng/g dw, n = 18, Hawaii, USA) and potential gold mining activities (283 – 566 ng/g dw, mean = 363 ng/g dw, n = 16, Bonzale, Republic of Congo).  $\delta^{202}\text{Hg}$  and  $\Delta^{199}\text{Hg}$  were regionally distinct suggesting differences in atmospheric Hg sources or preservation. Ombrotrophic peatlands had significantly higher concentrations of both total Hg and  $\delta^{202}\text{Hg}$ . Across all sites, percent sulfur explained variation in  $\delta^{202}\text{Hg}$  while percent nitrogen explained variation in  $\Delta^{199}\text{Hg}$ . Other trace metals including lead and cadmium were positively related to total Hg concentrations. A decrease of 0.20 to 0.40‰ in  $\delta^{202}\text{Hg}$  from 70 cm to surface samples was consistently found at two undisturbed peatland sites in Indonesia and Brunei, suggesting a possible modern atmospheric signal from forest fires. We found a wide range in Hg stocks (6 – 52 mg/m<sup>2</sup>) in the upper 70 cm across sites, with estimates equivalent or higher than values reported for Canadian boreal and Western Siberian peatlands. This work demonstrates that loss of tropical peat forests has important implications for global Hg releases and ecosystem health.

## Geomorphic and Biogeochemical Controls on Methylmercury Production in Western United States Beaver Meadows

Adamchak C<sup>1</sup>, Miller H<sup>1</sup>, Lininger K<sup>1</sup>, Hinckley E<sup>1</sup>

<sup>1</sup>University Of Colorado, Boulder

Land managers are reintroducing North American beaver (*Castor canadensis*) into Western United States (U.S) waterways to restore degraded riparian ecosystems. Beavers create cascades of sequential dams that alter river corridor (the channel and adjacent landscape) geomorphology and redox chemistry. These changes can produce conditions conducive to the production of methylmercury (MeHg), a bioaccumulating neurotoxin. Increasing atmospheric mercury (Hg) deposition in the western U.S., combined with beaver expansion, has the potential to dramatically change aquatic biogeochemical cycling and ecological processes, particularly rates of methylmercury (MeHg) production. In this study, we investigated the degree to which beaver activity expands anoxic conditions, influences the interaction of carbon (C), sulfur (S), and Hg cycles, and increases potential rates of Hg methylation in montane ecosystems. We present results from water and sediment samples from Coal Creek (Crested Butte, CO), Trout Creek (Colorado Springs, CO), and Sagehen Creek (Truckee, CA). We quantified total Hg and MeHg concentrations in water and sediment and further developed a technique to quantify sulfate reduction rates in sediment using the radioisotope <sup>35</sup>S. Preliminary results indicate that periodically inundated sediment within a beaver meadow had on average, higher MeHg concentrations ( $2.15 \pm 3.32$  ng/g) than the stream sediment ( $0.93 \pm 1.51$  ng/g,  $p < 0.05$ ). Additionally, MeHg concentrations in pond surface water ( $0.322 \pm 0.041$  ng/L) and the beaver pond outlet ( $0.11 \pm 0.41$  ng/L) were elevated compared to the inlet ( $0.05$  ng/L). Although not significant ( $p > 0.05$ ), the results suggest that beaver ponds may be associated with higher production of MeHg, which can be transported downstream. Overall, this study expands our understanding of MeHg production in high-elevation beaver meadows and provides insights for mountain communities and land managers regarding the consequences of continued beaver expansion for water quality.

## Mercury Cycling in High Elevation Mountain Wetlands Under a Changing Climate

Miller H<sup>1,2</sup>, Adamchak C<sup>1,2</sup>, Thornton P<sup>3</sup>, Driscoll C<sup>5</sup>, Janssen S<sup>4</sup>, Hinckley E<sup>1,2</sup>

<sup>1</sup>University Of Colorado Boulder, <sup>2</sup>Cooperative Institute for Research in the Environmental Sciences, <sup>3</sup>GoGuide, <sup>4</sup>United States Geological Survey, <sup>5</sup>Syracuse University

Wetlands are important areas for methylmercury (MeHg) production and bioaccumulation. In mountain environments, wetlands generally increase in extent and density with elevation; however, there is a paucity of research regarding Hg cycling within these environments. Moreover, climate change is disproportionately impacting mountain regions which likely alters Hg cycling and MeHg production in interconnected wetlands. For example, thawing permafrost within mountain environments is increasing weathering rates of geogenic substrates, including pyrite, resulting in higher sulfate concentrations in runoff. Elevated export of sulfate could alter redox conditions and promote microbial MeHg production in downstream wetland environments. We examined Hg storage, transformations, and transport in high elevation alpine (~3,000m) and subalpine (~2,500m) environments in the U.S. Rocky Mountains. We find that alpine ( $0.6 \pm 0.5 \text{ ng/g}$ ) and subalpine wetland ( $6.4 \pm 2.2 \text{ ng/g}$ ) soils have elevated MeHg concentrations compared to surrounding dry soils, with concentrations comparable to Arctic wetlands. Mercury methylation assays in soils demonstrate that MeHg production is significantly higher (3-fold;  $p < 0.05$ ) in subalpine wetlands ( $2.88 \pm 0.63 \%$  MeHg<sub>201</sub>) compared to alpine wetlands ( $-1.94 \pm 0.02 \%$  MeHg<sub>201</sub>) and dry soils ( $-0.14 \pm 0.00 \%$  MeHg<sub>201</sub>). Also, subalpine wetlands appear sulfate-limited, with significantly higher rates of MeHg production with 50 and 100  $\mu\text{M}$  sulfate additions. Loads of THg in runoff were significantly higher in the subalpine stream ( $11.0 \pm 13.4 \text{ ng/day/km}^2$ ) compared to the alpine stream ( $1.7 \pm 2.0 \text{ ng/day/km}^2$ ) and peaked in early June during peak snowmelt, demonstrating the ability for subalpine systems to transport Hg downstream. Production and transport of MeHg in mountain wetland environments appear to impact local wildlife with 100-fold higher concentrations of MeHg in the tissues of aquatic-feeding organisms compared to terrestrial-feeding organisms. Overall, we demonstrate the importance of mountain wetlands in storing and transforming Hg, as well as potential impacts related to climate change, such as increased sulfate export driving increased MeHg production and bioaccumulation.

## Alternate materials for the capture and quantification of gaseous oxidized mercury compounds from the atmosphere

Lown L<sup>1</sup>, Dunham-Cheatham S, Lyman S, Murray P, Carlson K, Gustin M

<sup>1</sup>University Of Nevada, Reno

Methodologies for identifying atmospheric oxidized mercury (HgII) compounds by gas chromatography mass spectrometry (GC-MS) are currently under development. This method requires a sorbent material to preconcentrate atmospheric mercury above method detection limits for analysis. The objective of this work was to identify and validate materials for quantitative capture of HgII from the gas phase, and to suggest potential surfaces onto which HgII can be collected, thermally desorbed, and characterized using GC-MS methods. Six compounds were identified as potential sorbents and tested in the laboratory for sorption of gaseous elemental (Hg<sup>0</sup>) and HgII in ambient air. Chitosan, alpha alumina, and gamma alumina demonstrated HgII capture in ambient-air laboratory tests, when loaded with a NIST-traceable HgBr<sub>2</sub> permeation source, without sorbing Hg<sup>0</sup> under the same conditions. However, these candidate materials demonstrated poor HgII recovery compared to cation exchange membranes when deployed in the field. Additional sorbent materials were also tested, and results demonstrate a need for matrix-specific certified reference materials and digestion methods for new materials.

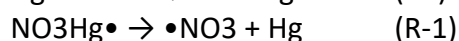
## Computational Chemistry Re-interprets Lab and Field Studies of Nitrate Radical Initiation of Oxidation of Hg(0)

Hewa Edirappulige D<sup>1</sup>, Cheng L<sup>2</sup>, Castro P<sup>1</sup>, Dibble T<sup>1</sup>

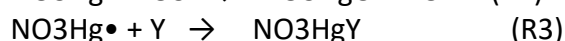
<sup>1</sup>SUNY College Of Environmental Science and Forestry, Department of Chemistry, <sup>2</sup>Johns Hopkins University, Department of Chemistry

Without knowing the redox chemistry of Hg in the atmosphere we can't understand the contribution of atmospheric deposition to mercury biogeochemical cycling. Peleg et al., (2015) observed a strong correlation between nighttime [NO<sub>3</sub>] and gaseous Hg(II), and previous studies had speculated about the role of NO<sub>3</sub> in nighttime oxidation of Hg(0).

Hence, we explored reaction (R1) oxidizing Hg(0) to Hg(I):



followed by two types of reactions oxidizing NO<sub>3</sub>Hg• to Hg(II):



where Y = BrO, NO<sub>2</sub>, NO<sub>3</sub>, HO<sub>2</sub>, and O<sub>2</sub>. The thermodynamics of NO<sub>3</sub>Hg• calculated at CCSD(T)//DFT with respect to R2 and R3 strongly resembled that of BrHg• and HOHg•. However, NO<sub>3</sub>Hg• will dissociate much faster than BrHg• and HOHg• due to its low bond energy (6.5 kcal/mol) compared to that of BrHg• and HOHg• (15.5 and 11.0 kcal/mol, respectively).

Sommar et al., (1997) reported an upper limit to k<sub>1</sub> of 4 × 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Our analysis indicates that Sommar et al. would not have found evidence for R1 even if k<sub>1</sub> was 10,000 times higher than the reported upper limit, so that result is not valid.

Peleg et al. concluded that NO<sub>3</sub> was associated with nighttime formation of gaseous Hg(II). Our kinetic simulations using the maximum reported values of [Hg], [O<sub>3</sub>] and [NO<sub>3</sub>] from Peleg et al. indicate that even with high values of k<sub>1</sub> and k<sub>2</sub> (1×10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>), production of Hg(II) (~6 pg/m<sup>3</sup>) was lower than the maximum, or even the average, [Hg(II)] observed by Peleg et al (97 and 25 pg/m<sup>3</sup>, respectively). Hence, we conclude that NO<sub>3</sub>-initiated oxidation of Hg(0) did not cause the elevated levels of Hg(II) observed by Peleg et al.



93

## Optimized method for direct analysis of mercury in ores and minerals

Egorov A<sup>1</sup>

<sup>1</sup>Lumex Instruments Canada

The AAS method is used for the determination of mercury throughout the world. However, the method has many limitations when analyzing rich organic and inorganic matrix samples. The new rapid and accurate direct method are presented for determining mercury in ores and minerals. The direct thermal decomposition AAS was used wherein a small sample of finely pulverized ore or mineral is heated via step heating program up to 850C, and the vaporized Hg is detected by atomic absorption spectrometry at 254 nm with Zeeman High Frequency Polarization Modulation background correction. This method is suitable for determining Hg in the 0.001–500.0 ppm range, and the precision is about 10% coefficient of variation.

## Mercury Biomagnification on aquatic trophic webs: A meta-analysis of the Southern Hemisphere

Quesada-Alvarado F<sup>1,2</sup>, Chiang G<sup>1,3,4</sup>

<sup>1</sup>Universidad Andrés Bello, <sup>2</sup>PhD program in Conservation Medicine, <sup>3</sup>Sustainability Research Centre, <sup>4</sup>Department of Ecology and Biodiversity, Faculty of Life Sciences

Environmental concentrations of Hg have increased since industrial revolution, posing a threat to environmental and human health. Mercury can bioaccumulate and biomagnified, with the latter process measurable through trophic magnification slope (TMS) and trophic magnification factor (TMF), with an increase at higher latitudes. Unfortunately, most studies have historically been conducted in the Northern Hemisphere, and there is a huge gap of information regarding biomagnification in aquatic ecosystems of the Southern Hemisphere (SH), especially taking in account the differences in bioclimatic zones, continents, and country.

The objective of our study was to perform a metanalysis of the current biomagnification of Hg in aquatic ecosystems studies in the last 20 years, by ecoregion and continent in the SH. The research utilized Google Scholar, WOS, and Elsevier search engines with the keywords Hg+biomagnification+Country. We considered only studies between 2000 to 2023. At the same time, we used Copernicus Marine Data Store engine to obtain remote physicochemical information and assess the possible influence on TMS and TMF.

Simple regressions were performed to determine the relationship between TMS and TMF based on latitude by continent, climate, and habitat. Differences in TMS and TMF values were also assessed by continent, climate, and trophic network. To marine ecosystems we did a GLM to determine what physicochemical variables influenced the biomagnification. The study concluded that latitude, ecosystem type, and trophic network did not significantly influence biomagnification values, but continent and climate type did. In marine ecosystems TMS was influenced by chlorophyll, dissolved oxygen and pH, while TMF only by pH. Biomagnification values were attributed more to anthropogenic activities near the evaluated system, regardless of whether it was located near the poles or in the equatorial zone. While marine ecosystems biomagnification could be due to productivity which can be measured by oxygen availability and water pH.

96

## Long-term monitoring of atmospheric mercury and its source contributions in Kennaook/Cape Grim, Australia

Rawat B<sup>1</sup>, Fisher J<sup>1</sup>, Deutscher N<sup>1</sup>, Powell J<sup>2</sup>, Keywood M<sup>2</sup>, Williams A<sup>3</sup>, Chambers S<sup>3</sup>, Griffiths A<sup>3</sup>

<sup>1</sup>Centre for Atmospheric Chemistry, University of Wollongong (UOW), <sup>2</sup>Climate, Atmosphere & Ocean Interactions Research Program, CSIRO Environment, <sup>3</sup>Australian Nuclear Science Technology Organization (ANSTO)

Mercury, seasonal variation, Southern Ocean, Cape Grim

## New measurements of mercury contamination in air, soil, sediments, and tailings at artisanal and small-scale gold mining sites across Côte d'Ivoire

Kpokro B<sup>1</sup>

<sup>1</sup>University Of Wollongong

Among the many anthropogenic mercury sources ASGM remains the largest (about 38%). ASGM largely occurs in developing countries, including more than thirty-five countries in Sub-Saharan Africa. While environmental mercury contamination has been measured in locations surrounding ASGM sites, almost no data is available from within artisanal mining sites.

The current study investigates mercury contamination from soils and tailings directly sampled in informal Cote d'Ivoire ASGM sites; sediments from adjacent rivers and wetlands of these sites; as well as air from the nearest towns to these ASGM sites.

Preliminary results reveal high mercury levels in tailings, soils, and air from sites using mercury. These levels decrease but are still elevated at the non-mercury ASGM sites. Tailings remain the most polluted environmental compartment followed by topsoil. Riverine sediments from non-mercury use ASGM sites had average concentrations representing, respectively, 11 and 20 times standards in developed countries. Passive air samplers deployed monthly, for one year, in the towns nearest to each of the four soil sampling sites showed a similar spatial distribution to the soils, with high mercury concentration in the air near sites where mercury was actively used in ASGM. Atmospheric mercury peaks during the dry season found were consistent with the expected occurrence of ASGM activity during that season. However, high atmospheric mercury concentrations during both the rainy season and the dry-to-wet transition period were also observed, implying a paradigm shift with ASGM practice now taking place year-round and no longer being a seasonal activity.

Supplementing environmental measurements with social science interviews, a better understanding of mercury use dynamics in ASGM activity was provided. Informality of ASGM has resulted in illegality of sites. Once dismantled by regulators, these sites subsequently become abandoned mercury-contaminated sites. The favourable market for mercury use in ASGM is generally backed up by informality.

## Forest harvesting impacts on methylmercury production and export in central Canadian boreal watersheds

Mitchell C<sup>1</sup>, Huang H<sup>1</sup>, Lam W<sup>1</sup>, Mangal V<sup>2</sup>, Lajoie C<sup>3</sup>, Mackereth R<sup>4</sup>, Melles S<sup>5</sup>, Kidd K<sup>3</sup>, Emilson E<sup>6</sup>

<sup>1</sup>University Of Toronto Scarborough, <sup>2</sup>Brock University, <sup>3</sup>McMaster University, <sup>4</sup>Ontario Ministry of Natural Resources and Forestry, <sup>5</sup>Toronto Metropolitan University, <sup>6</sup>Natural Resources Canada

Boreal forests are a strong sink of atmospheric mercury. Landscape disturbances such as forest harvesting, however, may lead to wetter soil conditions, greater erosion and stronger hydrological connectivity, which can lead to both greater production and export of bioaccumulative methylmercury. To broaden the relative paucity of data from managed North American boreal forests, we undertook a multi-year, multi-watershed experimental study in the central Canadian boreal forest to examine the effect of forest harvesting and certain management approaches on methylmercury production and export. In relation to pre-harvest conditions, we found that harvesting led to methylmercury production that was most strongly affected in stream sediment, compared to wetland and upland soils. Harvesting impacts were not strong in watersheds where <75% of watershed area was harvested, where substantial (30 m) streamside buffers were kept intact and where stream crossings by machinery were not observed. Significantly elevated methylmercury export from watersheds was only observed when there was evidence of physical disturbance by upstream machine crossing and weak buffer protection. In trying to mitigate mercury-related issues due to forest harvesting, the protection of stream integrity, especially for smaller tributaries, and practices similar to the management of erosion and material fluxes into streams are paramount.

## The current evidence of the effects of mercury exposure on hypertension

Chan L<sup>1</sup>, Loan A<sup>1</sup>, Hu X<sup>1</sup>

<sup>1</sup>University Of Ottawa

Mercury (Hg) is a chemical pollutant of human health concern worldwide. Although the health impacts of mercury have been primarily focused on its neurotoxicity, there is increasing evidence that exposure to Hg is a risk factor for cardiovascular diseases (CVD). Hypertension has long been recognized as a leading risk factor for CVD that affects millions globally, leading to many morbidities and fatalities. Therefore, the relationship between Hg exposure and hypertension has been a topic of interest in recent years.

According to the World Health Organization, in 2019, an estimated 1.28 billion adults aged 30–79 years worldwide have hypertension, most living in low- and middle-income countries. The prevalence of hypertension varies across countries and regions, with higher rates observed throughout central and eastern Europe, central Asia, Oceania, southern Africa, and some countries in Latin America and the Caribbean. Many populations in these regions also have fish and seafood as a staple food and, therefore, may have higher Hg exposure. Several possible underlying mechanisms for mercury-induced hypertension have been identified. They include: 1) oxidative stress, 2) inflammation, 3) dyslipidemia, 4) mitochondrial dysfunction, 5) lipid peroxidation, and 6) endothelial dysfunction. A number of epidemiological studies have also identified the dose-response relationship between Hg exposure and hypertension. We have published two systematic reviews and meta-analyses showing the significant relationship between hypertension, CVDs and Hg exposure in the last five years, and more evidence has emerged since.

We will present the results of a review carried out through database searches on the effects of Hg at the tissue and organ level and the underlying mechanisms contributing to hypertension onset and update the latest epidemiological evidence between Hg exposure and hypertension. We will summarize the latest evidence and discuss the potential use of the results for the health risk assessment for global exposure to Hg.

## High Mercury Concentrations in Some California Rockfish Species

Lamborg C<sup>1</sup>, Tseng C<sup>2</sup>, Garza C<sup>3</sup>, Cui X<sup>1</sup>, Calvin J<sup>1</sup>

<sup>1</sup>University Of California-Santa Cruz, <sup>2</sup>National Taiwan University, <sup>3</sup>(3) National Marine Fisheries Survey

There is a growing recognition that in addition to top predator, pelagic fish such as tuna, demersal fish can have high mercury concentrations as well. We investigated the mercury content of Rockfish (Sebastes), a genus with numerous species that is widely distributed, often long-lived and is a popular and economically important fishery. This genus is important to investigate not only for its value as a fishery but because the family of fish contains species with widely varying life histories that can be used to examine the factors controlling mercury bioaccumulation. Samples were collected off the coast of central California as part of the annual US National Marine Fisheries Rockfish survey. The concentration of mercury was measured in muscle and fin clips as well as fin clips from an archive of tissue. We found 1) that fin clips were a good proxy for muscle with a near universal relationship across species, 2) a curvilinear relationship between length or weight and mercury content, but a linear relationship between age and mercury content, suggesting age is the master variable, and 3) some of the species for which we had tissues showed quite high mercury content, well above recommended consumption limits, while others never exceed limits. We examine the factors that determine whether or not a particular species may have high mercury contents.

## Mercury speciation across the South Pacific and Southern Ocean on the U.S. GEOTRACES (GP-17 OCE): a preliminary evaluation

Despins M<sup>1</sup>, Lamborg C<sup>1</sup>, Mason R<sup>2</sup>, He Y<sup>2</sup>, Hammerschmidt C<sup>3</sup>

<sup>1</sup>University Of California-Santa Cruz, <sup>2</sup>University of Connecticut, <sup>3</sup>Wright State University

Mercury (Hg) species exhibit either a nutrient-like or hybrid-like distribution in the marine water column but, the relative concentrations of Hg species and the depth of Hg species maxima differ across ocean basins. Currently, little is known regarding the distribution of Hg species across the South Pacific Ocean. Here we present preliminary data showing Hg speciation for samples collected across a section of the South Pacific and Southern Oceans, through biological gradients, across hydrothermal vents, and along continental margins aboard the 2022-23 U.S. GEOTRACES cruise (GP-17 OCE), which sailed from Papeete, Tahiti to Punta Arenas, Chile. Three dissolved species, monomethyl mercury (MMHg), total Hg (HgT), and elemental mercury (Hg<sub>0</sub>), and two particulate species, total methylated mercury (MeHg) and HgT, were measured in high vertical and horizontal resolution across this transect. Dissolved HgT below the surface remained consistent with increasing latitude, while dissolved Hg<sub>0</sub> increased with latitude. Across many stations increases in dissolved HgT was seen in the benthic waters along in the South Pacific, suggesting a benthic flux. The amount of MMHg relative to HgT was predicted to increase across the Southern Ocean biological gradients as this proportion (MMHg: HgT) is predicted to be associated with MMHg formation in marine snow and during remineralization. A higher flux of particulate MeHg and HgT out of the surface waters to depth is expected south of the Sub-Tropical Front due to increased particulate organic carbon production and export. The data available to date will be presented and the factors controlling the distributions and relative concentrations examined.

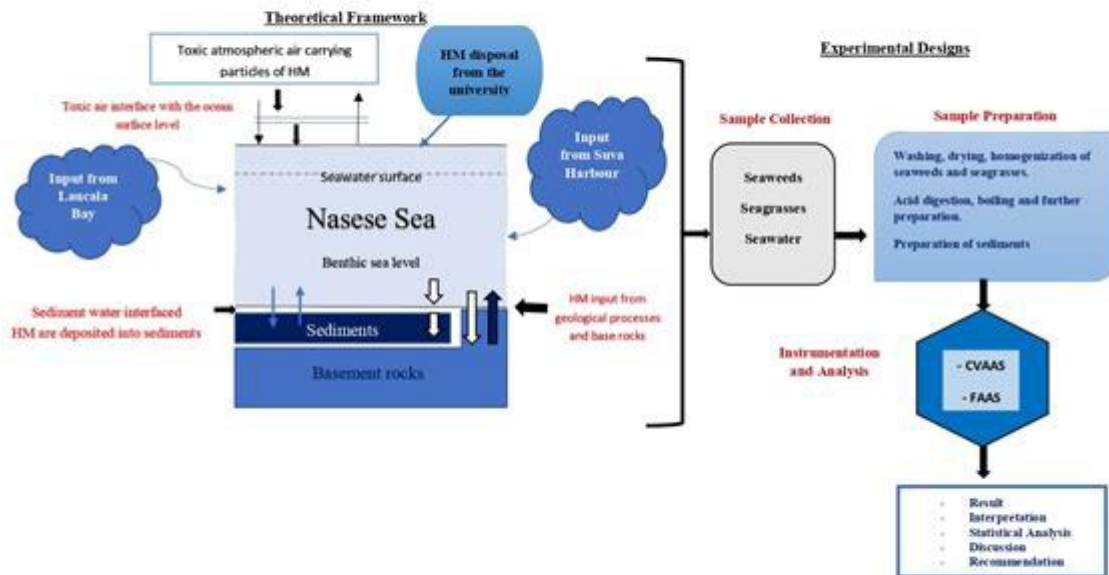
## Cold Vapour Determination of Mercury in Seaweeds and Seagrasses Collected Along Nasese Seashore in Suva, Fiji

Otiwa S<sup>1,3</sup>, N'Yeurt A<sup>2</sup>, Prasad S<sup>1</sup>

<sup>1</sup>Discipline of Biological and Chemical Sciences, School of Agriculture, Geography, Environment, Ocean and Natural Sciences (SAGEONS), The University of South Pacific, Suva, Fiji, <sup>2</sup>Pacific Centre for Environmental and Sustainable Development (PaCE-SD), The University of the South Pacific, Suva, Fiji, <sup>3</sup>Department of Biochemistry, Faculty of Physical Science, University of Cross River State

Seaweeds have long been an integral part of the South Pacific diets for centuries, forming a rich cultural food heritage on different islands of the region. Together with seagrasses, they serve as the primary source of food for aquatic animals. Mercury has been accumulated by these species through various natural and anthropogenic sources in the water environment. This study is aimed at determining the mercury concentration in selected seaweeds and seagrasses collected from the Nasese Seashore, Suva, Fiji. Based on ecological relevance and prevalence, a total of six species of seaweed and seagrass were harvested from the sampling area, washed, and oven-dried for 48 hours. 0.5 g of each sample underwent digestion with a specific combination of three different acids (1 mL HCl, 5 mL HNO<sub>3</sub>, and 2.5 mL H<sub>2</sub>SO<sub>4</sub>). Subsequently, samples were analyzed by cold vapour atomic absorption spectroscopy (CVAAS). The results revealed varying levels of Hg bioconcentration among the studied species. Notably, *Halodule uninervis* exhibited the highest concentration at 0.19 mg/kg, whereas the lowest level of mercury was found in the red seaweed *Gracilaria edulis* at 0.02 mg/kg. The sample reading RSD ranged from 1-7%, with a consistently stable peak area. The trend in mercury concentration amongst samples is *H. uninervis*>*A. spicifera*>*S. polycystum*>*H. ovalis*>*U. intestinalis*>*G. edulis*. Except for *H. uninervis*, all the selected species had mercury concentrations below the WHO permissible limit of 0.1 mg/kg. As a quality control measure, two spiked samples demonstrated a remarkable recovery in the range of 99.2 to 111.2%, affirming the accuracy and reliability of the results. The observed variations in Hg concentration among species prompt further investigations into the ecological and physiological factors influencing Hg accumulation.

### Abstract Graphics



103

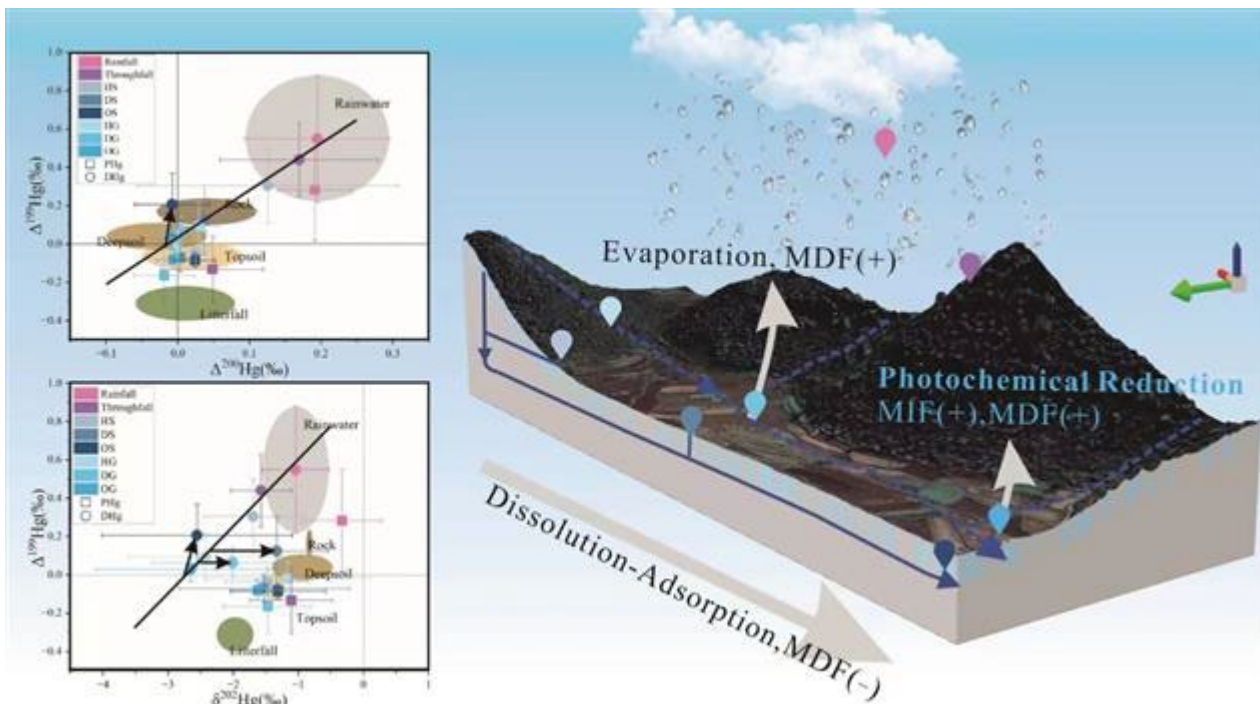
## Mercury Isotope Fractionation in Natural Hydrological Processes and Environmental Implication

Li R<sup>1</sup>, Li P

<sup>1</sup>State Key Laboratory Of Environmental Geochemistry, Institute Of Geochemistry, Chinese Academy Of Sciences

Water runoff serves as a vital pathway for mercury (Hg) migration from terrestrial sources into aquatic ecosystems. However, quantifying the specific sources and transformation processes of Hg in water runoff has been challenging due to the complex and diverse conditions presented in the natural environment. In this study, the problem was solved by determining the mechanism of Hg isotope fractionation during the generation and convergence processes of hydrologic runoff. In cases of highly mobile surface or subsurface runoff, the contribution of Hg to the water body can be directly assessed using the  $\Delta^{199}\text{Hg}$ - $\Delta^{200}\text{Hg}$  ternary mixing model. However, in surface water bodies with long residence time, dissolved Hg (DHg) exhibits a positive odd mass-independent fractionation (MIF) that requires special correction. Hg transformations in the runoff waters primarily occur through dissolution-adsorption processes, resulting in a higher contribution of Hg from terrestrial sources (from 46% to 83%). Runoff originating from agricultural areas facilitates the transfer of Hg from the water body to the atmosphere through evaporation. When the upstream water source of surface water is disconnected or limited, photochemical reduction plays a crucial role in the transformation of DHg. Our study provides new insights into the identification and characterization of sources and transformations of Hg in water bodies. It establishes the scientific basis for a comprehensive understanding of the role of runoff in the global biogeochemical cycle of Hg.

### Abstract Graphics



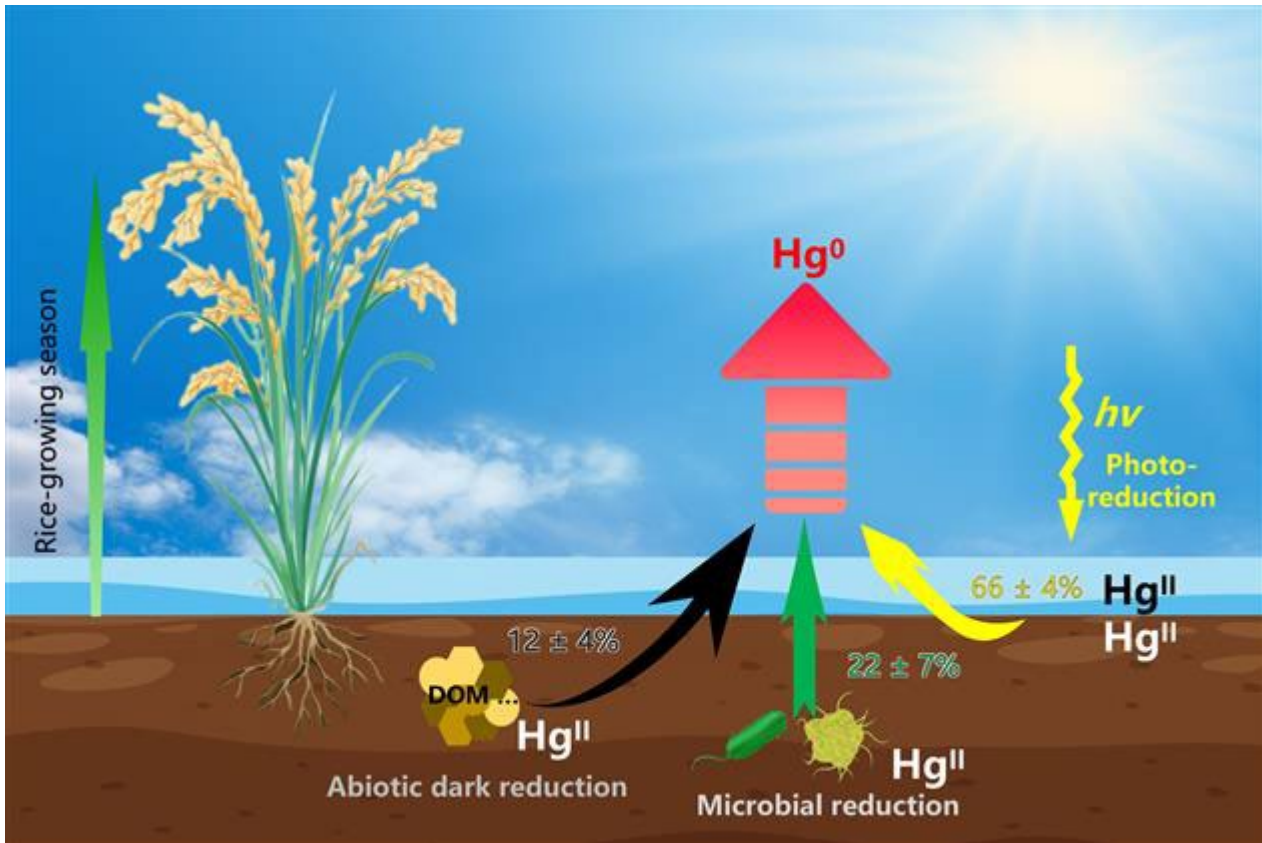
## Using mercury stable isotopes to quantify directional soil-atmosphere Hg(0) exchange in rice paddy ecosystems: implications for Hg(0) emission to atmosphere from land surfaces

Zhang K<sup>1</sup>, Meng B<sup>1</sup>, Feng X<sup>1</sup>

<sup>1</sup>Institute of Geochemistry, Chinese Academy of Sciences

Mercury (Hg) reduction processes are the primary driving force of gaseous elemental mercury (Hg(0)) emissions from soils. Current assessments of Hg(0) emissions have primarily focused on the photoreduction process and have overlooked other processes, which is attributed to the limitations of traditional methods in distinguishing and quantifying different reduction processes. This could result in an underestimation of soil Hg(0) emissions into the atmosphere. In this study, the main Hg reduction processes (photoreduction, microbial reduction, and abiotic dark reduction) in paddy soils were distinguished and investigated using Hg isotopes in a typical rice paddy in the Wanshan Hg mining area, SW China. The results revealed significant differences in the isotopic compositions of Hg(0) yielded from photoreduction ( $\delta^{202}\text{Hg} = -0.80 \pm 0.34\text{‰}$ ,  $\Delta^{199}\text{Hg} = -0.38 \pm 0.09\text{‰}$ ), microbial reduction ( $\delta^{202}\text{Hg} = -1.55 \pm 0.10\text{‰}$ ,  $\Delta^{199}\text{Hg} = 0.29 \pm 0.19\text{‰}$ ), and abiotic dark reduction ( $\delta^{202}\text{Hg} = -2.50 \pm 0.12\text{‰}$ ,  $\Delta^{199}\text{Hg} = 0.50 \pm 0.11\text{‰}$ ). Paddy soil-atmosphere exchange at three different stages was dominated by net Hg(0) emissions, with the average exchange fluxes ranging from 2.2 to 16.8 ng/(m<sup>2</sup> h), which produced significantly different isotopic compositions of exchanged Hg(0) (mean  $\delta^{202}\text{Hg}$ : -1.54 to -0.81‰; mean  $\Delta^{199}\text{Hg}$ : -0.45 to 0.06‰). A ternary mixed model revealed that photoreduction was the primary factor (mean: 37 to ~100%) contributing to Hg(0) emissions from paddy soils. Considering the whole rice growth period, the contributions of photoreduction, microbial reduction, and abiotic dark reduction were  $66 \pm 4\%$ ,  $22 \pm 7\%$ , and  $12 \pm 4\%$ , respectively. The results can be applied to wetland ecosystems. Future assessments of Hg(0) emissions from wetlands should fully consider the contributions of microbial and abiotic dark reductions, given the large Hg(0) emission potential of wetland ecosystems.

### Abstract Graphics



## Low Soil Mercury Caused High Rice Mercury in High Geological Background Region and Its Possible Mechanism

Wei L<sup>1</sup>, Li P<sup>1</sup>

<sup>1</sup>Institute of Geochemistry, Chinese Academy of Sciences

Rice has been confirmed as the principal pathway of methylmercury (MeHg) exposure to inhabitants in mercury (Hg) mining areas in China. However, the profiles of Hg contamination for high geological background regions (with high heavy metal concentrations originated from geological background) are overlooked. Here, we selected Dahao and Boli sites in Guizhou province, southwest China for study. The results showed that total mercury (THg) concentrations in the soil of Dahao and Boli averaged at  $386 \pm 90.7$  ng/g ( $n = 131$ ) and  $224 \pm 36.3$  ng/g ( $n=142$ ), which indicated low levels. However, the averages of rice THg concentrations in Dahao and Boli were  $21.8 \pm 13.2$  ng/g ( $n=130$ ) and  $3.49 \pm 2.69$  ng/g ( $n=142$ ), respectively, and 48.5% of rice THg concentrations in Dahao site exceeded national limit (20 ng/g). The rice MeHg concentrations in Dahao site averaged at  $20.1 \pm 11.01$  ng/g ( $n=25$ ), which was higher than those of Wanshan Hg mining area ( $7.23 \pm 3.96$  ng/g,  $n=24$ ). However, the rice MeHg concentrations in Boli were relatively low ( $1.52 \pm 3.96$  ng/g,  $n=25$ ). Moreover, the soil MeHg concentrations in Dahao ( $0.75 \pm 0.42$  ng/g,  $n=25$ ) and Boli ( $1.24 \pm 0.69$  ng/g,  $n=25$ ) were much lower than those in Wanshan Hg mining area ( $2.79 \pm 1.24$  ng/g,  $n=124$ ). The Bioaccumulation factor (BAF, ratio of MeHg in rice to soil MeHg) of MeHg in Dahao rice averaged at  $42.4 \pm 50.1$ , which was significantly higher than those in Boli site ( $1.64 \pm 1.18$ ,  $n=25$ ) and Wanshan Hg mining area ( $5.61 \pm 10.3$ ,  $n=32$ ). These results indicated that the rice in Dahao site can enrich THg and MeHg even with extremely low soil Hg. It's urgent to explore the key factors controlling the Hg bioaccumulation in rice of Dahao site. This study firstly evaluated Hg pollution issues in paddy ecosystem in high geological background areas.

## Exploring biogeochemical cycling of mercury in hypersaline environments

Sephus C<sup>1</sup>, Schartup A<sup>1</sup>, Bowman J<sup>1</sup>, West J<sup>1</sup>, Schmidt B<sup>2</sup>

<sup>1</sup>Scripps Institution Of Oceanography, <sup>2</sup>Cornell University

Brine systems are used as analogs to better understand ancient environments that existed on Earth as well as environments that exist on other planets. Studying brines can help us understand the biogeochemical cycling potentials of mercury during terrestrial life's past and extraterrestrial life's possibilities. Here, we investigated the potentials of microbial mercury cycling in ephemeral salt lakes across Western Australia and in the deep anoxic Orca Basin in the Gulf of Mexico. In Western Australia, an analog site for Martian lakes, we took water samples from 30 independent lake environments ranging in pH from 2.7 - 9.2 and total dissolved solids (TDS) from 15.3 – 320 g/L (TDS of seawater is ~35 g/L). Despite the combined environmental stressors of extreme pH and redox conditions, high salinities, and unusual ionic compositions, we found evidence of methylated mercury (MeHg) production of in all the lakes. MeHg concentrations ranged in value from 0.04 - 4.11 pmol kg<sup>-1</sup>. In the deep anoxic hypersaline Orca Basin, an analog for early Earth, we searched for evidence of mercury cycling in a poly-extreme environment with no sunlight, sustained anoxia, low temperatures, and high salinity, pressure, and metal concentrations. We report high concentrations of total mercury (0.41 -109 pmol kg<sup>-1</sup>) and exceptionally high levels of MeHg (1.8-21.1 pmol kg<sup>-1</sup>) coinciding with peak cell density. Depth profiles also reveal that total dissolved mercury concentrations correlate with the diagenetic profile of manganese (Mn<sup>2+</sup>) in a manner distinct from other anoxic basins, suggesting a possible role of microbial-mediated mercuric oxide cycling in the environment. In this presentation, we will discuss the biogeochemical cycling of mercury under a wide range of conditions, providing insight into the potentials of microbial and mercuric interactions both on Earth and beyond.

## Mercury stress and methylation promote carbon emission from rice paddy soils

Liu J<sup>1,2</sup>, Huang R<sup>1</sup>, Zhou Q<sup>1</sup>, Meng B<sup>2</sup>, Jiang T<sup>3</sup>, Feng X<sup>2,4</sup>

<sup>1</sup>College Of Resources, Sichuan Agricultural University, <sup>2</sup>State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, <sup>3</sup>Interdisciplinary Research Centre for Agriculture Green Development in Yangtze River Basin, Department of Environmental Sciences and Engineering, College of Resources and Environment, Southwest University, <sup>4</sup>University of Chinese Academy of Sciences

Methane (CH<sub>4</sub>) emission from rice paddy fields is one of environmental concerns with changing climate. Mercury (Hg) methylation in flooded paddy soils poses significant methylmercury (MeHg) exposure risks for global populations. However, these two issues were yet being linked previously. Recently, the up-to-date studies reported that methanogens and methanotrophs, both of which mediated CH<sub>4</sub> production, were not only involved in Hg methylation but also played roles in MeHg demethylation (Lu et al., 2017; Wu et al., 2020; Kang-Yun et al., 2022; Hao et al., 2024). These understandings shining some lights on the linkage between CH<sub>4</sub> emission and MeHg production. However, direct relationship between methane emission and mercury methylation remains unclear. Here, we use natural paddy soils with different Hg concentration gradients and also an exogenous Hg(NO<sub>3</sub>)<sub>2</sub> spiking experiment to reveal responses of greenhouse gas emission on Hg stress and Hg methylation. Emission fluxes and accumulative emissions of CO<sub>2</sub> and CH<sub>4</sub> during rice growing was monitored. Substrates of soil organic carbon (SOC) pools were considered by measuring particulate organic carbon (POC), mineral-associated organic carbon (MAOC), microbial biomass carbon (MBC), microbial necromass carbon (MNC), and dissolved organic carbon (DOC). Both total Hg and MeHg in paddy soils and in rice plants were also determined. The results showed that Hg stress and Hg methylation significantly promoted carbon emission from paddy soils. Concentrations of MeHg in paddy soils were positively co-varied with both respiration quotient (RQ) and metabolic quotient (qCO<sub>2</sub>). In addition, emission of CH<sub>4</sub> was determined by the different substrate of SOC, and soil DOC was associated with MAOC. Overall, this study is a preliminary attempt to link CH<sub>4</sub> emission and Hg methylation in paddy fields, which provides foundations to limit both greenhouse gas emission from paddy fields and MeHg accumulation in rice.

## Ecotoxicological Impacts of Mercury Cyanide in Zebrafish (*Danio rerio*): effects of chronic exposure

Guimaraes J<sup>1</sup>, Silva H<sup>1</sup>

<sup>1</sup>UFRJ

Ecotoxicological Impacts of Mercury Cyanide in Zebrafish (*Danio rerio*): effects of chronic exposure.

Mercury amalgamation is a widespread practice among over 15 million artisanal and small-scale gold miners in more than 70 countries. In many developing nations, residues from the amalgamation process undergo further processing through cyanidation, primarily using sodium cyanide (NaCN) or a combination of these extraction methods. Despite the prevalence of such practices, there is a notable scarcity of data regarding the interaction between cyanide and mercury, as well as the formation and dissociation of the mercury cyanide complex (Hg(CN)<sub>2</sub>). This chronic study spans 16 weeks, comprising 8 weeks of exposure and 8 weeks of recovery, delving into the repercussions of cyanide exposure and the bioavailability of mercury in the form of Hg(CN)<sub>2</sub> (0.08 and 0.12 mg.L<sup>-1</sup>). Using the *Danio rerio* model, our investigation includes a comprehensive analysis, examining oxidative stress, hematological parameters, and histological assessments. Furthermore, we aim to quantify total mercury (THg) levels in the gill, liver, and renal tissues, while also measuring free cyanide concentrations in the surrounding water. Our preliminary results indicate an increase in total leukocytes, especially neutrophils. Significant alterations associated with oxidative stress were also observed; catalase and superoxide dismutase activities increased in the gills, liver, and kidneys. Meanwhile, glutathione peroxidase and malondialdehyde levels increased only in the liver and kidneys. Additionally, a significant weight reduction of up to 20% compared to the control group was demonstrated. Approximately 50% of the animals also exhibited discoloration of the characteristic zebrafish stripes. The observed physiological and biochemical changes in *D. rerio* highlight the potential environmental risks associated with mercury cyanide exposure. Further research is essential to develop strategies for mitigating these risks and promoting sustainable mining practices on a global scale

## Zooplankton as an indicator of mercury pollution in the three Baltic estuaries

Panasiuk A<sup>1</sup>, Wojdasiewicz A<sup>1</sup>, Kornijów R<sup>2</sup>, Woźniczka A<sup>2</sup>, Bełdowska M<sup>1</sup>

<sup>1</sup>University of Gdańsk, <sup>2</sup>National Marine Fisheries Research Institute

Mercury is a dangerous element and its high concentration may be very dangerous both for the marine environment and its biotic components, as well as for humans in the context of obtaining living marine resources. Zooplankton is an important ecological formation which is a food for many marine predators, hence mercury concentrations in zooplankton organisms can be an important indicator of its presence in the seas, as well as enable obtaining information on the amount of mercury that can be potentially transferred to the higher trophic levels. Baltic Sea is a semi-closed reservoir surrounded by highly industrialized countries, hence it is particularly exposed to the mercury pollution and its high concentrations. The research was conducted in the three different estuaries in southern parts of the Baltic Sea, and zooplankton was collected from different research stations and during warm and cold seasons, as seasonality in temperate areas may affect the recorded mercury concentrations. Representatives of zooplankton were identified to the lowest possible taxonomic position in order to assess which species could potentially be vectors of the highest mercury concentrations. Obtained results are extremely important in the context of research on the safety of marine living resources, and in particular the role of zooplankton in the transfer of toxic compounds to the higher trophic levels, in marine waters that can be particularly at risk. The study was funded by a research project titled "Primary producers as a key entry point of historical and present-day mercury into the estuarine trophic web", National Science Centre 2022/45/B/ST10/00368.

## Mercury in the Antarctic pelagic ecosystem – krill *Euphausia superba* and *Pygoscelis* penguins – transfer from the food to the top predators

Panasiuk A<sup>1</sup>, Hoszek K<sup>1</sup>, Korejwo E<sup>2</sup>, Fudala K<sup>3</sup>, Bialik R<sup>3</sup>, Bełdowska M<sup>1</sup>

<sup>1</sup>University Of Gdańsk, <sup>2</sup>The Institute of Oceanology of the Polish Academy of Sciences (IO PAN), <sup>3</sup>The Institute of Biochemistry and Biophysics of the Polish Academy of Sciences

Increased mercury concentrations in the Antarctic environment may lead to disturbances in the population dynamics of marine pelagic fauna, affecting its reproduction, health and increased mortality. Antarctic krill *Euphausia superba* is a key species in the functioning of the Antarctic environment, and it is the primary food for the most Antarctic predators. Among Antarctic predators, penguins constitute an important bird biomass - their breeding colonies are located in many different locations throughout the Antarctic Peninsula region. They are considered to be good bioindicators of environmental pollution, including mercury. Research shows that penguins, feeding in the marine environment and breeding on a land, can transfer pollutants from the marine environment to the land. In winter, representatives of *Pygoscelis* (*P. adeliae*, *P. antarcticus*) make long feeding migrations and *P. papua* penguins feed close to their colonies. Comparing the results of mercury concentrations from these three species allows to assess the state of the environment both locally as well as far away from the colonies. Research has shown that *E. superba* crustaceans are a carrier of mercury in the Antarctic food web, and thus may be its vector to the higher trophic levels. Studies have shown statistically significant differences in the accumulation of total mercury both between the species of penguins which were examined, as well as between different colonies of the same species.

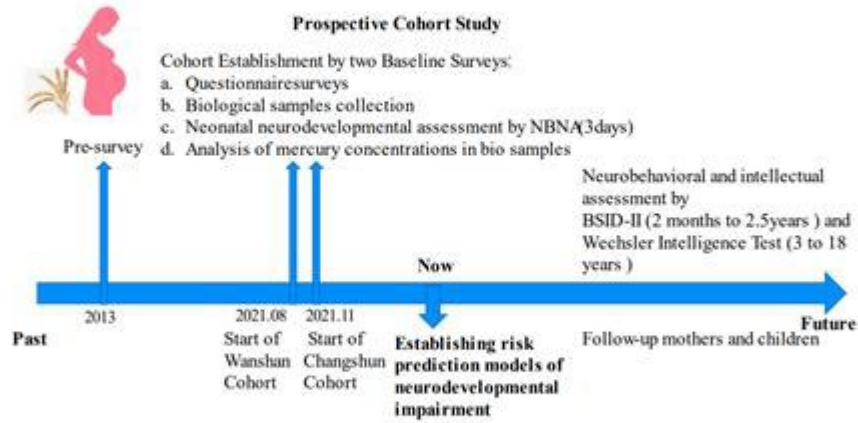
## The Relationship between Maternal Prenatal Mercury Exposure and Neonatal Neurodevelopment: A Prospective Cohort Study in Wanshan Mercury Mining Area, Guizhou Province

Gan C<sup>1</sup>

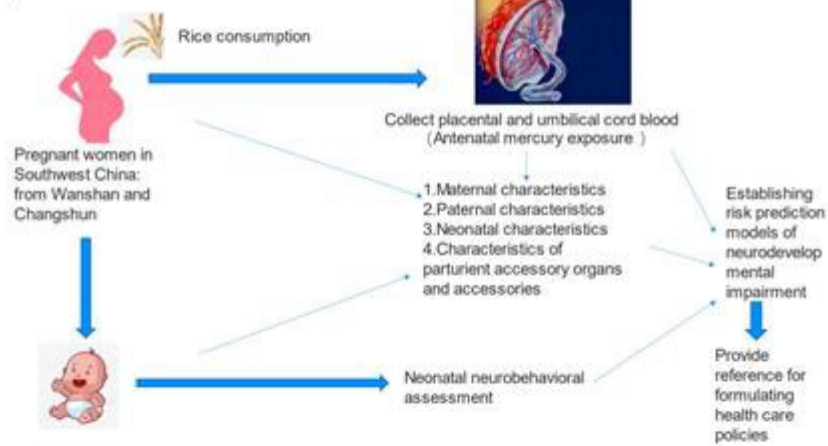
<sup>1</sup>Institute Of Geochemistry, Chinese Academy Of Sciences/Guizhou Medical University  
Rice serves as a prominent source of methylmercury exposure in China inland regions. In Wanshan District and Changshun County of Guizhou Province, where rice is a dietary staple, we investigated the correlation between maternal prenatal mercury exposure and neonatal behavioral neurodevelopment, developing a risk prediction model. The study encompassed 320 women in Wanshan and 306 in Changshun, along with their newborns. The research team conducted behavioral neurological assessments on 206 three-day-old newborns in Wanshan and 214 in Changshun, analyzing factors influencing neurodevelopmental damage and the dose-effect relationship. Among the 206 mothers in Wanshan, the average placental methylmercury content was 2.88 ng/g (range: 0.17-18.09 ng/g), with the average umbilical cord blood methylmercury content at 2.84 ug/L (range: 0.05-24.47 ug/L). In Changshun, among the 214 mothers, the average placental methylmercury content was 0.8 ng/g (range: 0.05-4.47 ng/g), and the average cord blood methylmercury content was 0.84 ug/L (range: 0.06-3.1 ug/L). In the total population model without covariate adjustment, placental methylmercury emerged as a risk factor for neurological impairment in the general population. With every 1 ng/g increase in placental methylmercury content, the risk of neonatal neurological damage increased by 1.23 (OR=1.23, 95%CI=1.11-1.36). Considering all covariates, the risk of neonatal neurological damage increased by 1.39 for each 1 ng/g increase in placental methylmercury content (OR=1.39, 95%CI=1.01-1.94). The logistic regression prediction model for the total population utilized the ROC curve, with AUCs of 0.905 and 0.863 for the validation and training sets, respectively, indicating a robust predictive effect. Neurodevelopmental impairment in neonates commenced when placental methylmercury content exceeded 0.98 ng/g (OR>1).

### Abstract Graphics

**Graphical Abstract 1**  
**Wanshan and Changshun : Mercury exposure and Health Effects**



**Graphical Abstract 2**



113

## Spatial narrative of the status of Hg in selected South African freshwaters: a story map approach

Somerset V<sup>1</sup>, van der Horst C<sup>1</sup>, Walters C<sup>2</sup>

<sup>1</sup>Cape Peninsula University of Technology, <sup>2</sup>Council for Scientific and Industrial Research

Mercury (Hg) is known to be a persistent and toxic heavy metal that can bio-accumulate in the aquatic environment and lead to serious human health effects. Hg is released into the atmosphere from both natural and anthropogenic sources, where in the atmosphere it can be present in a gaseous phase or in particulate matter [1].

It is also known that aquatic ecosystems have been affected by various types of contaminants in recent decades. Various anthropogenic activities can be attributed to this. The concern is the release of these contaminants from multiple regulated and unregulated sources. As for many heavy metals, once they are released into rivers, they may dissolve to form ions or complexes, suspended as particulate matter, or settled down as bed sediments. Through bioaccumulation they may enter the food chain and lead to human health issues [2].

Spatial assessments and GIS-based story maps will be used to visualize trends to inform the status of Hg concentrations between the 2010 and 2022/23 assessments in surface water and sediment in the Breede-Gouritz and Berg-Olifants water management areas (WMAs). This will be the first data since 2010 for the WMAs involved. The 2022/2023 assessments will include soil concentrations as well. It is hoped that evidence will be provided as to whether Hg concentrations in the freshwater ecosystem remain the same or to suggest which factors are responsible for possible changes observed.

## Are future oil and gas decommissioning sites potential sources for mercury contamination in the deep sea?

Paton L<sup>1</sup>, Marczinczik N<sup>1,2</sup>, Moro T<sup>1,3,4</sup>, Gonzalez de Vega R<sup>1</sup>, Lindsay T<sup>1</sup>, Clases D<sup>4</sup>, Feldmann J<sup>1</sup>  
<sup>1</sup>TESLA, University Of Graz, <sup>2</sup>University of Muenster, <sup>3</sup>NanoMicroLab, University of Graz,  
<sup>4</sup>Universidade Federal de Santa Catarina

Oil and gas pipelines installed in the deep sea have a finite lifetime, at the end of this period a strategy is required for the decommissioning of this infrastructure[1]. From an industrial perspective, this approach must be time and cost effective but equally, must adhere to contemporary regulations which require that decommissioning strategies protect the marine environment to the greatest degree possible[2,3]. Current regulations on mercury (Hg) cannot be specific as any threat of contamination is unknown with limited available data on the extent of Hg contamination within subsea pipelines[4,5]. It is essential that the concentrations of Hg accumulated on the surfaces of steel pipelines is understood. Similarly, the Hg species which are present and could leach into the environment must be identified, as any leaching of bioavailable species could have a significant impact on Hg bioaccumulation which is already significant in the marine food web.

We have previously stated that Hg adsorption on pipeline surfaces may represent a percent level increase oceanic Hg concentration[4]. Now, through the application of cold vapour atomic fluorescence spectrometry, single particle inductively coupled plasma mass spectrometry and synchrotron-based spectroscopic techniques we show that of the total Hg which is accumulated on pipeline surfaces a majority is immediately solubilised when the steel is treated with seawater. Furthermore, within this fraction it is possible to identify nanoparticulate Hg which would interact with biota entirely differently, relative to soluble Hg species, resulting in two potential routes for Hg to enter the food chain. Therefore, it is possible that pipelines left in the deep sea, following corrosion-induced breakdown, may act as a source of reactive Hg species in environmentally significant concentrations. Research in this area must be promoted to allow for appropriate risk assessment of oil and gas decommissioning projects and to ensure that the environment is protected.

## Hg isotope evidence for deep sea dark demethylation in the western North Pacific

Takeuchi A<sup>1</sup>, Okabe N<sup>1</sup>, Tada Y<sup>2</sup>, Marumoto K<sup>2</sup>

<sup>1</sup>National Institute for Environmental Studies, <sup>2</sup>National Institute for Minamata Disease

Factors affecting natural variations of methylmercury (MeHg) and dissolved elementary mercury (DEM) concentrations in the open sea water columns are not fully understood. The highest MeHg concentrations in the water columns are often observed in mesopelagic zones (200–1,000m), and DEM is ubiquitously present throughout the ocean. Vertical profiles of dark demethylation and reduction potential in the western North Pacific (NP) seawater were determined by enriched stable Hg isotope tracer experiments to reveal presence or absence of the dark demethylation and reduction in epipelagic (0–200m) and bathypelagic (1,000–4,000m) zones. Up to 8% of the spiked amount of <sup>201</sup>Hg (approx. 120pg) and up to 15% of the spiked monomethyl-<sup>199</sup>Hg (MM<sup>199</sup>Hg; approx. 27pg) were detected as DEM after 24-hr incubations of the spiked seawater. The produced <sup>201</sup>Hg<sup>0</sup> was observed in all the samples. This indicates that the dark chemical reduction may occur throughout the water columns in the western NP, and DEM in the deep sea can be derived from the in-situ chemical reduction of Hg<sup>2+</sup> in the aphotic zone. On the other hand, the determined amount of <sup>199</sup>Hg<sup>0</sup> derived from dark demethylation of MM<sup>199</sup>Hg was increased with increasing depth. No <sup>199</sup>Hg<sup>0</sup> was observed in the epipelagic zone whereas the larger amount of <sup>199</sup>Hg<sup>0</sup> was detected in the samples collected below oxygen minimum zone. Vertical variations of the detected amount of <sup>199</sup>Hg<sup>0</sup> indicate the absence of the dark demethylation in the upper ocean and the higher magnitude of the demethylation in the bathypelagic zone of the western NP. These suggest that the dark demethylation is not responsible for the low concentrations of MeHg in the upper ocean but can influence the reducing concentrations of MeHg and production of DEP in the deep sea.

116

## Decoding Mercury Dynamics in Two Meromictic Lakes using Low-molecular-weight Acids and Metagenomic Analyses

Todorova S<sup>1</sup>, Green H<sup>2</sup>, Qasim G<sup>1</sup>, Jazdyk A<sup>2</sup>, Driscoll C<sup>1</sup>

<sup>1</sup>Syracuse University, <sup>2</sup>SUNY Environmental Science and Forestry

The abstract was uploaded as a separate document because italicized words and power on numbers were not displayed properly here.

## Multi-model mercury simulation and analysis initiative to inform the Minamata and Long-Range Transboundary Air Pollution Conventions

Dastoor A<sup>1</sup>, Angot H, Bieser J, Brocza F, Edwards B, Feinberg A, Feng X, Geyman B, Gournia C, He Y, Hedgecock I, Ilyin I, Keating T, Kirk J, Lin J, Lehnerr I, Mason R, McLagan D, Muntean M, Rafaj P, Roy E, Ryjkov A, Selin N, De Simone F, Soerensen A, Steenhuisen F, Travnikov O, Wang S, Wang X, Wilson S, Wu R, Wu Q, Zhang Y, Zhou J, Zhu W, Zolkos S

<sup>1</sup>Environment and Climate Change Canada

The Multi-Compartment Hg (mercury) Modeling and Analysis Project (MCHgMAP) is an international multi-model research initiative to analyze environmental Hg levels to inform the effectiveness evaluations of the Minamata Convention on Mercury (MC) and Convention on Long-Range Transboundary Air Pollution (LRTAP). This paper presents the MCHgMAP experimental design (modeling architecture, inputs and evaluation data, simulations, and analysis) and progress to date. The study design exploits recent advances in Hg modeling, emissions and observations for addressing the key policy questions of the Conventions: (1) What are the contributions of anthropogenic emissions and releases and other Hg sources to current environmental Hg levels?, (2) How have these contributions changed over the timeline of the Conventions?, (3) How do the contribution levels and trends vary geographically?, (4) What are the contributions of anthropogenic emissions and releases and other drivers to the temporal trends in Hg levels across global regions? and (5) How are Hg levels expected to change in the future?

Once released from primary sources, Hg recycles between the atmosphere, land, and ocean (i.e., secondary emissions and releases), and as a result, past and present Hg emissions continue to affect the environment from decades to centuries. In MCHgMAP, a novel harmonized simulation approach between atmosphere, land, and ocean, and multi-media Hg models is employed to account for the changes in secondary Hg exchanges on Hg cycling. The MCHgMAP objectives include detection and attribution of recent and future global spatial patterns and temporal trends of environmental Hg, and identification of key knowledge gaps to advance Hg science and modeling to support policies. Modeling consistency is enhanced by utilizing a common set of emissions, environmental conditions, and observation datasets. A series of model experiments are developed and prioritized to ensure a systematic analysis and participation of a variety of models from the scientific community.

## Blue vs Humpback whales, frenzy for food or contaminants? Trophodynamics of mercury in Patagonia.

Hirmas A<sup>2</sup>, Molina B<sup>1,2,4</sup>, O'Driscoll N<sup>6</sup>, Bahamonde P<sup>3,8</sup>, Chiang G<sup>1,2</sup>

<sup>1</sup>Centro de Investigación para la Sustentabilidad (CIS), <sup>2</sup>Departamento de Ecología y Biodiversidad, Universidad Andrés Bello, <sup>3</sup>Núcleo Milenio INVASAL, <sup>4</sup>Facultad de Medicina Veterinaria y Agronomía, Universidad de las Américas, <sup>5</sup>Department of Animal Science, Facultad de Ciencias Veterinarias, Universidad de Concepción, <sup>6</sup>Department of Earth & Environmental Sciences, Acadia University, <sup>7</sup>Instituto de Ciencias Naturales Alexander Von Humboldt, Universidad de Antofagasta, <sup>8</sup>Center of Resilience, Adaptation & Mitigation, Universidad Mayor

Patagonia is considered a remote ecosystem, characterized by oceanographic, topographic and geological conditions that, together with the large contributions of fresh water in the sector (rain, melting of glaciers and rivers), allow the existence of a complex and dynamic marine ecosystem that produces one of the largest estuarine systems in the world, characterized by a high primary productivity that supports a great diversity of organisms. The northern sector of Patagonia has been described as a feeding site for large cetaceans such as blue whales (*Balaenoptera musculus*) and humpback whales (*Megaptera novaeangliae*), due to the large existing populations of their main preys, krill (*Euphausia* sp.) and squat lobster (*Munida* sp.) respectively. Mercury is a global pollutant of concern. It transforms to an organic form known as methylmercury in aquatic ecosystems, one of the most toxic forms due to its potential to bioaccumulate, and its efficient trophic transfer through marine food webs (biomagnification). The aim of this study was to assess the trophic interactions between two baleen whale species and different zooplanktonic organisms, and trophodynamics of Hg in whales in the Chilean Patagonia. Prey items were collected through net trawls and whales were sampled by collecting skin and blubber biopsies. Stable isotope analysis helped to determine that krill was the main prey item for blue whales, and for humpback whales it was the squat lobster. Humpback whales also presented a higher trophic level. MeHg was detected both in prey items and whale species, being significantly higher in whales than in preys. The biomagnification factor (BMF) calculated, indicate that diets generate a significant contribution of MeHg through biomagnification processes which was also supported by positive values of trophic magnification factor (TMF) that help us conclude that besides both whales are feeding in the same area, they accumulate different concentrations of MeHg.

## Health effects and economic benefit of pollution remediation in typical mercury mining area

Li P<sup>1</sup>, Jiang H<sup>1</sup>

<sup>1</sup>Institute of Geochemistry, Chinese Academy of Sciences

Methylmercury (MeHg) is a potent neurotoxin which poses health risk to local residents living in mercury (Hg) mining areas via the consumption of MeHg contaminated rice. To protect the environment and human health, ecological remediations have been carried out by local authorities in Wanshan Hg mining area (WSMA). However, the benefits of health risks of human MeHg exposure after ecological remediation are still unclear. Hence, based on previous studies conducted in WSMA, rice MeHg concentrations in different villages were modelled by the inverse distance weighting method at the time point of 2007, 2012, 2017, and 2019. The probabilistic model and risk assessment model were used to characterize the changes of human MeHg exposure and health benefits under different ecological remediation in WSMA, which the parameters of the model were adopted from rice consuming population. The results revealed a decrease of 3.88  $\mu\text{g}/\text{kg}$  in rice MeHg concentrations and a corresponding reduction of 0.039  $\mu\text{g}/\text{kg}/\text{d}$  in probable daily intake (PDI) of MeHg in 2019 compared to 2007 in WSMA on average. Ecological remediation in the WSMA resulted in a substantial reduction in economic losses, amounting to \$38.7 million. Pollution source treatment and planting structure adjustment contributed 84% and 16% of the total economic benefits, respectively. However, the flooding event in 2016 led to an economic loss of \$2.43 million (4.48% of total GDP in 2016) in the WSMM. The benefits analysis suggests that planting restructure adjustment generates the greatest benefits in the short term, whereas pollution source control maximizes health benefits in the long term. These findings can provide scientific advices for ecological remediation in the Hg polluted areas. As well, it can provide the foundation for health benefit assessment for human MeHg exposure via rice consumption.

120

## Westerlies-driven transboundary transport of atmospheric mercury to the north-central Tibetan Plateau

Sun S<sup>1</sup>

<sup>1</sup>Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences

The transboundary mercury (Hg) pollution has caused adverse effects on fragile ecosystems of the Tibetan Plateau (TP). Yet, knowledge of transport paths and source regions of atmospheric Hg on the inland TP remains poor. First continuous measurements of atmospheric total gaseous mercury (TGM) were conducted in the central TP (Tanggula station, 5100 m a.s.l., June-October). Atmospheric TGM level at Tanggula station ( $1.90 \pm 0.30$  ng m<sup>-3</sup>) was higher than the background level in the Northern Hemisphere. The identified high-potential source regions of atmospheric TGM were primarily located in the northern South Asia, Southeast Asia, West Asia, and northwest China. TGM concentrations were lower during the Indian summer monsoon (ISM)-dominant period ( $1.81 \pm 0.25$  ng m<sup>-3</sup>) than those of the westerly-receding period ( $2.18 \pm 0.40$  ng m<sup>-3</sup>) and westerly-intensifying period ( $1.91 \pm 0.26$  ng m<sup>-3</sup>), contrary to the seasonal pattern in southern TP. The distinct TGM minima during the ISM-dominant period indicated lesser importance of ISM-transported Hg to Tanggula station located in the northern boundary of ISM intrusion, compared to stations in proximity to South and Southeast Asia source regions. Instead, TGM concentrations showed an increasing trend as westerlies intensified, indicating the key role of westerlies in transboundary transport of atmospheric Hg to the inland TP.

## Mercury threat to declining migratory shorebirds along the East Asian-Australasian Flyway

Ma Y<sup>1</sup>, Choi C<sup>2</sup>, Shang L<sup>3</sup>, Klaassen M<sup>4</sup>, Ma Z<sup>5</sup>, Chang Q<sup>6</sup>, Jaspers V<sup>7</sup>, Bai Q<sup>8</sup>, He T<sup>9</sup>, Leung K<sup>10</sup>, Hassell C<sup>11</sup>, Jessop R<sup>12</sup>, Gibson L<sup>13</sup>

<sup>1</sup>Guangxi Normal University, <sup>2</sup>Duke Kunshan University, <sup>3</sup>Chinese Academy of Sciences, <sup>4</sup>Deakin University, <sup>5</sup>Fudan University, <sup>6</sup>Nanjing Normal University, <sup>7</sup>Norwegian University of Science and Technology, <sup>8</sup>Dandong Forestry and Grassland Development Service Center, <sup>9</sup>Zhanjiang Mangrove National Nature Reserve Bureau, <sup>10</sup>Hong Kong Waterbirds Ringing Group, <sup>11</sup>Australasian Wader Studies Group, <sup>12</sup>BirdLife Australia, <sup>13</sup>Southern University of Science and Technology

Exposure to pollutants is a potential but overlooked driver for population declines in shorebirds along the East Asian-Australasian Flyway. We combined knowledge of moult strategy and life history with a standardised sampling protocol to assess mercury (Hg) contamination in 984 individuals across 33 migratory shorebird species on an intercontinental scale. Feather Hg concentration was substantially higher in South China, Australia and Yellow Sea than in northern temperate and Arctic breeding ranges. Over one-third of sampled individuals exceeded toxicity benchmarks. Feather Hg was best explained by the moulting region, while habitat preference (non-coastal obligate or coastal obligate), the proportion of invertebrates in diet and forage stratum (foraging mostly on the surface or at depth) also contributed, but were less pronounced. Populations of the *Tringa* genus were at highest risk of Hg contamination. It is important to continue biomonitoring and expanding research to other pollutants to guide conservation of threatened shorebirds.

## Global survey of *hgcA*-carrying genomes in marine and freshwater sediments

Wang Y<sup>1</sup>, Ikuma K<sup>2</sup>, Brown A<sup>1</sup>, Deonaraine A<sup>1</sup>

<sup>1</sup>Texas Tech University, <sup>2</sup>Iowa State University,

Mercury (Hg) methylation is a microbially mediated process that produces methylmercury (MeHg), a bioaccumulative neurotoxin. A highly conserved gene pair, *hgcAB*, is required for Hg methylation, which provides a basis for identifying Hg methylators and evaluating their genomic composition. In this study, we conducted a large-scale omics analysis in which 281 metagenomic freshwater and marine sediment samples from 46 geographic locations across the globe were queried. Specific objectives were to examine the prevalence of Hg methylators, to identify horizontal gene transfer (HGT) events involving *hgcAB* within Hg methylator communities, and to identify associations between *hgcAB* and microbial biochemical functions/genes. Hg methylators from the phyla Desulfobacterota and Bacteroidota were dominant in both freshwater and marine sediments while Firmicutes and methanogens belonging to Euryarchaeota were only identified in freshwater sediments. Novel Hg methylators were found in the Phycisphaerae and Planctomycetia within the Planctomycetota, including potential *hgcA*-carrying anammox metagenome-assembled genomes (MAGs) from Candidatus Brocadiia. HGTs of *hgcA* and *hgcB* were identified in both freshwater and marine methylator communities. Spearman's correlation analysis of methylator genomes suggested that in addition to sulfide, thiosulfate, sulfite, and ammonia may be important species for Hg methylation processes in sediments. Overall, our results indicate that the biochemical drivers of Hg methylation vary between marine and freshwater sites, lending insight into the effectiveness of remediation strategies and the influence of a changing climate on Hg methylation processes.

## Microbial Mercury Methylation in Tibetan Thermokarst Lakes

Lu X<sup>1</sup>, Liu X<sup>1</sup>, Li L<sup>1</sup>, Yang Z<sup>1</sup>, Mu C<sup>1</sup>, Yang M<sup>2</sup>, Liu Y<sup>2</sup>, Gu B<sup>3</sup>

<sup>1</sup>Lanzhou University, <sup>2</sup>Huazhong Agricultural University, <sup>3</sup>Oak Ridge National Laboratory

Mercury (Hg) is a global pollutant that can be transformed to the neurotoxin, methylmercury (MeHg), under anoxic conditions by certain microorganisms. MeHg can bioaccumulate and biomagnify in aquatic food webs to concentrations that pose a threat to the health of humans and wildlife. With global warming, the permafrost on the Tibetan Plateau has been degrading over the past few decades, leading to the release of nutrients and organic carbon, as well as the remobilization of the stored Hg. This also creates thermokarst landscapes such as thermokarst lakes and ponds, which have been known to be hotspots for Hg(II) methylation in the Arctic, potentially increasing MeHg and its transport to neighboring aquatic ecosystems. However, our knowledge of MeHg formation and the dominant Hg(II) methylators in these Tibetan thermokarst lakes is limited. Here we analyzed total Hg (THg) and MeHg concentrations in the thermokarst lake water bodies and sediments on the central Tibetan Plateau. We found that, while Hg levels were lower than those in the Arctic and most other parts of the Tibetan Plateau, MeHg%, as an indicator of the net production level of in situ Hg methylation, was higher, suggesting that the formation of thermokarst lakes increased MeHg production. We confirmed the presence of microbial genera associated with Hg(II) methylation through substrate and inhibitor addition experiments. The results showed that molybdate addition was effective in inhibiting Hg(II) methylation in all three lakes, indicating that sulfate-reducing bacteria were the dominant Hg(II) methylators. Our study reveals that thermokarst lakes formed by permafrost degradation on the Tibetan Plateau could potentially lead to elevated MeHg levels in Tibetan ecosystems and may thus pose health risks to humans and wildlife, particularly under future climate warming scenarios.

## Mercury Bioaccumulation and Transfer in Subtropical Forest Bird Food Chains Insights from vivo-Nest Videorecording and Mercury Isotopes

Luo K<sup>1</sup>, Yuan W<sup>1</sup>, Wang X<sup>1</sup>, Feng X<sup>1</sup>

<sup>1</sup>State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences

Forests serve as the largest atmospheric Hg sink in terrestrial ecosystems, with  $\sim 1200 \text{ Mg yr}^{-1} \text{ Hg}^0$  being deposited onto the forest floor via litterfall. This process is particularly significant in subtropical and tropical regions, which are also renowned for their rich biodiversity in terrestrial ecosystems. However, the lack of established connections between Hg accumulation in forest organisms, such as birds, and atmospheric Hg deposition limits our understanding of Hg bioaccumulation pathways and ecological risks in forest ecosystems. This limitation hinders the effectiveness evaluation of the Minamata Convention on Mercury. This study employed a multidisciplinary approach (video observations and isotopic tools) to identify the key factors determining Hg exposure in forest birds and quantify the contribution of Hg sources in forest bird food chains, within a primary subtropical forest with high atmospheric Hg<sup>0</sup> deposition of  $50\text{--}80 \mu\text{g m}^{-2} \text{ yr}^{-1}$ . Our findings reveal that foraging niche determines the Hg exposure risk of sympatric forest insectivorous birds, highlighting the ecological risk of MeHg exposure for understory insectivorous birds (especially the riverine insectivorous songbirds) due to atmospheric Hg<sup>0</sup> deposition and methylation in the forest floor. We recommend further assessments of MeHg exposure for understory insectivorous birds and its ecological implications, to better understand how atmospheric Hg loading can influence the risk of remote wildlife subject to global Hg pollution.

## Mercury Levels and Potential Methylation/ Demethylation Rates in Canadian High Arctic Sea and Lake Ice Cores

Gigi S<sup>1</sup>, Huang H<sup>1</sup>, Mitchell C<sup>1</sup>, Lehnherr I<sup>2</sup>, Bergquist B<sup>3</sup>, Steffen A<sup>4</sup>, Criscitiello A<sup>5</sup>, Myers A<sup>5</sup>

<sup>1</sup>University of Toronto Scarborough, <sup>2</sup>University of Toronto Mississauga, <sup>3</sup>University of Toronto St. George, <sup>4</sup>Environment and Climate Change Canada, <sup>5</sup>University of Alberta

The Canadian High Arctic is being disproportionately affected by climate change, with for example, enormous contemporary losses of multi-year sea ice. These dramatic changes affect arctic marine, aquatic and terrestrial ecosystems as well as people and wildlife living in or around these areas. Before coastal, multi-year sea ice is entirely lost, it is important to better understand whether mercury biogeochemistry varies significantly between multi-year and first-year sea ice. This study therefore examined total mercury, methylmercury, and dimethylmercury concentrations, as well as enriched stable isotope-based methylation and demethylation potential rate constants in several ice cores (first-year and multi-year sea ice, as well as inland freshwater lake ice) from the northernmost place in Canada – Alert, Nunavut on the northern tip of Ellesmere Island. Based on other high latitude sea ice research, we hypothesized that first year ice cores will likely have more elevated mercury levels than the multi-year ice cores due to processes that expel ions or affect light penetration. We also hypothesize that the degradation of dimethylmercury to monomethyl mercury is a greater source of methylmercury in ice than is in situ methylation of inorganic mercury. The currently ongoing accumulation of results from this study will help to compare methylation and demethylation processes in different ice types so that we might ultimately predict how the climate change-driven shift from multi-year to first-year sea ice will impact net methylmercury production and bioaccumulation in local marine food webs.

126

## Japan's International Cooperation to Support Implementation of Minamata Convention

Kuroda I<sup>1</sup>

<sup>1</sup>Ministry of the Environment of Japan

At the Diplomatic Conference where Minamata Convention on Mercury was adopted, Ministry of Environment of Japan (MOEJ) expressed its intention to promote the voices and messages of Minamata and to support developing countries' efforts including monitoring of mercury in the environment and in humans through actions entitled "MOYAI Initiative".

Since then, MOEJ has been implementing various activities including trainings on atmospheric monitoring and analysis techniques for technicians of monitoring organizations.

It has started in the Asi-Pacific region and partnership and cooperation has expanded to African region.

At this session, I would like to introduce current activities as well as future collaboration.

127

## Linking Dimethylmercury and Monomethylmercury in a North Pacific Upwelling Region

West J<sup>1</sup>, Adams H<sup>1</sup>, Paulson E<sup>1</sup>, Kubler-Dudgeon I<sup>1</sup>, Choy C<sup>1</sup>, Schartup A<sup>1</sup>

<sup>1</sup>Scripps Institution of Oceanography, University Of California San Diego

More than three decades ago, measurements revealed that methylated mercury (Hg) in the open ocean consists of mono- (MMHg) and dimethylmercury (DMHg). Despite years of field- and experimental investigations, the dynamics between these two Hg species remain unclear. A question persists – Is DMHg primarily a precursor for or a product of MMHg? To answer this question, we studied Hg speciation in the California Current Ecosystem, an important ecological region where upwelling supplies nutrients and Hg to productive surface waters. We report methylated and total Hg concentrations from four full-depth profiles sampled twice daily in October 2023. These profiles extend from the nearshore continental shelf to the oligotrophic open ocean (33° 11'N, 118° 23'W – 30°N, 124° 40'W), and water samples were collected from a maximum depth of 3500 m. We observe an increase in DMHg from a few fM above 110 m depth up to ca 0.9 pM at ~400 m depth, just above the oxygen minimum zone (~500 m depth). MMHg concentrations were ~30 fM or below across all profiles and depths. The concentrations of DMHg and the DMHg:MMHg ratios we report here are among the highest measured in seawater. To understand why these waters are enriched in DMHg, we pooled water samples of each profile into depth groups based on their oxygen and DMHg concentrations (corresponding to depth ranges of ≤ 110 m, 111-750 m, and >750 m) and incubated them with isotopically labeled Hg species. These experiments reveal that DMHg forms exclusively from MMHg at all depths at rates around 0.01 d<sup>-1</sup>, with the fastest DMHg formation at depths below 750 m. No DMHg formed from divalent inorganic Hg. Finally, our results suggest that DMHg remains stable for weeks. In this presentation, we will explore the implications of these findings for the marine methylated Hg cycle.

128

## Advancements in Mercury Measurement and Global Comparability: Insights from Inter-Laboratory Exercises and Proficiency Testing Programs

Haraguchi K<sup>1</sup>

<sup>1</sup>National Institute for Minamata Disease

In order to evaluate the effectiveness of the Minamata Convention, multiple laboratories will analyze samples using different methods and equipment. It is crucial to ensure that the measurements obtained by the different labs can be compared. We establish reliability and international comparability in analyzing biological samples by providing reference materials such as hair, urine, and blood, aiming for consistency and accuracy. Proficiency testing, including samples of hair and fish, were also conducted. During the presentation, we will discuss the extent to which analytical variations and biases will influence the consistency and accuracy of the evaluation process.

## Mercury levels in some locally consumed freshwater fish, bivalves and canned tuna from selected areas of Viti Levu, Fiji.

Shah S<sup>1</sup>, Lal V<sup>2</sup>, Mani F<sup>1</sup>

<sup>1</sup>SAGEONS, USP, <sup>2</sup>IAS, USP

This study looked into the mercury (Hg) levels of locally consumed freshwater fish and bivalves collected within the vicinity of Ba River, Fiji Islands. Locally produced canned tuna was purchased from supermarkets. Canned fish products serve as a significant source of nutrition in the Pacific Islands Countries and Territories (PICTs). Dependence on canned fish products has increased in majority PICTs as a result of rapid population growth; which has exceeded the capability of well-managed coastal fisheries to supply necessary quantities of fish. Mercury; which is naturally present in the environment and is also anthropogenically introduced; is a concern in fish intake, particularly for vulnerable populations due to its potential adverse health and bioaccumulative effects. Human activities such as industrial processes and coal combustion releases additional Hg into the environment; leading to elevated levels in some aquatic organisms. Mercury is a non-essential, toxic, persistent and bioaccumulative element; a toxin to the central nervous system and readily crosses the placental barrier. Mercury bioaccumulates up the food chain, with large predatory fishes acquiring the greatest concentrations of Hg. The total Hg levels, as per Food and Agriculture Organization/World Health Organization (FAO/WHO) Codex Alimentarius Commission guidelines is 1 mg/kg for predatory fish and 0.5 mg/kg for smaller fish. In this study, fish and bivalve samples were allowed to undergo acid digestion and analysed via cold vapor atomic absorption spectroscopy (CVAAS). It is noted from this study that certain predatory fish have mercury concentrations close to the /FAOWHO limit of 1 mg/kg; whilst the smaller herbivorous fishes have Hg levels less than 0.5 mg/kg. The Hg levels in canned tuna were below the FAO/WHO regulatory guidelines. The bivalves had an average of 0.2 mg/kg of Hg.

## Artisanal and Small-scale Gold Mining and Biodiversity: A Global Literature Review

Dossou Etui I<sup>1</sup>, Stylo M<sup>1</sup>, Davis K<sup>1</sup>, Evers D<sup>2</sup>, Slaveykova V<sup>3</sup>, Burton M<sup>2</sup>, Wood C<sup>1</sup>

<sup>1</sup>United Nations Environment Programme, <sup>2</sup>Biodiversity Research Institute, <sup>3</sup>University of Geneva

ASGM is crucial to the livelihoods of about 20 million people in over 80 countries, mainly in rural areas. ASGM is largely informal, which increases the challenge of addressing negative social and environmental effects including on biodiversity. However, with proper guidance, ASGM can operate in a responsible manner, using cleaner production methods that minimize impacts on human health and the environment. The global literature review jointly conducted by the UNEP Global Mercury Partnership, the Biodiversity Research Institute and the University of Geneva, outlines interactions between ASGM and biodiversity based on findings from 27 ASGM NAPs, along with a review of more than 100 publications. According to the literature reviewed, the interrelationship between ASGM and biodiversity, including protected areas, is pervasive at every stage of ASGM operations, from extraction to mine closure, and generates significant impacts on the surrounding ecosystems. These include deforestation, soil degradation, chemical contamination of aquatic and terrestrial systems, and alteration in waters turbidity. These environmental stressors lead to loss or deterioration of habitat and, by extension, indigenous biodiversity and ecosystem services. Moreover, legal, institutional, and regulatory frameworks and related measures, inadequate or non-existent in some cases, may not necessarily support sustainable practices, often resulting in exploited sites abandoned without remediation, reclamation, rehabilitation, or restoration measures. To mitigate such impacts, a key recommendation arising is to strengthen the integration of the interrelationship between ASGM and biodiversity in the implementation of national strategies. The work also led to the mapping of ASGM sites reported in the NAPs that are located in or within 5km of key biodiversity areas. Further investigations relating to the visualisation of the impacts of ASGM on biodiversity and a mapping of the interactions between the above-mentioned sites and protected areas are being developed as a support to global action towards preserving biodiversity and ecosystem services.

132

## Application of *Leucaena leucocephala* modified biochar as a novel material for controlling the release and exposure of mercury in the soil: From human health risk perspective.

Yoashi N<sup>1</sup>, Hsi H<sup>1</sup>, Chien L<sup>2</sup>

<sup>1</sup>Graduate Institute of Environmental Engineering, National Taiwan University, <sup>2</sup>School of Public Health, Taipei Medical University

Mercury (Hg) contaminated agricultural soil have received wide attention because of the adverse risk posed towards food security, environmental and human health. In addition, climate change altered Hg transmission and mobility in the soil limiting soil productivity and nutrients bioavailability hence elevated health risk. In order to adapt the aforementioned risks, incubation and pot experiments were employed to showcase the impacts of novel synthesized biochar without any modification (BC) and modified (NH<sub>4</sub>P-BC) on the Hg immobilization, nutrients accessibility (phosphorous, nitrogen, calcium, magnesium, and potassium), and human health risk.

Results showed that impregnation increased the surface area, available nutrients, and ox-nitrogenated function groups (O-N, O-P, C=O-C, and O-H). Specifically, elemental analysis proved an increase of nitrogen and oxygen from 0.47% and 9.47% to 3.01% and 21.4% respectively.

Pot experiment indicated the effectiveness of NH<sub>4</sub>P-BC in immobilizing soil Hg, compared to the control and biochar without any modification groups reducing the quantity of Hg absorbed by *Lactuca sativa*. Notably, the soil available nutrients under NH<sub>4</sub>P-BC amendment were the highest followed by BC and the control group demonstrating exceptional impregnation contribution to climate change adaptation.

Furthermore, the bioaccessible fraction of Hg exhibited a notably higher level in the control group compared to the BC group, with a further reduction observed under NH<sub>4</sub>P-BC treatment. NH<sub>4</sub>P-BC treatment demonstrated a low non-carcinogenic health risk for farmers, considering oral food intake, oral soil ingestion, and dermal contact exposure routes. Additionally, in the context of the general public accounting for food ingestion, a diminished health risk was observed for both adults and children.

With multifaceted capabilities, NH<sub>4</sub>P-BC emerges as a practical and sustainable alternative to conventional adsorbents in Hg removal technologies. It not only addresses the impact of climate change on Hg pollution in agricultural farmland but also presents a green and sustainable remediation technology applicable globally.

## Factors and processes controlling Hg methylation in soils of Northern Poland

Płońska P<sup>1</sup>, Saniewska D<sup>1</sup>, Łęczyński L<sup>2</sup>, Bełdowska M<sup>1</sup>

<sup>1</sup>Department of Chemical Oceanography and Marine Geology, Faculty of Oceanography and Geography, University of Gdańsk, <sup>2</sup>Department of Geophysics, University of Gdańsk

The soil, similar to the sediment in the marine environment, serves as a storage reservoir for various toxic substances, including mercury and its compounds. However, beyond its role as a storage medium, soil can also function as a source of numerous substances to the aquatic environment. Methylmercury (MeHg) stands out as one of the most toxic forms of mercury (Hg) present in the environment. Certain studies designate Poland as a significant 'emitter' of mercury into both the European atmosphere and the Baltic Sea. Consequently, the objective of this study was to identify the factors influencing the formation and retention of MeHg in the soil, as well as its remobilization into the river in southern Baltic Sea catchment area.

During the fall and winter of 2021/2022, fifteen soil core samples on fifteen stations, each with a length of 200 cm, were collected. Stations were located on meadows, in for forests and in anthropogenic sites. Stations were selected with guide of geological map to ensure sampling of different soil type, e.g.: peats, brown earth and sand. The concentration of mercury and its fractions was determined using the thermodesorption method, while methylmercury concentration was measured through cold vapor atomic fluorescence spectroscopy.

Factors contributing to the influx and formation of methylmercury included precipitation, distance from the riverbank, soil moisture, and the bioavailability of organic matter. Mercury sulfide is transported to the soil surface with precipitation and undergoes relatively rapid conversion to methylmercury. Additionally, an increase in MeHg concentration was noted in moist soils located near the riverbank. Soil with degraded organic matter had lower mercury methylation potential compared to soil with fresh organic matter.

134

## Reducing mercury use in Uganda's Artisanal and Small Scale Gold Mining sector: interventions through National Action Plans and planetGOLD

Nakafero A<sup>1</sup>

<sup>1</sup>National Environment Management Authority

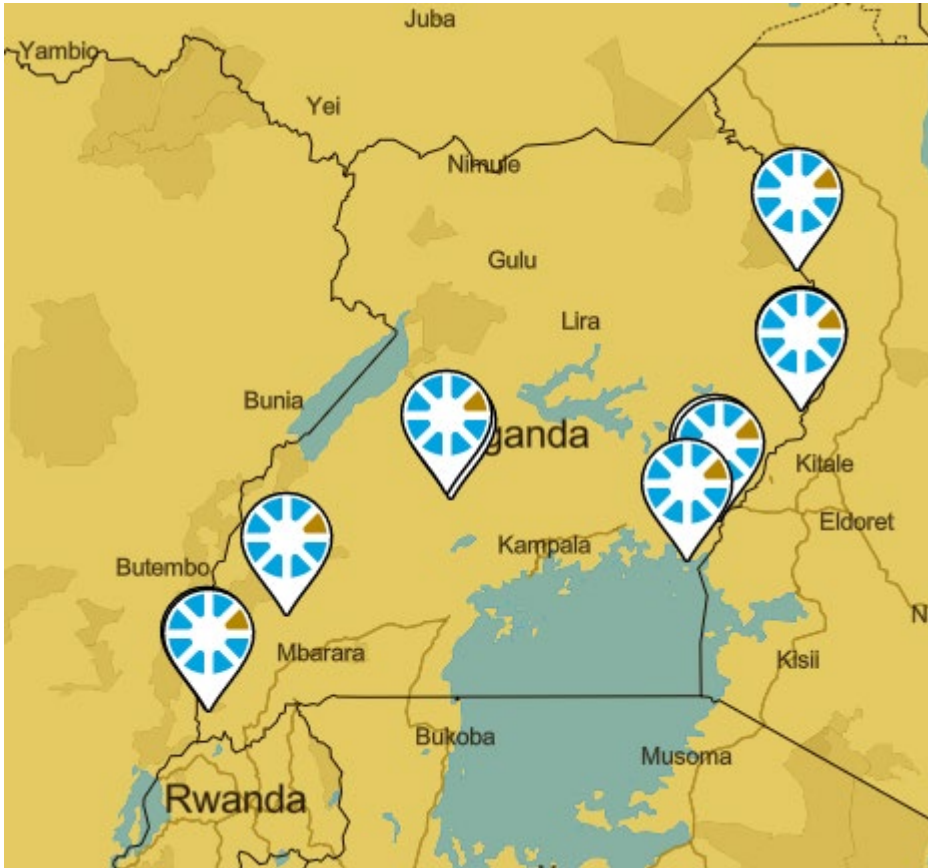
An estimated 400,000 to 600,000 women and men work in the wider artisanal small-scale mining (ASM) sector, according to the Directorate of Geological Survey and Mines, thus supporting an additional estimated 2 million people indirectly (<https://www.planetgold.org/uganda>). The total Artisanal and Small Scale Gold Mining in Uganda (ASGM) workforce in Uganda to be over 31,000 whereas the entire ASGM value chain population is about 391,347 people (NEMA, 2019).

However, Uganda's ASGM sector is the highest contributor (18496kg/yr) of mercury emissions in Uganda (refer to figure 1 indicating mercury sources & emissions in Uganda). A study on baseline estimates of mercury use and practices in Uganda carried out by NEMA in 2018 equated mercury use in Artisanal and Small-Scale Gold Mining to 15,000kgs of mercury per year (figure 2 showing ASGM sites using mercury).

In response to the above; a National Action Plan for Artisanal and Small Scale Gold Mining in Uganda, (NAP) was developed in 2019 with an objective of reducing the use of mercury and mercury compounds in, and the emissions and releases to the environment of mercury from, ASGM in accordance to Annex C of the Minamata Convention. This not only enabled Uganda to comply with the text of the Minamata Convention, but fostered cooperation with stakeholders including development partners in implementing the NAP strategies including .

Uganda is implementing the planetGOLD Uganda project's objective is to reduce the use of mercury in the country's ASGM sector through a holistic, multisectoral integrated formalization approach and to increase access to finance, leading to adoption of sustainable mercury-free technologies and access to traceable gold supply chains (<https://www.planetgold.org/uganda>). The planetGOLD Uganda project plans to support 4,500 men and women at 11 mine sites in the country, reducing mercury use by 15 tonnes over the course of the five-year project (IBID).

### Abstract Graphics



135

## Mercury Isotopic Evidences Reveal Precipitation Controls Mercury Accumulation in Soils of Tianshan No. 1 Glacier Retreat Area

Liu N, Wang X<sup>1</sup>, Feng X<sup>1</sup>

<sup>1</sup>State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences

Glacier melting due to global warming can significantly affect the fate of mercury (Hg) in local terrestrial ecosystems. However, there are significant knowledge gaps in the understanding of the source contribution and factors influencing Hg accumulation in continental glacier-retreated areas, which limits understanding of Hg cycling in terrestrial ecosystems under global change. In this study, we comprehensively investigated Hg concentrations and isotopic signatures on a 250-year scale in Tianshan No. 1 Glacier retreat area. Results showed that the Hg concentration in the surface 0-15 cm soil increased with the increase of glacier retreat time. The 0-15 cm soil Hg pool increased by approximately 1.71 times over a period of approximately 250 retreat years. The surface 0-15 cm soil in glacier-retreated areas shows distinctive positive  $\Delta^{199}\text{Hg}$  ( $0.43 \pm 0.21$  ‰) and  $\Delta^{200}\text{Hg}$  ( $0.06 \pm 0.04$  ‰). The Hg isotopic mixing model indicates that atmospheric Hg<sup>0</sup> and atmospheric Hg<sup>2+</sup> contribute approximately half of the soil Hg sources ( $51 \pm 12\%$  and  $44 \pm 14\%$ , respectively), while geogenic input contribute about  $4 \pm 2\%$  of the Hg sources. The significant positive correlation between soil Hg concentration and atmospheric Hg<sup>2+</sup> contribution highlights the key role of precipitation in the accumulation of soil Hg. The average atmospheric Hg<sup>2+</sup> deposition flux in Tianshan No. 1 Glacier retreat area was estimated with  $6.12 \pm 20.75$   $\mu\text{g m}^{-2} \text{ yr}^{-1}$  in this study.

136

## Advanced Mercury Speciation Analysis in Fish Samples using NexSAR Speciation Solution

Wagener V<sup>1</sup>

<sup>1</sup>Perkin Elmer

Mercury Speciation Analysis in Fish Samples Using NexSAR Speciation Solution

This study presents an investigation into mercury speciation analysis, focusing on the application of the NexSAR speciation solution and an innovative methodology for the rapid and accurate determination of methylmercury (MeHg) and elemental mercury (HgO) in freeze-dried fish samples. The key objectives of this research include aqueous extraction optimization, achieving baseline separation of HgO and MeHg, and evaluating the robustness and repeatability of the NexSAR Speciation Solution.

The aqueous extraction methodology is developed to efficiently extract MeHg and HgO from freeze-dried fish samples. Chromatographic analyses reveal that the tuna fish matrix has minimal impact on chromatography, with peak shapes and retention times comparable to standards. The method achieves accurate measurements within a timeframe of 3 minutes, emphasizing the system's efficiency in mercury speciation analysis.

In this work robustness and repeatability are demonstrated across multiple analyses, ensuring consistent and reliable results. The chromatographic analysis demonstrates baseline separation of HgO and MeHg, a critical aspect for precise quantification and characterization of each species.

Overall, this study highlights the capabilities and efficiencies of this solution, providing a powerful tool for scientists engaged in mercury speciation analysis. The findings Advanced contribute to the understanding of mercury distribution, bioaccumulation, and potential health risks associated with fish consumption. The presented methodology holds promise for enhancing environmental monitoring, food safety assessment, and regulatory compliance in mercury speciation analysis.

137

## Improved mechanistic modeling on reproducing particulate bound mercury in the marine atmosphere

Chen L<sup>1</sup>, Zhang Y, Zhou Q, Han G, Xu Z

<sup>1</sup>East China Normal University

Mercury (Hg) is a neurotoxic pollutant and ubiquitous on the planet, which receives a global concern owing to its adverse health outcomes. The formation of Hg(P) mainly stems from the adsorption of Hg(II) on aerosol particles such as nitrate aerosols, sulfate aerosols, and sea salt aerosols. However, limitation exists for the employment of the traditional gas-solid partitioning schemes which is based on observations in the continents to modeling Hg(P) in the marine atmosphere. This study employed an improved mechanism in an atmospheric chemical transport model to simulate the mechanistic processes of Hg(P) cycling in the marine atmosphere, such as the hygroscopic growth of sea salt particles, the adsorption of Hg(II) on particles, and the desorption of Hg(P) from particles. Observations from cruises and offshore islands collected from peer-review literature were employed to evaluate the model performance and improvement. We find the gas-solid partitioning scheme on the basis of primary and secondary processes can successfully reproduce atmospheric Hg(P) concentrations over coastal and inland areas, but fails to reproduce the concentrations over the ocean. The new process-based scheme significantly elevates the simulated atmospheric Hg(P) concentrations in the marine atmosphere. Finally, we revisit a new budget of global atmospheric Hg cycling in the marine atmosphere, including 160 Mg yr<sup>-1</sup> and 1360 Mg yr<sup>-1</sup> of Hg for dry deposition and wet deposition fluxes of seasalt-bound Hg(P), respectively, which provides a new understanding of the global pollutant.

## My mom gives me Hg: Evaluation of mercury contamination in South American fur seal pups and females (*Arctocephalus australis*).

Peña Galindo I<sup>1</sup>, Bernaldes B<sup>9</sup>, Montalva F<sup>9</sup>, Gutiérrez J<sup>6</sup>, Arancibia A<sup>8</sup>, Angel A<sup>8</sup>, Gómez A<sup>7</sup>, Robbins V<sup>11</sup>, Arakawa N<sup>10</sup>, Pérez-Venegas D<sup>7</sup>, Seguel M<sup>3</sup>, Cortés-Hinojosa G<sup>2</sup>, Chiang G<sup>4</sup>

<sup>1</sup>Programa de Medicina de la Conservación, Universidad Andrés Bello, <sup>2</sup>Escuela de Medicina Veterinaria, Pontificia Universidad Católica de Chile, <sup>3</sup>Department of Pathobiology, Ontario Veterinary College, University of Guelph, <sup>4</sup>Centro de Investigación para La Sustentabilidad, Facultad de Ciencias de la Vida, Universidad Andrés Bello, <sup>5</sup>Departamento de Ecología y Biodiversidad, Facultad de Ciencias de la Vida, Universidad Andrés Bello., <sup>6</sup>Programa de Doctorado en Ciencias, mención Ecología y Evolución, Universidad Austral de Chile, <sup>7</sup>Centro de Investigación y Gestión de Recursos Naturales (CIGREN), Instituto de Biología, Facultad de Ciencias, Universidad de Valparaíso, <sup>8</sup>Facultad de Ciencias de la Vida, Universidad Andrés Bello., <sup>9</sup>Facultad de Ciencias Biológicas, Pontificia Universidad Católica de Chile, <sup>10</sup>Faculty of veterinary medicine, Kagoshima University, <sup>11</sup>Emergency and Referral Hospital of West Toronto

In Chile, numerous mines (mainly gold and copper) but also, other human activities are important sources of mercury (Hg), a global pollutant and object of long-range transport. The discharges from mines and metal-related industries flow into rivers and the ocean, where this metal accumulates in sediment deposits on the bottom of the ocean, in biota, and it is transferred from lower to upper trophic levels. Marine mammals, are useful bioindicator species for monitoring metal contamination in aquatic ecosystems because, they are crucial for determining the potential risk of contaminated food consumption. In pinnipeds, the accumulation in high concentrations of Hg is toxic and can induce clinical disease with neurological manifestations. Pinnipeds are excellent valuable indicators of pollutants accumulated in the marine environment as a top predator, and their biological and ecological characteristics. The current study estimates bioaccumulation and compares the levels of Total Hg (THg) in blood and milk samples of fur seal adult females and their pups during the first days of life, in the largest breeding colony of South American fur seals (*Arctocephalus australis*) in Guafo Island, a remote oceanic island in the South of Chile. THg, was analyzed using a Direct Mercury Analysis System (DMA-80evo, Milestone). The main objective of this study is to try to evidence the horizontal transfer of this metal. Preliminary results in females showed a range of THg 15.65-618.24mg/kg ww, with an average of 201.5 mg/kg ww. In pups, showed a range of THg between 358.77-6.54 mg/kg ww, with an average of  $77.54 \pm 6.71$  mg/kg ww. These preliminary results are higher to those found in serum of fur seal (*Arctophoca australis* ssp.) from Perú (levels found in females  $0.0028 \pm 0.0021$  ug/g ww, and  $0.018 \pm 0.007$  ug/g ww in pups). Our results confirm transfer of THg from mother to pup.

### Abstract Graphics

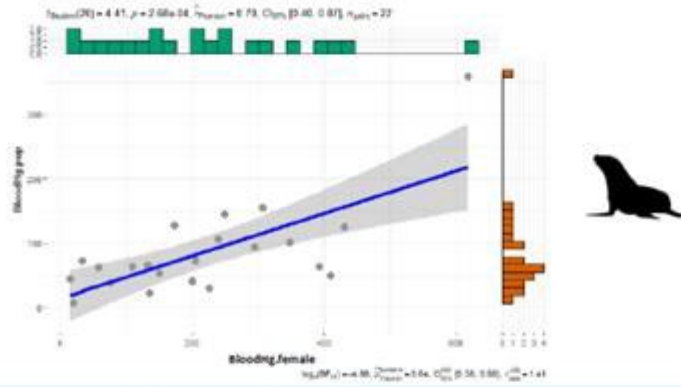


Figure 4: Relationship between blood [THg] ( $\mu\text{g}/\text{kg ww}$ ) of pups and females.

139

## From toxic to non-toxic

### What options are available to prevent mercury blowouts in flue gas systems

Frank S<sup>1</sup>

<sup>1</sup>New Environmental Technology GmbH

How much mercury is dissolved in the circulation of a scrubber system?

Is it really many kilograms? Or just a few grams?

How is this Hg present in acidic and alkaline scrubbers?

What happens to this dissolved Hg in scrubber systems when unpredictable events occur?

Can dissolved Hg be converted to Hg(0) by reducing agents (e.g. SO(2) gas)? Does dissolved Hg(0) remain in the scrubber liquid?

At this point, no activated carbon filter can retain the enormous amount of elemental Hg, and Hg escapes into the environment in very high concentrations via the gas phase.

Is there a difference between "brominated and iodised or chlorinated" Hg compounds? Are brominated Hg compounds stable against SO(2) reductions?

Does Hg(0) condense at "cool" spots in the gas purification system? How can permanent Hg(0) emissions be avoided?

How can such events be prevented permanently and safely?

By converting mercury into an insoluble form!!!!

Does this only work in an alkaline scrubber? Why not start in an acidic scrubber?

But how can this work in a strongly acidic scrubber (pH < 1!!)?

Are there already incinerators that work according to such a principle?

How many incinerators work according to this principle? How many incinerators exceed the limit values? Does this work in all incinerator systems? Is it possible to control scrubber systems analytically?

Are there any developments for dry sorption systems? For power stations? For soil remediation?

Our presentation addresses these questions and explains a solution and its advantages for the sustainable prevention of unwanted Hg blowouts.

#### **Abstract Graphics**

**From Toxic to Non-Toxic**



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Frank Scharrenbach, [fscharrenbach@netgmbh.com](mailto:fscharrenbach@netgmbh.com)  
New Environmental Technology GmbH  
Gutenbergstrasse 7  
69214 Eppelheim

## Methylmercury Export from a Headwater Peatland Catchment Decreased with Cleaner Emissions Despite Opposing Effect of Climate Warming

Mccarter C<sup>1</sup>, Sebestyen S<sup>2</sup>, Jeremiason J<sup>3</sup>, Nater E<sup>4</sup>, Kolka R<sup>2</sup>

<sup>1</sup>Nipissing University, <sup>2</sup>USDA Forest Service Northern Research Station, <sup>3</sup>Gustavus Adolphus College, <sup>4</sup>University of Minnesota

Peatlands are sources of bioaccumulating neurotoxin methylmercury (MeHg) that is linked to adverse health outcomes. Yet, the compounding impacts of climate change and reductions in atmospheric pollutants on mercury (Hg) export from peatlands are highly uncertain. We investigated the response in annual flow-weighted concentrations (FWC) and yields of total-Hg (THg) and MeHg to cleaner air and climate change using an unprecedented hydroclimatic (55-years; streamflow, air temperature, precipitation, and peatland water tables), depositional chemistry (21-years; Hg and major ions), and streamwater chemistry (~17-years; THg, MeHg, major ions, total organic carbon, and pH) datasets from a reference peatland catchment watershed in Minnesota, USA. Over the hydroclimatic record, annual mean air temperature increased by ~1.8°C, while baseflow and the efficiency that precipitation was converted to runoff (runoff ratio) decreased. Concurrently, precipitation-based deposition of sulfate and Hg declined, where wet Hg deposition declined by ~3-4 µg Hg/m<sup>2</sup>. Despite declines in wet Hg deposition over the study period, the catchment accumulated on average 0.04±0.01 g Hg/ha/yr based on wet Hg deposition minus THg yield alone and will likely never flush the anthropogenic Hg from the catchment when including other Hg deposition and emission pathways. Annual MeHg FWC was positively correlated with mean annual air temperatures (p=0.03, r=0.51), runoff ratio (p<0.0001, r=0.76), and wet Hg deposition concentration (p<0.0001, r=0.79). Decreasing wet Hg deposition and annual runoff ratios counterbalanced increased peatland MeHg production due to higher air temperatures, leading to an overall decline in streamwater MeHg FWC. Streamwater MeHg export may continue to decrease only as long as declines in runoff ratio and wet Hg deposition persistently outpace effects of increased air temperature.

## EDGARv8 anthropogenic speciated mercury emissions: hotspots, shift of key emitting sources on global gridmaps and trend analysis over five decades.

Muntean M<sup>1</sup>, Crippa M<sup>2</sup>, Crippa M<sup>1</sup>, Guizzardi D<sup>1</sup>, Pagani F<sup>2</sup>, Becker W<sup>2</sup>, Banja M<sup>1</sup>, Schaaf E<sup>1</sup>, Darras S<sup>1</sup>  
<sup>1</sup>European Commission, Joint Research Centre, <sup>2</sup>Unisystems S.A.

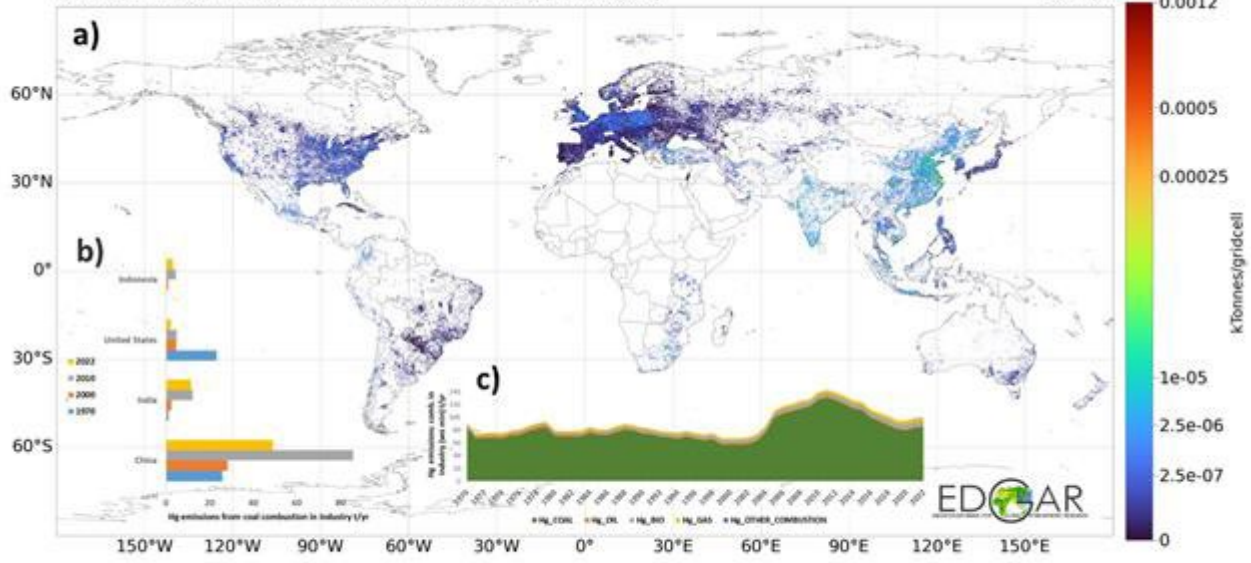
Scientific findings related to mercury emissions, which are affecting human health and the environment globally, are essential for the implementation of both the Minamata and Long-Range Transboundary Air Pollution Conventions. Besides total mercury, speciated and gridded mercury emissions are of utmost importance for impact evaluation throughout chemical transport modelling, in particular the estimation of mercury deposition that is the primary pathway from emissions sources to the exposure.

The Emissions Database for Global Atmospheric Research (EDGAR) develops independent estimates of total mercury (Hg) by country and sector for all countries focusing on key anthropogenic mercury emitting sources by using as input activity data from international statistics and emissions factors from official guidebooks. The methodology and the results of a trend analysis by region and top emitting countries for the period 1970-2022 will be discussed, highlighting the impact of shift of key sources on emissions pattern over this period. EDGARv8 inventory includes emissions of elemental mercury (Hg<sup>0</sup>) that can be transported over long distances, and gaseous oxidised mercury (Hg<sup>2+</sup>) and particle bound mercury (Hg-P), which are the reactive forms of mercury with shorter lifetimes. A comprehensive analysis of regional contributions to both elemental and reactive mercury emissions will be provided and the hotspots of emissions will be presented on global gridmaps of 0.1 x 0.1 degree resolution for the year 2022. As an example, for coal combustion in industry, Figure 1 illustrates the hotspots in 2022, the changes in emissions levels over five decades in top emitting countries and trends by fuel for this sector. An insight on the drivers for temporal and spatial changes of the emissions patterns over five decades will be provided by highlighting the impact of increases in fuel consumption and production of different commodities together with the implementation of mitigation technologies on the levels of mercury emissions.

### Abstract Graphics

Hg emissions:  
Coal combustion in coal fired industrial boilers (Year 2022)

Global total: 85.17t  
EDGARv6.0



*Figure 1. Mercury emissions from coal combustion in industry: a) hotspots of emissions in 2022, b) the changes in emissions levels over five decades in top emitting countries, c) trends by fuel type.*

143

## Examining the uptake of Methylmercury by the mixotroph *Ochromonas* during heterotrophic or autotrophic growth

Sanchez M<sup>1</sup>, Mason R<sup>1</sup>, Chen C<sup>2</sup>, Taylor V<sup>2</sup>

<sup>1</sup>University Of Connecticut , <sup>2</sup>Dartmouth College

Photosynthetic plankton, both algae and bacteria, constitute the foundation of the marine food web. Recent studies looking at Mixotrophs, distinguished by their ability to use photosynthetic and heterotrophic nutrition, have been revealed to be the majority of single-celled and multicellular plankton. The impact of these organisms within marine food chains is being recognized and advanced, but there is an urgent need for understanding the role of mixotrophs in the trophic transfer of contaminants. The bioaccumulation of methylmercury (MeHg) by microbes has been recognized as its key entry point into aquatic food webs. The bioconcentration of MeHg in marine phytoplankton is recognized as the largest bioconcentration step in the marine food chains. Certainly, incorporating mixotrophic variation in nutrition may account for differences among MeHg algal uptake and therefore most likely impact Earth's Mercury cycling. Therefore, developing biogeochemical models that focus on incorporating mixotrophs into oceanic food web structures and their impact on MeHg bioaccumulation is the next step toward understanding the role of these important organisms. To understand how different feeding modes drive changes in MeHg uptake a feeding/light experiment was conducted. The uptake of MeHg by the mixotrophic *Ochromonas*, characterized as a facultative mixotroph, was examined under different environmental factors, such as light levels and prey availability. Dissolved MeHg concentrations, particulate MeHg concentrations, and Volume Concentration Factors (VCFs) were calculated. An increase of MeHg uptake by *Ochromonas* during heterotrophy conditions suggests feeding modes most likely play a role in the increase of bioaccumulation of MeHg via algal cells. Further research is needed to examine mixotrophs' implications in the 21st century. Mixotrophs' role within marine food chains and likely in MeHg bioaccumulation, will impact the fate, transport, and transformation of mercury in our oceans.

144

## planetGOLD programme as a vehicle for implement of National Action Plan and ultimately reporting progress on the Minamata Convention

Bernaumat L<sup>1</sup>, Keane S

<sup>1</sup>UNEP

Artisanal and small-scale miners are responsible for producing 20 percent of the world's gold each year. Many of these small-scale mining operations use mercury to extract their gold, making this sector the largest source of mercury pollution in the world. The Minamata Convention on Mercury requires countries with "more than insignificant ASGM" to reduce and where feasible eliminate the use of mercury in the sector and to develop a National Action Plan (NAP) which includes elimination of the four worst practices, establishing baseline estimates, targets for reduction, timelines, strategies for formalization, involvement of stakeholders, managing mercury trade, public health and sharing information. The planetGOLD programme, funded by the Global Environment Facility and under implementation since 2018 now support 25 countries in implementing measures to formalize the sector, improve access to finance and markets, implement mercury-free extraction technologies and share information. The programme represents an ideal tool for countries to implement their NAPs and the monitoring system put in place under the programme will allow countries to gather the necessary data for reporting on the progress toward its implementation which is due every 3 years. Having consistent metrics to measure mercury reduction will strengthen the confidence in the data reported but we now need to focus on updating of the baseline data with the knowledge and experience accrued through planetGOLD implementation. The scientific community can contribute to these efforts by developing new techniques for characterizing baselines, within the context of resource constraints typical of countries where ASGM is practiced.

145

## Quantity and Fate of Mercury in Crude Oil

Maxson P<sup>1</sup>

<sup>1</sup>Concorde East/West Srl

Mercury mobilized during oil and gas production and processing has not been widely discussed until relatively recently, while this industry remains a major source of global mercury releases and wastes. It has been assumed that mercury in crude oil was less of a problem than gas. However, there is evidence that mercury in crude oil is also significant, even as global crude production continues to increase.

This presentation focuses on the mercury in crude oil:

- How much mercury is mobilized annually, in which geographical regions, and at which parts of the production process?
- How much of the mobilized mercury is recovered or recycled, in which geographical regions?
- For the mercury that is not recovered or recycled, what are the typical disposal practices?
- During the process of mercury mobilization, mercury recovery, and mercury waste disposal, what are the pathways and quantities of mercury emissions to the air, and mercury releases to water and soil?
- Where can we most effectively intervene to reduce the quantities of these mercury emissions and releases, and their impacts on human health and the environment?

While the Middle East, North America and the CIS countries are responsible for 75% of global oil production and are themselves faced with concerning levels of mercury contamination in crude, the average mercury contamination in Southeast Asian crude is five to ten times higher. Preliminary calculations suggest that the production and processing of crude oil mobilizes at least 100 metric tons of mercury, of which some 40% likely occurs in the Asia-Pacific region.

This information will 1) help to motivate industry to implement responsible mercury release, emission and waste management practices, and will 2) provide researchers (e.g., developing the next Global Mercury Assessment) with improved data on mercury pathways and emissions linked to global oil production.

## Monitoring of Atmospheric Mercury in the Northern Cape Province of South Africa

Mashile T<sup>1</sup>, Martin L<sup>1</sup>

<sup>1</sup>Sol Plaatje University

The Minamata Convention requires improved monitoring of atmospheric Hg and characterization of Hg sources across the globe. The environmental and air pollution due to mercury emission needs to be monitored and investigated as studies have shown that it is harmful to the environment and has severe effects on human health. In this investigation, a network of passive air samplers (PAS) were deployed across various towns in the Northern Cape (NC) Province for continuous monitoring, evaluation and measurements of atmospheric Hg levels and determination of the spatial distribution of atmospheric Hg across the province. The PAS captures gaseous Hg on sulfur-impregnated activated carbon after it passes through a radon diffusive barrier. Since the PASs are small, relatively low in cost and require no power source, they can be deployed at multiple location sites, yielding a much greater spatial range and resolution of gaseous Hg measurements. The PAS were deployed and exposed for time periods between 1 month and 3 months for three years. The Tekran 2537B Mercury Vapour Analyzer instrument was used for determinations of concentrations of total gaseous mercury (TGM). The instrument operates by passing air over two gold cartridges (traps) working in tandem to capture and determine the concentration of TGM in the air. The results showed a presence of substantial amounts of Hg in some of the monitoring sites across the NC Province. The accurate measurement of gaseous Hg concentrations in the atmosphere is important to understand its source, cycling, distribution and temporal trends.

147

## Feeding strategy as a key driver of mercury (Hg) bioaccumulation at the base of the marine food web.

Amptmeijer D<sup>1</sup>, Bieser J<sup>1</sup>, Schrum C<sup>1,2</sup>

<sup>1</sup>Helmholtz-zentrum Hereon, <sup>2</sup>Universität Hamburg

Feeding strategy as a key driver of mercury (Hg) bioaccumulation at the base of the marine food web.

Mercury (Hg) and methylmercury (MeHg) bioaccumulation in the marine food chain can lead to unsafe levels of MeHg in seafood for human consumption. While the process of bioaccumulation at the top of the food web is relatively well understood, less is known about the bioaccumulation of Hg and MeHg at the base of the food web. This study models the impact of different feeding strategies on the bioaccumulation of both inorganic Hg and MeHg.

Our findings reveal a strong correlation between MeHg bioaccumulation and trophic level, contrasting with the absence of such a relationship for inorganic Hg. Given that inorganic Hg can constitute the majority of Hg at the food web's base, lower trophic animals may contain higher Hg levels than their predators. Since inorganic Hg is considerably less toxic than MeHg, this disparity can lead to a misperception of the risk certain low trophic level benthic species pose when consumed, particularly if only total Hg is measured.

This study highlights the complexity of bioaccumulation at the food web's foundation and underscores the importance of measuring both inorganic and MeHg content when assessing seafood toxicity. These results emphasize the need for a comprehensive approach to ensure accurate evaluations of seafood safety.

## An approach to effectively characterizing a river impacted by a historical mercury mine using a combination of abiotic and biotic media

Dent S<sup>1</sup>, Silvertooth J, Eckley C, Eagle-Smith C, Crawford J

<sup>1</sup>Cdm Smith

Black Butte Mine is a former cinnabar mine that drains into the headwaters of the Coast Fork Willamette River, which flows through the United States (U.S.) Army Corp of Engineers managed flood control reservoir, the Cottage Grove Reservoir (Oregon, USA). The river between the mine and reservoir is predominantly high-energy and drains a watershed that consists of forested and agricultural areas. Discharge is highly variable between storm events and baseflow conditions, affecting the chemical and physical processes in surface water, riverbank/floodplain soil, sediments, porewater, and hyporheic zone water. Sport fish within Cottage Grove Reservoir contain mercury concentrations above the U.S. Environmental Protection Agency's fish consumption advisory threshold of 0.3 µg/kg. This study involved sampling of surface water, riverbank soil, porewater, and periphyton for analysis of total mercury, methylmercury, and relevant ancillary parameters that relate to both the mobility and methylation of mercury. Sediment and porewater sampling results suggest that pockets of sedimentation zones within the stream corridor are active zones of methylmercury production; however, their footprint composes less than 3% of the total riverbed area. Parallel food-web studies in this drainage showed elevated mercury concentrations in young-of-year fish within this river system, and considering the seemingly small footprint of sediment methylation zones it appeared there was a missing piece of the puzzle for methylmercury sources. Periphyton, a biotic media far more ubiquitous than sedimentation zones in the channel, was sampled at the study site and showed total mercury and methylmercury concentrations comparable to and often greater than sediment concentrations. Using a generalized linear model, periphyton mercury concentrations tracked significantly with dissolved fractions of mercury in surface water. If the approach had been limited to abiotic media, this investigation may have missed an important mercury methylation pathway, demonstrating the importance of using a whole ecosystem approach when evaluating mercury contaminated sites.

## Assessment of elemental mercury outgassing from groundwater and subsurface soils using passive air samplers

Alten A<sup>1</sup>, Biester H<sup>1</sup>, McLagan D<sup>2</sup>

<sup>1</sup>Technische Universität Braunschweig, <sup>2</sup>Queen's University

Gaseous elemental mercury ( $\text{Hg}^0$ ) as the dominant Hg species in the atmosphere can be transported globally. Contaminated groundwater and soil are important sources and sinks for atmospheric  $\text{Hg}^0$ , so it is important to understand biogeochemical processes and fluxes of  $\text{Hg}^0$  within these systems. Compared to high-temporal resolution fluxes measured by active monitoring systems, the  $\text{Hg}^0$  passive air sampler (MerPAS) excels at assessing spatial concentration gradients of Hg and these data have been used to effectively produce time-averaged, above-ground emissions fluxes. Here we aim to investigate the expansion of the MerPAS flux assessments into the subsurface environment to better understand Hg cycling and the redox processes driving Hg releases to the atmosphere in different soil-groundwater systems. MerPAS samplers were deployed within the soil and at different heights within groundwater wells at two former wood treatments ( $\text{HgCl}_2$  pollution) facilities (Germany), and a Hg contaminated chemical plant landfill area (Switzerland).  $\text{Hg}^0$  were also monitored by LumexRA-915M for comparison. Groundwater and sub-soil samples were collected to provide critical metadata. Various redox and Hg concentration gradients were observed in groundwater among different sampling locations. Horizontally, MerPAS  $\text{Hg}^0$  concentrations at the surface of groundwater wells correlated with Hg contamination in groundwater. While vertically, MerPAS  $\text{Hg}^0$  concentrations increased with well depths ( $26 \pm 58$  times), which confirms groundwater as the main source of  $\text{Hg}^0$  in the wells. MerPAS well  $\text{Hg}^0$  concentrations ( $10\text{-}100,000 \text{ ng/m}^3$ ) were significantly higher than those in soil ( $1\text{-}100 \text{ ng/m}^3$ ), suggesting Hg redox processes are more dynamic and  $\text{Hg}^0$  outgasses more readily from groundwater than subsurface soils.  $\text{Hg}^0$  levels measured by MerPAS and LumexRA-915M were consistent in order of magnitude. Our results demonstrate the applicability of subsurface MerPAS deployment methods to derive unique information on Hg biogeochemistry and potentially fluxes within contaminated soil-groundwater systems.

150

## Associations between in utero methylmercury exposure and child's weight from birth to 36 months in rural China and Norway

Rothenberg S<sup>1</sup>

<sup>1</sup>Oregon State University

**Background:** Most studies investigating the associations between prenatal methylmercury (MeHg) exposure and child's birthweight were conducted in populations, where fish ingestion was the primary dietary source of MeHg. Inconsistent results were reported, potentially reflecting confounding by beneficial nutrients naturally present in fish. Rice ingestion is also an important dietary source of MeHg, however, rice does not contain the same beneficial nutrients as fish, and thus confounding may be minimized.

**Methods:** The associations between child's weight (birth, 12 months, and 36 months) (z-scores, adjusted by age and sex) and prenatal MeHg exposure (maternal blood mercury) were investigated in two cohorts, where the dietary sources of MeHg differed (China, n=382; Norway, n=2,822). To investigate associations, we used a linear mixed model for repeated measures, and included a 2-way interaction term between maternal blood mercury and study location.

**Results:** Among Chinese mothers, the median daily rice ingestion rate was significantly higher (213 g/day), compared to Norwegian mothers (24 g/day) (Wilcoxon rank sum test,  $p < 0.0001$ ). Conversely, all Norwegian mothers ingested fish weekly, while 43% of Chinese mothers rarely or never ingested fish (Chi-squared test,  $p < 0.0001$ ). Blood mercury levels were significantly higher among Chinese mothers (median: 1.2  $\mu\text{g/L}$ ), compared to Norwegian mothers (median: 1.0  $\mu\text{g/L}$ ) (Wilcoxon rank sum test,  $p < 0.0001$ ). In adjusted models, among Chinese mothers, a negative association between weight-for-age z-scores and maternal blood mercury (log<sub>10</sub>-transformed) was observed (beta: -0.32, 95% confidence interval (CI): -0.65, -0.0016), while the association for Norwegian mothers was null (beta: -0.0074, 95% CI: -0.09, 0.08).

**Conclusions:** Prenatal methylmercury exposure was negatively associated with child's weight-for-age z-scores in rural China, where rice ingestion was the primary dietary source of MeHg, and confounding due to beneficial nutrients were minimized. These results are important because low birthweight and child's growth during infancy are associated with other adverse health outcomes.

## Exploring the sensitivity of Southern Ocean mercury cycling to uncertainties in ocean mercury processes

Fisher J<sup>1</sup>, Heimbürger Boavida L<sup>2,5</sup>, Petrova M<sup>2</sup>, Torres-Rodriguez N<sup>2</sup>, Puigcorbé V<sup>3</sup>, Angot H<sup>4,5</sup>, Dommergue A<sup>4</sup>, Huang S<sup>6</sup>, Zhang Y<sup>6</sup>, Wu P<sup>6</sup>

<sup>1</sup>University Of Wollongong, <sup>2</sup>Mediterranean Institute of Oceanography, <sup>3</sup>Institut de Ciències del Mar, <sup>4</sup>Institut des Géosciences de l'Environnement, <sup>5</sup>CNRS, <sup>6</sup>Nanjing University

A critical goal for the mercury science community is effectiveness evaluation: determining whether Minamata Convention actions have decreased mercury in the environment. The atmosphere will be the first harbinger of change due to the short residence time of mercury in air. In the Southern Hemisphere, only three sites have ongoing records that can be used to evaluate pre- and post-Convention changes in atmospheric mercury: Kennaook/Cape Grim, Tasmania; Amsterdam Island; and Cape Point, South Africa. All three are coastal sites bordering the Southern Ocean and show significant influence from oceanic mercury released to the atmosphere through air-sea exchange. It is critical to understand how much of the atmospheric mercury at these sites comes from the ocean and how much from sources regulated by the Convention. These questions are best addressed using computational models that can distinguish between different sources. However, state-of-the-science models have repeatedly shown poor skill in simulating atmospheric mercury at the Southern Hemisphere monitoring sites.

In this work, we combine oceanic (MITgcm-Hg) and atmospheric (GEOS-Chem) mercury models to identify critical uncertainties in Southern Ocean mercury cycling. First, we run a suite of MITgcm-Hg ocean model sensitivity studies, perturbing uncertain parameters involved in abiotic ocean mercury cycling processes (e.g., particulate export flux, air-sea exchange). We use these sensitivity simulations to evaluate the extent to which each parameter impacts simulation of mercury in the surface ocean. From there, we use the modelled surface ocean mercury concentrations as input to the GEOS-Chem atmospheric model to determine the sensitivity of atmospheric mercury concentrations to uncertain ocean parameters. Throughout, we evaluate the model simulations using observations from Southern Ocean research voyages and ongoing atmospheric monitoring sites. Preliminary assessment of the parameter values that provide the most accurate simulations as well as key uncertainties to target in future measurement efforts will also be discussed.

## Metagenomic assessment of Hg methylating and demethylating communities in wastewater treatment plants

Wang Y<sup>1</sup>, Ikuma K<sup>2</sup>, Brown A<sup>1</sup>, Deonarine A<sup>1</sup>

<sup>1</sup>Texas Tech University, <sup>2</sup>Iowa State University,

Wastewater treatment plants (WWTPs) are a widely used biotechnology, in which highly diverse and dynamic microbial communities are utilized to break down organic substrates. There is concern about the risks associated with WWTPs as a source of mercury (Hg) and methylmercury (MeHg) to aquatic systems receiving treated effluent and to terrestrial systems where activated sludge is applied. In these environments, Hg can be transformed to the neurotoxin MeHg, which further accumulates in the food web. WWTP effluent and sludge can release microbes which carry Hg cycling genes (*hgcA*, *mer*), potentially impacting downstream microbial communities and Hg cycling. A comprehensive omics analysis was conducted on 342 sludge and 198 wastewater samples (including 19 effluent and 179 raw sewage) from WWTPs in various countries and regions across the globe. Objectives were to evaluate the prevalence of Hg methylation (*hgcA*) and demethylation (*merB*) genes in WWTP sludge, effluent, and sewage; to identify microbes carrying Hg-cycling genes; to assess horizontal gene transfer (HGT) in these microbial communities; and to determine potential biochemical drivers of Hg methylation and demethylation. The *hgcA* gene was detected in sludge and sewage from 34 WWTPs, and *merB* genes in 54 WWTPs. 142 *hgcA*-carrying and 31 *merB*-carrying metagenome-assembled genomes (MAGs) across over 15 phyla were identified, including *hgcA*-carriers involved in nitrogen fixation. A total of 336 HGT events from the sludge samples and 104 HGT events from the sewage and effluent samples within *hgcA* and *mer* communities were identified. Correlation analysis showed that nitrogen and sulfur metabolism were associated with Hg demethylation (*merB*) in sewage and sludge, while genes for nitrogen fixation (*nifT*, *nifB*, *nifN*) and iron uptake (*feoA*) were closely linked to *hgcA*. Overall, our study suggests that Hg cycling and methylation processes in systems receiving WWTP effluent and sludge warrant further study.

## Using systems analysis to evaluate interventions towards sustainability in artisanal and small-scale gold mining

Selin H<sup>1</sup>, Selin N, Goldstein R

<sup>1</sup>Boston University

Under the Minamata Convention on Mercury, parties with more than insignificant artisanal and small-scale gold mining (ASGM) within their territory must develop a national approach with the ultimate aim of phasing out mercury use in ASGM. Addressing mercury use in ASGM often poses complex challenges, and interventions aiming to reduce mercury use that do not account for on-the-ground conditions and interactions may be ineffective or have unintended negative consequences for environmental protection and human well-being. We apply a qualitative systems-level framework – the Human, Technical, Environmental (HTE) framework – to explore implications of potential interventions towards greater sustainability in the ASGM sector. We focus on a case study of the Madre de Dios region of Peru. We use the HTE framework to compare and contrast three different types of interventions: (1) legally-focused efforts such as formalization or permitting; (2) technological developments such as mercury-free mining techniques; and (3) market-based systems such as certification and labeling. We first construct a qualitative system description, identifying system components and classifying interactions among three categories of material system components (human, technological, and environmental) that are mediated by two categories of non-material components in the form of institutions and knowledge. We then use qualitative and quantitative network analysis to evaluate changes in interactions based on the three categories of interventions. Our analysis is based on interviews with government officials and representatives of stakeholders and indigenous organization, analysis of legal instruments and government documents, fieldwork in Madre de Dios, and insights from the existing ASGM literature. By examining quantitative changes in network structure related to mercury in ASGM, we show that this network approach represents dynamics of prior interventions, which have not altered the centrality of mercury in this system. Further analysis identifies key leverage points that could be targeted by future interventions.

## A decade of atmospheric mercury monitoring at Concordia Station in central Antarctica

Dommergue A<sup>1</sup>, Angot H<sup>1</sup>, Bertrand Y<sup>1</sup>, Magand O<sup>2</sup>, Pirrone N<sup>3</sup>, Sprovieri F<sup>3</sup>

<sup>1</sup>Univ. Grenoble Alpes, CNRS, INRAE, IRD, Grenoble INP, IGE, <sup>2</sup>Observatoire des Sciences de l'Univers à La Réunion (OSU-R), UAR 3365, CNRS, Université de La Réunion, Météo France, IRD, <sup>3</sup>NR-Institute of Atmospheric Pollution Research

Gaseous elemental mercury (Hg(0)) undergoes efficient global transport, with even polar regions receiving substantial inputs of anthropogenic mercury through long-range transport.

While extensive monitoring has been conducted in the Arctic atmosphere, there remains a significant knowledge gap concerning the vast 7 million km<sup>2</sup> Antarctic continent, particularly in the high-altitude plateau region. Previous studies (Brooks et al., 2008; Dommergue et al., 2012; Angot et al., 2016) have suggested a pronounced reactivity of mercury at the air–snow interface on the plateau in summer.

Since 2012, atmospheric Hg(0) has been continuously monitored using a Tekran 2537 instrument at the French/Italian Concordia Station (75S, 123E) located at an altitude of 3220m on the Antarctic plateau, approximately 1100 km away from the nearest coast of East Antarctica. The station experiences air temperatures ranging from -20°C in summer to -70°C in winter, with an annual mean temperature of -45°C. The region undergoes permanent daylight in summer and continuous darkness in winter, with a modest snow accumulation of about 10 cm/year.

Considering the challenging weather conditions and technical/logistical constraints, the presentation of such a record stands as a noteworthy achievement in itself.

Throughout the 10-year timeframe Hg(0) records exhibited a consistent annual and seasonal pattern, displaying relatively stable values ( $1.13 \pm 0.20$  ng/m<sup>3</sup>; median  $\pm$  SD) during the dark winter period (May–Aug). In contrast, there was a notably fluctuating signal in the summer months (Nov–Feb), with a median value of  $0.73 \pm 0.43$  ng/m<sup>3</sup> and a range extending from below detection limit up to 5 ng/m<sup>3</sup>. This variability can be attributed to the intense photoreactivity and the variability of the atmospheric boundary layer height during the summer season.

Angot, H., et al (2016). ACP 16(13): 8249-8264.

Dommergue, A., et al (2012). ACP 12(22): 11027-11036.

Brooks, S. et al (2008). Atmos Envir 42(12): 2877-2884.

## Top-down constraints on mercury emissions from diffuse sources

Roy E<sup>1</sup>, Feinberg A<sup>2,3</sup>, Fisher J<sup>4</sup>, Powell J<sup>5</sup>, Harnwell J<sup>5</sup>, Ward J<sup>5</sup>, Selin N<sup>1,2</sup>

<sup>1</sup>Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology,

<sup>2</sup>Institute for Data, Systems, and Society, Massachusetts Institute of Technology, <sup>3</sup>Department of Atmospheric Chemistry and Climate, Institute of Physical Chemistry Blas Cabrera, CSIC, <sup>4</sup>Centre for Atmospheric Chemistry, School of Earth, Atmospheric and Life Sciences, University of Wollongong,

<sup>5</sup>Climate, Atmosphere & Ocean Interactions Research Program, CSIRO Environment

Constraints on global mercury (Hg) cycling necessitate the development of improved emission estimates. Globally distributed atmospheric Hg measurement records offer an opportunity to quantify regional emission sources when incorporated into an appropriate inverse modeling framework. Since such techniques typically require observations with high frequency and accuracy, applications of inverse modeling for diffuse source quantification in Hg science have remained largely untapped.

This study extends traditional inverse modeling techniques to quantify regional Hg wildfire emissions using the GEOS-Chem chemical transport model and an eight-year Hg measurement record at Gunn Point, Australia by optimizing for statistical properties of the model and observations. Concentration signals represent the sensitivity of a measurement location to emissions from another region and are calculated as the difference between a baseline GEOS-Chem simulation and a sensitivity simulation in which local, regional, or global wildfire emissions are eliminated. We define a linear response function for the measurement site using the regional concentration signals and the emission magnitude from each respective region. We then use a Markov chain Monte Carlo sampling method to explore the sample space of emission inputs to the linear response function to minimize the difference of statistical properties of this function relative to observations while accounting for observational and model-based errors. Initial results that optimize emissions to match the 95th percentile range suggest that existing GEOS-Chem emissions for Australia's Northern Territory lie below the 25th percentile of the posterior distribution, which is robust to an increase in spatial and temporal resolution of the GEOS-Chem model used to define the linear response function. We compare these results with emissions derived from footprint-based source quantification techniques. We also show how these methods can be extended to other dominant diffuse emission sources including artisanal and small-scale gold mining.

## Strategies to reduce mercury use in the Artisanal and Small-Scale Gold Mining sector – evidence from Bolivia

Tarras-Wahlberg H<sup>1</sup>

<sup>1</sup>planetGOLD Bolivia

In the context of the Minamata Convention, this paper considers strategies to reduce mercury use in the Artisanal and Small-scale Gold Mining (ASGM) sector of Bolivia.

Mercury emissions from the approximately 1600 ASGM cooperatives in Bolivia are severe, despite the existence of relevant and controlling legislation. This policy failure has different causes. The large number of miners operating in remote areas makes supervision difficult. A further complication is the economic importance and political power of the ASGM sector which limits the government's ability to control it.

For miners, mercury amalgamation is attractive as it is simple and requires minimal operational control. It is, however, inefficient and in most cases, there are better methods available. Given the limitations of the regulatory approach, initiatives have been taken to assist Bolivian miners to use other technologies. Still, only minor, and temporary successes have been achieved. An important reason relates to how cooperatives are governed, with continuous changes in leadership which makes planning difficult. And in terms of initiatives taken to assist ASGM miners to become formal, there is no clear evidence that such operators use less mercury.

A case can be made for regulatory reform and improved supervision, and for introducing controls that reduces the availability of mercury - or raises its cost. Furthermore, efforts to improve awareness of the risks entailed in using mercury are worthwhile, and overall sensibilisation that creates concern and pressure by affected communities and other stakeholders has had positive impact in some cases.

In the shorter term, initiatives to assist miners to use alternative technologies should be considered. However, in the longer term, the preference given in Bolivian policy to ASGM should be evaluated critically, and consideration given to strategies that encourage small operators to become larger, and better organised entities, that can engage in responsible mining practices

158

## Mercury fluxes to the air and water following a wildfire in the mountains of the Pacific Northwest, USA.

Eckley C<sup>1</sup>, Johnson M<sup>1</sup>, Luxton T, Bollman M

<sup>1</sup>United States Environmental Protection Agency

Wildfires are occurring with increased frequency and severity and previous studies have shown that wildfires can release mercury (Hg) into the atmosphere through the burning of organic material and heating of soils. The objective of this study was to measure: 1) the potential for enhanced Hg volatilization from soils in the years following a wildfire and 2) the short- and long-term potential for post-wildfire soils and ash to sequester Hg in precipitation. To address the first objective dynamic flux chamber (DFC) measurements were conducted at forested and post-wildfire locations representing moderate and high severity burns. The second objective was addressed by conducting lab-based sorption experiments by mixing precipitation with soils and ash from moderate and high severity wildfires. The results showed that un-burned forests were net-sinks for atmospheric gaseous Hg (flux: -6 ng/m<sup>2</sup>/day); whereas the post-wildfire soils were a net Hg source (flux: 11 ng/m<sup>2</sup>/day), which was largely related to increased levels of solar radiation reaching the soil. The sorption experiments with Hg in precipitation showed that the freshly burned materials absorbed >95% of the Hg in precipitation. Over several years, the sorption efficiency of the soils and ash decreases, but is still represents a much larger sink for atmospheric inputs relative to un-burned soils. Overall, these results indicate that post-wildfire landscapes decrease atmospherically deposited Hg loading to water; however, a higher proportion of deposited Hg is re-emitted to the atmospheric and prolongs the active cycling of Hg in the environment.

## Beaver ponds are poisoning rivers of Tierra del Fuego

Lopez R<sup>1</sup>, Molina B, Astorga M, Hirmas A, Peña I, Quesada F, Chiang G

<sup>1</sup>Universidad Andrés Bello

River impoundments represent global threats to the integrity of freshwater ecosystems. Dams can be built by humans but also by environmental engineers, such as beavers. Damming of rivers changes all the natural flow of a stream system, increasing the deposition of sediments and nutrients, as well as a large amount of many toxic chemicals. In this new condition, Hg-methylating microorganisms thrive producing methylmercury, an organic form of mercury of human and environmental concern. Although artificial and natural reservoirs have similar biogeochemical effects, the role of beaver ponds in the cycling of some elements such as mercury tends to be underestimated by comparison. Beaver dams appear to play an important role as a source of toxic methylmercury in aquatic systems, but this effect has only been studied in the Holarctic area, where there is a historical record of anthropogenic mercury contamination in air and ecosystems. In this sense, southern Patagonia represents a good opportunity to study how this invasive species could influence the Hg cycle, because it has faced the presence of the North American beaver (*Castor canadensis*) since the second half of the last century. With the aim of evaluating the effect of beaver dams on the mercury cycle in rivers of Tierra del Fuego; total mercury (THg) and methylmercury (MeHg) concentrations in the beaver dam systems were determined twice a year (during the winter and summer months). Samples of water, sediment and organic matter were collected upstream of each beaver, in the reservoir itself and downstream of the dam. On the one hand, THg concentrations showed an increase in beaver ponds, although loads beyond the dam decreased again. On the other hand, methylmercury also increased in reservoirs, but loads also remained high downstream. Until now, beaver dams could be considered hotspots for methylmercury contamination.

## Over a decade of atmospheric mercury monitoring at Amsterdam Island (37°S) in the French Southern and Antarctic Lands

Dommergue A<sup>1</sup>, Angot H<sup>1</sup>, Bertrand Y<sup>1</sup>, Magand O<sup>2</sup>, Duperray S<sup>1</sup>, Collignon L<sup>4,1</sup>, Sonke J<sup>3</sup>, Laffont L<sup>3</sup>

<sup>1</sup>Univ Grenoble Alpes, <sup>2</sup>Observatoire des Sciences de l'Univers à La Réunion (OSU-R), UAR 3365, CNRS, Université de La Réunion, Météo France, IRD, <sup>3</sup>Géosciences Environnement Toulouse, CNRS/IRD, Université Paul Sabatier Toulouse 3, <sup>4</sup>GEOPS, Université Paris Saclay, CNRS

The monitoring of atmospheric mercury (Hg) levels has been suggested as a crucial indicator for periodically assessing the effectiveness of the Minamata Convention utilizing existing monitoring data and observed trends. Nonetheless, there are data gaps, particularly in the Southern Hemisphere.

In this context, we present a comprehensive dataset (see details in Magand et al 2023) spanning over a decade of atmospheric Hg monitoring at Amsterdam Island (37.80°S, 77.55°E) in the remote southern Indian Ocean. Amsterdam Island is situated midway between South Africa, Australia, and the Antarctic coast, and is predominantly influenced by marine air masses.

Datasets include gaseous elemental and reactive (oxidised) Hg species concentrations from either active/continuous or passive/discrete acquisition methods, and annual total Hg wet deposition fluxes. The mean gaseous elemental Hg concentration over the 2012–2022 period was  $1.05 \pm 0.14$  ng/m<sup>3</sup> (mean  $\pm 2\sigma$ , 95% confidence interval) and no significant trend was detected. Reactive Hg species concentrations showed median values of 1.7 and 4.7 pg/m<sup>3</sup> for active methods (Tekran speciation unit) and filter-based methods, respectively, with rare instances of concentrations reaching up to  $\sim 25$  pg/m<sup>3</sup>.

Regarding Hg wet deposition, the annual flux averaged  $2.04 \pm 0.80$   $\mu\text{g m}^{-2}$  year<sup>-1</sup> as published in Tassone et al (2023).

These datasets are made available to the community (<https://gmos.aeris-data.fr/>) to support policy-making and further scientific advancements.

### Reference

Magand, O., Angot, H., Bertrand, Y., Sonke, J. E., Laffont, L., Duperray, S., Collignon, L., Boulanger, D., and Dommergue, A.: Over a decade of atmospheric mercury monitoring at Amsterdam Island in the French Southern and Antarctic Lands, *Scientific Data*, 10, 836, 10.1038/s41597-023-02740-9, 2023.

Tassone, A., Magand, O., Naccarato, A., Martino, M., Amico, D., Sprovieri, F., Leuridan, H., Bertrand, Y., Ramonet, M., Pirrone, N., and Dommergue, A.: Seven-year monitoring of mercury in wet precipitation and atmosphere at the Amsterdam Island GMOS station, *Heliyon*, 9, e14608, <https://doi.org/10.1016/j.heliyon.2023.e14608>, 2023.

## Gold sampling for atmospheric mercury analysis: insights and limitations

Gačnik J<sup>1</sup>, Dunham-Cheatham S<sup>2</sup>, Lyman S<sup>3</sup>, Gustin M<sup>1</sup>

<sup>1</sup>Department of Natural Resources and Environmental Science, University of Nevada, Reno, <sup>2</sup>College of Agriculture, Biotechnology & Natural Resources, University of Nevada, Reno, <sup>3</sup>Bingham Research Center, Utah State University

Keywords: Atmospheric mercury; Calibration; Gold cartridge; Peak integration algorithm; Tekran 2537

Many atmospheric mercury (Hg) measurements are based on preconcentration of Hg by gold amalgamation and thermal desorption of Hg into a cold vapor atomic fluorescence spectrometer. This method has been used for decades; however, there is still debate as to whether only gaseous elemental mercury (Hg<sup>0</sup>) or both Hg<sup>0</sup> and gaseous oxidized mercury (Hg<sup>II</sup>) are collected on the gold cartridge. Additionally, there have been discussions regarding whether peak area or peak height of the desorption profile should be used to calculate concentrations. In our work, we addressed the uncertainty of whether Hg<sup>0</sup> or TGM (Hg<sup>0</sup> + Hg<sup>II</sup>) is measured when using a Tekran<sup>®</sup> 2537 analyzer. Experiments were performed using a newly developed Hg<sup>II</sup> permeation calibrator; extensive validation tests showed that the calibrator produced a reproducible and stable Hg<sup>II</sup> permeation rate. The results of Hg<sup>II</sup> sampling and analysis using gold amalgamation showed that the Tekran<sup>®</sup> 2537 analyzer measures an atmospheric Hg fraction that is somewhere between Hg<sup>0</sup> and TGM. By adding a thermolyzer upstream of the analyzer, all Hg<sup>II</sup> was measured as Hg<sup>0</sup>. We recommend the use of a thermolyzer or a cation exchange membrane upstream of the analyzer to enable TGM and Hg<sup>0</sup> measurements, respectively. A real-time peak height calculation algorithm was also developed that can be used with legacy Tekran 2537 analyzers, so both peak area and peak height integration results can be obtained simultaneously. The algorithm was used in combination with bell jar Hg<sup>0</sup> injections and permeation calibrator Hg<sup>0</sup> injections to obtain multipoint calibration curves for different Tekran 2537 analyzer models simultaneously. The results showed inconsistencies both between different Tekran 2537 models and calibration methods, showcasing the need for routine multipoint calibrations for atmospheric Hg measurements.

162

## Particulate-bound mercury sampling using membrane materials: biases due to adsorption of gaseous oxidized mercury

Gačnik J<sup>1</sup>, Allen N<sup>1</sup>, Dunham-Cheatham S<sup>2</sup>, Lyman S<sup>3</sup>, Gustin M<sup>1</sup>

<sup>1</sup>Department of Natural Resources and Environmental Science, University of Nevada, Reno, <sup>2</sup>College of Agriculture, Biotechnology & Natural Resources, University of Nevada, Reno, <sup>3</sup>Bingham Research Center, Utah State University

Keywords: Gaseous oxidized mercury adsorption; Membrane materials; Particulate-bound mercury; Permeation calibrator

Measurements of atmospheric mercury (Hg) still present analytical challenges and unknowns that limit the reliability of measured data. One of the unknowns is associated with membranes used for capturing particulate-bound mercury (PBM). PBM membranes are currently the most common sampling method for PBM utilized in atmospheric Hg measurement systems. It has been hypothesized that PBM membranes could also collect gaseous oxidized mercury (GOM), therefore, the selectivity of PBM membranes for just PBM compounds could be poor, leading to biases in measurement systems collecting PBM. In our work, we used both ambient air sampling and laboratory experiments (using a gaseous HgBr<sub>2</sub> calibrator) to study adsorption of GOM by PBM membranes. Controlled laboratory results revealed that membranes designed to retain only PBM accumulated significant amounts of GOM. Additionally, particulate matter adsorbed on PBM membranes provided an active surface area for GOM retention. Ambient air sampling revealed that GOM can be reduced to gaseous elemental mercury (GEM) on PBM membranes, further complicating and biasing measurement data. Our results lead to questions regarding the validity of many PBM measurements performed in past decades, including results obtained with Tekran analyzers, membrane-based designs, and certain dual-channel analyzers. We recommend the measurement of reactive mercury (RM, GOM + PBM) until new and bias-free methods for atmospheric Hg speciation are developed.

## A time series of mercury speciation at Scripps Pier, La Jolla, CA: Insights on methylmercury production and cycling in the surface ocean

Adams H<sup>1</sup>, West J<sup>1</sup>, Kubler-Dudgeon I<sup>1</sup>, Bowman J<sup>1</sup>, Lamborg C<sup>2</sup>, Schartup A<sup>1</sup>

<sup>1</sup>Scripps Institution of Oceanography, <sup>2</sup>University of California, Santa Cruz

The Ellen Browning Scripps Memorial Pier (Scripps Pier) is an integral aspect of the research conducted at Scripps Institution of Oceanography. Time series for various oceanographic properties have been established since the initial construction of the pier over 100 years ago, and more time series are added annually along with many other short-term experiments. This setting is unique due to the proximity of the deep La Jolla Submarine Canyon, which allows for the deep Canyon waters to mix with surface waters, stimulating biological productivity. The Scripps Pier is ideal for studying mercury (Hg) speciation in surface waters due to the occurrence of tidal internal waves; the heaving of these waves provides the opportunity to sample Canyon and surface waters from a fixed depth. Repeat sampling of these water masses can help elucidate the processes that drive Hg methylation. After 3.5 years of weekly sampling for total mercury (THg) and methylmercury (MeHg), and 2 years for dimethylmercury (DMHg), we are starting to discern seasonal trends for THg and DMHg. Concentrations are elevated between March and June (THg range: 0.32 – 6.8 pM, DMHg range: 0.01 – 0.098 pM) and depleted from September to December (THg range: 0.34 – 1.6 pM, DMHg range: 0.001 – 0.019). We propose that this seasonality results from the influence of upwelling in the region during the spring months, bringing Hg from depth to the surface waters off the Scripps Pier. The distinctive seasonality in DMHg, along with existing time series data for a range of ancillary parameters, enables us to conduct incubation studies during seasons of contrasting DMHg levels. This provides a better focus on the chemical and biological agents involved in Hg speciation. Here, we present the results of our findings and discuss the implications for the Hg cycle.

## Global mercury cycling: An Earth System Modeling Approach

Zhang Y<sup>1</sup>, Zhang P, Yuan T, Peng D, Mao M

<sup>1</sup>Nanjing University

Mercury (Hg) cycles among different spheres of the Earth. Global models have been developed focusing on the atmosphere, land, and ocean, however, these models have not been properly coupled: i) different assumptions, e.g. meteorological fields and land cover/usage, are used by models that leads to inconsistency; ii) not all the major components of the Earth system are considered, e.g. lake and rivers and the Hg release to water/land. The Earth System Models provide a comprehensive platform for studying Hg cycling. Based on the Community Earth System Model 2, we develop the CAM6-Chem-Hg, CLM5-Hg, POP-Hg, and MOSART-Hg for the global atmosphere, land, ocean, and river, respectively. In this talk, we will show the progress of model development and new findings based on this new tool:

i) The CAM6-Chem/Hg model simulates the atmospheric redox chemistry, transport, and deposition of Hg species with an online configuration. The model shows good agreement with available observations. We also diagnose the drivers for the seasonal variation of surface concentrations. ii) The CLM5-Hg model simulates the vegetation uptake of elemental Hg, land re-emissions, and transport between the soil pools. We find a lagging effect between Hg vegetation uptake and litter concentration, implying a buffering effect of vegetation on the atmosphere-land exchange. iii) The development of the MOSART-Hg model is based on the land erosion and riverine transport model, which simulates the processes of Hg from land to ocean under both natural and anthropogenic conditions. The model results show significant inter-annual and seasonal variations in riverine Hg, while quantifying the contribution of rivers in different regions. iv) We couple the CAM6-Chem/Hg and CLM5-Hg with online calculated fluxes. The model results indicate substantial inter-annual variability in wildfire Hg emissions and provides insights for the magnitude of the vegetation sink of atmospheric Hg.

## Synthesis of phosphorylated chitosan cross-linked graphene oxide polymer nanocomposite, and phosphorylated chitosan cross-linked graphene oxide doped sulphur polymer nanocomposite.

Molete P<sup>1</sup>, Leudjo-Taka A<sup>1</sup>, Klink M<sup>1</sup>, Martin L<sup>2</sup>

<sup>1</sup>Vaal University Of Technology, <sup>2</sup>Cape Point Global Atmosphere Watch Station, <sup>3</sup>Chemical Resource Beneficiation, Atmospheric Chemistry Research Group

Mercury is a well-known heavy metal pollutant that is highly toxic to humans, animals, and plants. The presence of mercury in water bodies can disrupt ecological balance, affecting the breakdown of organic pollutants and the survival of microorganisms responsible for water purification processes. Thus, while mercury is classified as an inorganic pollutant, its presence and effects can indirectly influence other water pollutants in aquatic environments. This pursuit represents a current and challenging task (Leudjo Taka et al., 2019). Bio-polymers that are naturally derived polymers such as alginate, chitosan, cyclodextrin, lignin, and sericin proteins are good examples of eco-friendly materials. (Thakur et al., 2014, 2013). Biopolymer-based nanocomposites can be defined as macromolecular environmentally friendly materials made of multiple phases where one of the phases has nanoscale additives. These biopolymer nanocomposites possess excellent multifunctional properties from each component's combination (Jeon and Baek, 2010; Taka et al., 2018; Ramasami et al., 2018).

Therefore, creating adsorbent and efficient detection techniques that are selective, sensitive, and environmentally friendly is urgently needed. The use of sulphurised natural biopolymer-based nanocomposites for electrochemical mercury (II) adsorption and detection in aqueous solutions is our focus. The synthesized biopolymer nanocomposite materials were characterized using a number of techniques such as Brunauer-Emmett-Teller (BET), Fourier-transform Infrared (FTIR) Spectroscopy, Scanning Electron microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), UV-vis Diffuse Reflectance and UV-Vis Photoluminescence (PL). The developed biopolymer nanocomposite decorated with sulphur nanoparticles will be used as an adsorbent and a chemical sensor for mercury in water.

Keywords: mercury pollution; nanomaterials; chitosan; biopolymer nanocomposites

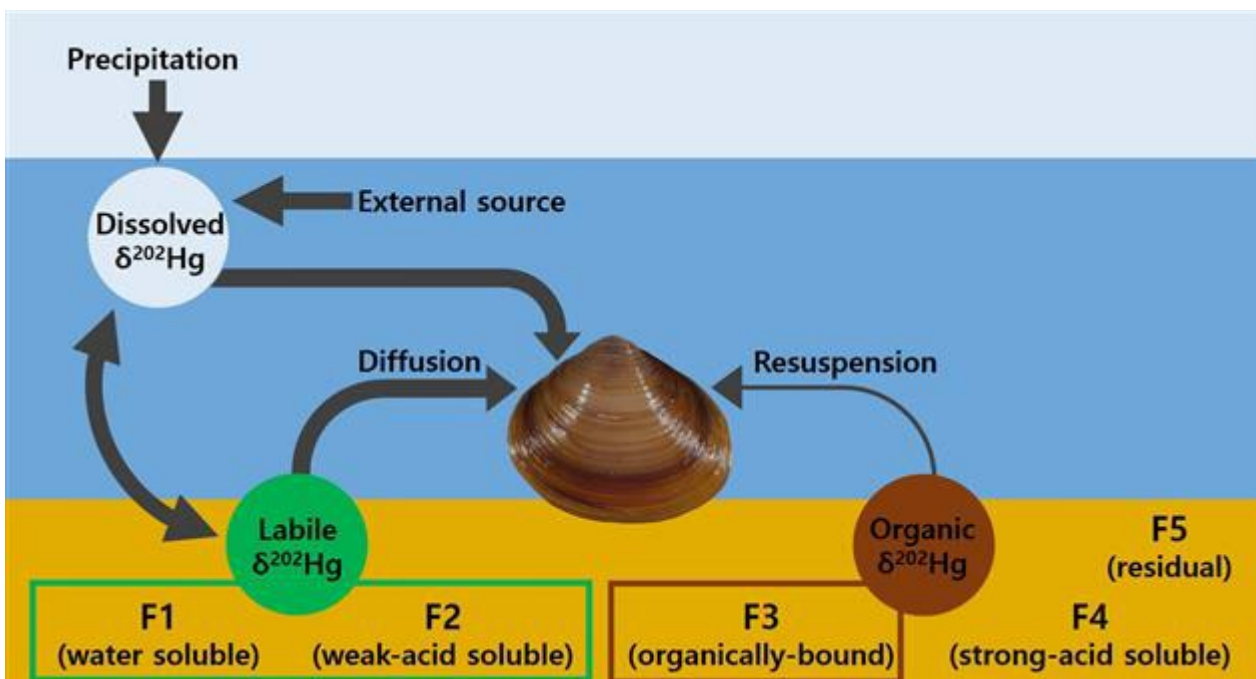
## Elucidating mercury sources and exposure pathways to bivalves using mercury stable isotopes.

Kim Y<sup>1</sup>, Kwon S<sup>1</sup>, Washburn S<sup>2</sup>, Brooks S<sup>3</sup>, Yoon J<sup>1</sup>, Besnard L<sup>1</sup>

<sup>1</sup>Pohang University of Science and Technology, <sup>2</sup>Geosyntec Consultants, <sup>3</sup>Oak Ridge National Laboratory

This study aims to enhance the applicability of bivalves as monitoring tools for sediment quality by identifying mercury (Hg) sources and exposure pathways, particularly in relation to sediment. Hg isotope ratios were applied to elucidate the sources and pathways of Hg accumulated in bivalves with field studies and in situ experiments. We characterized Hg isotope ratios of various geochemical pools (F1, F2; labile, F3; organically-bound, F4, F5; recalcitrant) in riverine sediment contaminated with liquid Hg in the Republic of Korea (Hyeongsan River; HS). Pristine Asian clams (*Corbicula fluminea*) were deployed at the contaminated sites to evaluate the isotopic turnover. They underwent isotopic shift for two-month period toward labile/exchangeable Hg pools (F1, F2 fractions) in the sediment. In contrast, Asian clams at control site with low sediment Hg concentration exhibited similar Hg isotope ratios with samples of precipitation and the dissolved phase of the water column. A similar trend was observed in East Fork Poplar Creek (Oak Ridge), U.S., where Asian clams exhibited Hg isotope ratios resembling those of the dissolved phase of the water column. It is attributed to in-stream processing and input from Hg-contaminated groundwater during high hydrologic flow seasons. These findings highlight that dissolved Hg phases within the water column, whether originating from sediment diffusion or external sources, serve as primary sources and exposure pathways for bivalves. This study contributes valuable insights into existing biomonitoring programs that employ bivalves as bioindicators for sediment quality, revealing the causes for isotopic deviations between bivalves and bulk sediment in estuarine, lake, and coastal systems. The sensitivity of bivalves to both in situ and externally derived dissolved Hg phases underscores the significance of considering these factors in biomonitoring strategies.

### Abstract Graphics



## Methodology of air mercury surveys at ore deposits in real time

Castro Alvarenga E<sup>1</sup>, Rukhlov A<sup>2</sup>, Shashko A<sup>1</sup>, Ryzhov V<sup>3</sup>, Pogarev S<sup>1</sup>, Perkins E<sup>4</sup>, Barnes W<sup>5</sup>

<sup>1</sup>Lumex-marketing LLC, <sup>2</sup>British Columbia Geological Survey, <sup>3</sup>Lumex-Analytics GmbH, <sup>4</sup>Anomalous Exploration, <sup>5</sup>Finlay Minerals Ltd

Mercury (Hg) is a pathfinder of most types of endogenic ore deposits forming lithochemical dispersion haloes in host rocks, overburden sediments, and vapour haloes in soil gas. Over the past few years, new data have been obtained with real-time air mercury survey of near-surface atmosphere at sediment-covered mineralization and ore-controlling fault zones.

A Lumex RA-915M portable analyzer based on Zeeman atomic absorption spectroscopy (ZAAS) enables direct mercury determination in air below the background level of 1-2 ng/m<sup>3</sup> even under unfavourable meteorological conditions such as strong wind and low ambient temperature. This analytical technique detects weak Hg emissions directly above geological sources: areas of mineralization, buried ore bodies and related fault zones. In contrast to soil gas sampling, gaseous Hg haloes in near-surface air can be detected over outcrops, wet soils, bogs, salt-marshes, permafrost, snow, and other types of surface. This study evaluates the effectiveness of real-time Hg vapour measurement in near-surface air above Hg, Au, Au-Ag-Cu, polymetallic, and rare-metal mineralization under various geochemical and climatic conditions in the polar, temperate, and arid areas.

Rapid air mercury surveys delineate mineralization under cover in real time and thus are effective for mineral prospecting in underexplored areas where other techniques might be less efficient (e.g., due to extensive transported overburden).

## Increasing anthropogenic emissions are inconsistent with the declining atmospheric mercury concentrations observed in the Northern Hemisphere

Feinberg A<sup>1,2</sup>, Selin N<sup>2</sup>, Braban C<sup>3</sup>, Chang K<sup>4,5</sup>, Jaffe D<sup>6</sup>, Kyllönen K<sup>7</sup>, Landis M<sup>8</sup>, Leeson S<sup>3</sup>, Molepo K<sup>9</sup>, Murovec M<sup>10</sup>, Nerentorp Mastromonaco M<sup>11</sup>, Aspmo Pfaffhuber K<sup>12</sup>, Rüdiger J<sup>13</sup>, Sheu G<sup>14</sup>, St. Louis V<sup>15</sup>

<sup>1</sup>IQF-CSIC, <sup>2</sup>Massachusetts Institute of Technology, <sup>3</sup>UK Centre for Ecology & Hydrology, <sup>4</sup>Cooperative Institute for Research in Environmental Sciences, University of Colorado, <sup>5</sup>NOAA Chemical Sciences Laboratory, <sup>6</sup>University of Washington, <sup>7</sup>Finnish Meteorological Institute, <sup>8</sup>United States Environmental Protection Agency, Office of Research and Development, <sup>9</sup>Institute of Coastal Environmental Chemistry, Helmholtz Zentrum Hereon, <sup>10</sup>Slovenian Environment Agency, Environment and Nature protection Office, Air Quality Division, <sup>11</sup>IVL Swedish Environmental Research Institute, <sup>12</sup>NILU, <sup>13</sup>Air Monitoring Network, German Environment Agency, <sup>14</sup>Department of Atmospheric Sciences, National Central University, <sup>15</sup>Department of Biological Sciences, University of Alberta

Anthropogenic activities emit ~2000 Mg / yr of the toxic heavy metal mercury (Hg) into the atmosphere, where it can be transported long distances and deposited to remote ecosystems. Existing global anthropogenic emissions inventories report increases in Northern Hemispheric (NH) Hg emissions during the last three decades, in contradiction with the observed decline in atmospheric Hg concentrations at NH measurement stations. Many factors can obscure the link between anthropogenic emissions and atmospheric Hg concentrations, including trends in the re-emissions of previously released anthropogenic (“legacy”) Hg, atmospheric sink variability, and spatial heterogeneity of monitoring data. Here we assess the observed trends in total gaseous mercury (TGM) in the NH and apply biogeochemical box modeling and chemical transport modeling (GEOS-Chem) to understand the trend drivers. Using linear mixed effects modeling of observational data from 51 stations, we find negative TGM trends in most NH regions, with an overall trend for 2005–2020 of  $-0.011 \pm 0.06$  ng / m<sup>3</sup> / yr. We attribute this trend to a decline in NH anthropogenic emissions of at least 165 Mg / yr between the years 2005 and 2020, using an ensemble of simulations in a three-box atmospheric model. Faster declines in 95th percentile TGM values than median values in Europe, North America, and East Asian measurement stations corroborate that the likely cause is a decline in nearby anthropogenic emissions rather than background legacy re-emissions. Our results are relevant for evaluating the effectiveness of the Minamata Convention on Mercury and demonstrate that existing emissions inventories are incompatible with the observed TGM declines.

## Sulfur decorated with some Functionalized Bio-polymer Nanocomposites as adsorbents for Mercury in Aqueous Solution

Goci M<sup>1</sup>

<sup>1</sup>Vaal University Of Technology

Mercury is a chemical element that is harmful to human health and the environment. In this regard, the present challenge is to advance efficient materials and techniques to eliminate mercury pollution in water, soil and atmosphere. In this study, an easy-to-use and fabricate, sulfur (S) nanoparticles decorated with modified bio-polymer nanocomposites (phosphorylated chitosan cross-linked multiwalled carbon nanotubes pCh-MWCNTs/Ag-TiO<sub>2</sub> and S@pCh-MWCNTs/Ag-TiO<sub>2</sub>) was synthesized using phosphorylation and cross-linking polymerization methods. The synthesized sulfur-decorated biopolymer nanocomposite material was characterized using a series of techniques such as Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy (SEM). The SEM images showed that the surface morphology of the treated adsorbents materials have a spherical and agglomerated morphology. Furthermore, the FTIR results revealed that the adsorbents had functional groups such as carboxyl (-COOH), hydroxyl (-OH), and carbonyl (-C=O). The developed sulfur decorated phosphorylated chitosan-based polymer nanocomposite materials were then used as an adsorbents to remove mercury in aqueous solution through batch adsorption study, whereby one parameter at a time was varied while all others were fixed. The removal of mercury was carried out by studying the effect of pH 2, 4, 6, 8, and 10. On the other hand, the adsorbent dosage were 0.0025, 0.0030, 0.00355, 0.0040, and 0.0045 g, and initial concentration were conducted using different Hg<sup>2+</sup> solution concentrations of 1.9, 3.9, 7.9, 11.9, 15.9, and 19.9 ppb. The results revealed the effect of variables and optimum conditions on the removal of mercury ions on pCh-MWCNTs/Ag-TiO<sub>2</sub> and S@pCh-MWCNTs/Ag-TiO<sub>2</sub>, respectively (pH of the solution = 4,3 and 6, adsorbent dosage = 0.0025 g and 0.0035g) under 25°C for 24 hours. The optimization of each parameter was done to determine the conditions in which the adsorbents work best in the uptake of Hg (II). These adsorbents presented acceptable adsorption performance for removal of Hg (II) from aqueous solutions.

## Use of bitter cassava as an alternative to gold amalgamation

Silva E<sup>1</sup>, Torkaman P<sup>2</sup>, Barreto M<sup>3</sup>, Mariz J<sup>4</sup>, Veiga M<sup>2</sup>, de Tomi G<sup>1</sup>

<sup>1</sup>NAP.Mineração/USP Centre for Responsible Mining, University of São Paulo, <sup>2</sup>Norman B. Keevil Institute of Mining Engineering, University of British Columbia, <sup>3</sup>Maná Alimentos Agroindústria, <sup>4</sup>Computer Center, Federal University of Pernambuco

Worldwide, more than 2,000 tonnes of mercury are released annually into the environment by 20 million artisanal miners, representing the world's largest source of mercury pollution through human action. However, the artisanal miners usually extract less than 30% of the relatively coarse gold with amalgamation. We have explored "manipueira," a cyanide-rich liquid by-product from the cassava root starch industry, as an alternative to the traditional amalgamation process for gold extraction. Manipueira contains approximately 30% w/w of the cassava. We conducted our study using two samples from Artisanal and Small-Scale Gold Mining (ASGM): a Brazilian sample with 15.8 ppm Au and a Colombian one with 48.9 ppm Au. These samples, ground to -200#, were subject to lab agitated leaching tests at various times, using Solid: Liquid ratios ranging from 10 to 20 while maintaining a pH of 10.5. The "manipueira" used in these tests contained free cyanide (CN-) concentrations ranging from 200 to 600 ppm. Our results were promising. From the Brazilian ore sample, up to 61.5% of gold was extracted in a single 8-h extraction with "manipueira" with 300 ppm of free CN- while 78.4% of the gold was extracted in two 8-h cycles. Regarding the Colombian ore, 51% of gold was extracted with "manipueira" with 267 ppm of free CN- in 24 hours whereas 82.4% of gold was extracted in 24 h with 600 ppm of free CN-. Particularly In Brazil, the geographical proximity of the mine to a starch production factory (<200 km), which processes up to 400 tonnes/day of cassava and generates up to 128,000 L/day of "manipueira", stands out as a strategic advantage. This proximity could facilitate the adoption of this eco-friendly method over amalgamation. This process has potential to be used in African countries like Nigeria, Congo and Ghana, among the world's largest cassava producers.

## Obtaining Gold and Mercury Losses in an Artisanal Mining Site in Nigeria

Anene N<sup>1</sup>, Musa B<sup>2</sup>, Mohammed Y<sup>1</sup>, Robert-Lemire C<sup>3</sup>, Yeomans C<sup>3</sup>, Veiga M<sup>4</sup>

<sup>1</sup>Dept of Artisanal and Small-scale Mining, Ministry of Mines and Steel Development, <sup>2</sup>Zinariya Kyautar Allah Venture Uke Ltd, <sup>3</sup>Alinea International, <sup>4</sup>Norman B. Keevil Institute of Mining Engineering, University of British Columbia

The number of artisanal gold miners in Nigeria ranges from 260,000 to 1 million miners producing from 6 to 20 t/a of gold and releasing over 20 t/a of mercury. A short-term project sponsored by the Global Affairs Canada and implemented by Alinea International, the Technical Assistance Partnership (TAP), provided technical assistance to the ASM department of Ministry of Mines working with miners in the Uke and Minna region. In the Uke, samples from feed and tailings were systematically sampled every 15 min. for 4 hours in sluice boxes and sent for gold analysis. Mercury losses in 17 operations were obtained by weighing the initial and final mercury in the amalgamation of the concentrates. After analyses in 5 operations, the average gold grade in the feed resulted in 3.80 ppm STD = 0.76 ppm. The Gold recovery was 29.24% STD = 6.62% which is low due to lack of liberation of the fine gold particles. Finer grinding would be necessary. The mercury balance revealed that 42% of the mercury is lost, in which 26% with tailings and 16% evaporated to the air. The ratio of HgLost to AuProduced was found to be at 3.4 which is very high for this type of amalgamation process. Mercury is openly sold in the sites, and the price ranges from US\$ 113/kg to US\$ 123/kg, which is not expensive compared with the price in similar countries which ranges from US\$ 200/kg to US\$3000/kg. The Hg-contaminated tailings and primary tailings are sold to local cyanidation plants and this forms toxic soluble Hg(CN)<sub>2</sub> in the process. The results were brought to the attention of the miners and now the project is planning a pilot project of further training to Ministry staff and the possibility to establish a demonstration plant to increase gold production with Hg-free methods.

## How Projects on Mercury-Free for AGM Could be More Effective

Veiga M<sup>1</sup>

<sup>1</sup>Norman B. Keevil Institute of Mining Engineering, University of British Columbia

Most projects to demonstrate mercury-free techniques to Artisanal Gold Miners (AGM) intends to bring a technique to concentrate gold to a smeltable grade. This must be above 30,000ppm Au, otherwise gold would be lost to the slag. Conventional gold mining companies remove the coarse (>0.1 mm) gold specks by gravity concentration before sending the tailings to flotation or cyanidation. The gravity concentrate is then upgraded before intensive cyanidation or smelting. Rarely, a conventional gold mine recovers more than 30% of the gold by gravity concentration. Most interventions in artisanal mining sites do not report the existing %gold recovery and the miners have as the only control of their plants, the amount of gold they put in their pockets. The intervention does not work if miners do not understand the simple concept of % gold recovery. If the gold grade of concentrates is high, the % gold recovery is low. How can an interventionist convince a miner to lose most of the gold in the tailings to have a rich smeltable concentrate? The proposed steps tested is: 1) assess the current gold recoveries (and losses) of the existing processes by systematic sampling of feeds and tailings; 2) assess mercury losses by measuring the Hg entering the system and recovered by filtration of retorting; 3) involve miners in all processes to demonstrate how to calculate the %gold recovery; 4) implement a Hg-free pilot plant with simple changes in the concentration circuit to operate in closed circuit (size classification) recirculating tailings. Miners can compare the existing % gold recovery with the new circuit. Miners will understand the process control using chemical analyses and calculating % gold recovery of their concentration circuit, with consequent abandonment of amalgamation. Examples of metallurgical balances of gold and mercury in different countries are demonstrated in the presentation.

## Identifying Spatial Patterns of Mercury and Methylmercury Concentrations and Loads Downstream of Historical Mining Areas in the Western USA

Thoms B<sup>1</sup>, Eckley C<sup>2</sup>, Stanfield B<sup>2</sup>, Crawford J<sup>2</sup>, Dent S<sup>3</sup>, Silvertooth J<sup>4</sup>

<sup>1</sup>Oregon DEQ, <sup>2</sup>USEPA, <sup>3</sup>CDM Smith, <sup>4</sup>CDM Smith

Thousands of abandoned mines are located within the western region of the USA and may continue to cause negative impacts on downstream water quality. In addition to mobilization directly from the historical mine site, tailings and other mine materials have often been redistributed downstream of the sites and can continue to be secondary sources of contamination, especially during periods of elevated discharge. This presentation will look at mercury (Hg) loading and methylation factors in three watersheds in the Pacific Northwest of the United States impacted by legacy mining. Each of the watersheds have synoptic sampling data that look at secondary sources downstream, areas of increased methylmercury (MeHg) production, and differences in low and high flow events. The Black Butte Mine in the Coast Fork Willamette River (CFWR) watershed in Oregon and the Cinnabar mine in Idaho are both former primary Hg mines whereas the Jordan Creek historic mining area was impacted by legacy amalgamation activities in the Silver City mining District in SE Idaho. In the CFWR, mercury methylation in the river system is mostly associated with periphyton growth, whereas in the downstream reservoir most methylation occurs within the sediment and in the water column during periods of thermal stratification. Methylation in the Jordan Creek watershed is affected by seasonal irrigation withdrawal, and increases from nutrients from agriculture, including secondary sources of Hg. The Cinnabar Mine Site is in a mountainous landscape and its stream conditions (steep gradient/high velocity) are less conducive to MeHg production. All watersheds downstream of the mines show increased loading with distance downstream, suggesting that the remobilization of historically deposited Hg remains an important source to the watersheds.

## Investigating mercury uptake, release, chemical speciation, and isotope fractionation in native and transplanted lichens at legacy mercury mine and background locations

Weiss-Penzias P<sup>1</sup>, Straw B<sup>1</sup>, Rothman M<sup>1</sup>, Seelos M<sup>2</sup>, O'Day P<sup>3</sup>, Rivas Meraz E<sup>3</sup>, Tate M<sup>4</sup>, Janssen S<sup>4</sup>, Alpers C<sup>5</sup>

<sup>1</sup>University Of California, Santa Cruz, <sup>2</sup>Santa Clara Valley Water District, <sup>3</sup>University of California, Merced, <sup>4</sup>US Geological Survey, Mercury Lab, <sup>5</sup>US Geological Survey, California Water Science Center

Legacy mercury (Hg) mines in the California Coast Range act as point sources of emissions of gaseous elemental mercury (GEM), which can then be redeposited locally through uptake by foliar species. We used six species of lichens that grow around former mines, New Almaden and Sulphur Bank, along with passive GEM samplers to determine the locations of GEM emission hot spots. The genera of three main lichen types sampled were Evernia, Ramalina, and Usnea; total Hg (THg) concentrations agreed to within 20% across species at a given location. THg in lichens ranged from 45,348 ng/g at Sulphur Bank, to 20,083 ng/g at New Almaden, to 53 ng/g at our background location. We also transplanted intact clumps of lichens from a background location to a mining site (and vice-versa) by hanging the lichens in mesh bags. We observed a 61% increase in THg in background lichen and a 14% decrease in New Almaden lichen after 120 days. Hg stable isotope mass-independent fractionation (MIF) was more negative (-0.69‰) for background lichen samples compared with those from New Almaden (-0.02‰), which may be attributed to differences in atmospheric processes resulting in a proxy for long-range transport vs local emissions. Chemical speciation of Hg in lichen from the mine sites was investigated using High Energy Resolution Fluorescence Detection (HERFD) XANES where we found that Hg species were dominated by either meta-cinnabar or cinnabar, and Hg coordinated by cysteine-type ligands. As Hg in lichen is not easily washed off with DI water or EDTA solution, we hypothesize that Hg enters the lichen tissue primarily as Hg<sup>0</sup> and is oxidized within the lichen leading to Hg<sup>2+</sup> and Hg<sup>0</sup> concentrations that reach equilibrium over time with atmospheric concentrations. We conclude that lichens can be a cost-effective tool to reveal contamination from atmospheric Hg point sources.

### Abstract Graphics



## The mechanism of foliar physiological parameters restricting foliar assimilation of atmospheric mercury in typical forest ecosystems

Luo K<sup>1</sup>, Wang X<sup>1</sup>, Yuan W<sup>1</sup>, Liu N<sup>1</sup>, Jia L<sup>1</sup>, Feng X<sup>1</sup>

<sup>1</sup>State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

Forest ecosystem is an important Hg reservoir globally. Mercury (Hg) deposition through foliar uptake of gaseous elemental mercury (Hg<sup>0</sup>) has been regarded as the main input of atmospheric Hg<sup>0</sup> into terrestrial ecosystems. However, present knowledge on the mechanism of atmospheric Hg<sup>0</sup> uptake by foliage remains deficient. In this study, we investigated the foliar net Hg accumulation rate of eight typical dominant tree species in typical tropical rainforests, tropical sparse shrubs and subtropical evergreen broad-leaved forests in China during different growth seasons, coupled with the key foliar physiological parameters of net photosynthetic rate (A), stomatal conductance (g<sub>sw</sub>), transpiration rate (E) and water vapor pressure deficit (VPD). Our results showed that the foliar Hg content increased with foliage age, but the increase rate of different tree species was significantly different (131.9829 ng m<sup>-2</sup> month<sup>-1</sup> ~ 772.8460 ng m<sup>-2</sup> month<sup>-1</sup>). A and g<sub>sw</sub> showed a significant positive correlation with foliar net Hg accumulation rate throughout the growing season, which was speculated to be a major functional trait restricting the foliar Hg accumulation, suggesting stomatal uptake of atmospheric Hg<sup>0</sup> was the most essential Hg uptake pathway. Additionally, foliar Hg uptake was inhibited under high VPD conditions. Stomatal closure and mesophyll conductance decrease in foliage drove the reduced diffusion of Hg<sup>0</sup> from atmosphere to binding sites may be the primary cause of the decrease of net Hg accumulation rate under most water stress conditions.

## Modeling the uncertainties in the atmospheric redox chemistry of mercury (Hg)

Feinberg A<sup>1</sup>, Sonke J<sup>2</sup>, Saiz-Lopez A<sup>1</sup>

<sup>1</sup>IQF-CSIC, <sup>2</sup>Géosciences Environnement Toulouse

Anthropogenic emissions of the toxic heavy metal mercury (Hg) threaten human health and ecosystems. The elemental form of emitted gaseous mercury, Hg(0), can be transported globally in the atmosphere due to its long lifetime of 4–6 months, but upon oxidation it forms soluble divalent mercury, Hg(II), which is rained out within days. However, there are many uncertainties associated with atmospheric Hg chemistry, leading to uncertain predictions of its fate and ecosystem impacts. To address these knowledge gaps, we integrate the latest knowledge from laboratory kinetics, computational and isotope chemistry, and field measurements into global atmospheric Hg models, WACCM and GEOS-Chem. We assess the uncertainties of Hg chemical reactions from previous laboratory studies and quantum chemical calculations, as well as hypothesize unmeasured reactions that could occur involving atmospheric Hg. By applying statistical methods from the field of global sensitivity analysis, we identify the key chemical reaction rates that contribute the most to the uncertainty in the atmospheric Hg lifetime and Hg deposition. As well, by identifying the chemical reaction rates that play negligible roles in the global Hg cycle, we can suggest new reduced chemical mechanisms that will be more computationally efficient for long-term atmospheric simulations, while retaining the accuracy of more complex models. We explore the parametric uncertainty space to find reaction rate combinations that best match available field measurements of Hg(0) and Hg(II) concentrations and Hg wet deposition. In doing so, we aim to reduce existing model biases for oxidized Hg species and improve predictions of the environmental consequences of Hg.

## Long-term air mercury monitoring at Listvyanka station, Siberia

Castro Alvarenga E<sup>1</sup>, Sholupov S<sup>1</sup>, Pogarev S<sup>1</sup>, Obolkin V<sup>2</sup>, Khodzher T<sup>2</sup>, Kalinchuk V<sup>3</sup>, Ryzhov V<sup>4</sup>

<sup>1</sup>Lumex-marketing LLC, <sup>2</sup>Limnological Institute SB RAS, <sup>3</sup>Il'ichev Pacific Oceanological Institute FEB RAS, <sup>4</sup>Lumex Analytics GmbH

The Minamata Convention on Mercury stipulates the developing of global and national air mercury observation networks, such as GMOS and GOS4M. Background air monitoring provides information on the environmental cycle, transport, and fate of mercury, as well as revealing emissions sources. As part of the GMOS (Global Mercury Observation System) project (2011-2015), Standard Operating Procedures (SOPs) and a QA/QC system were established and implemented at all monitoring sites to ensure full comparability of the network observations (Sprovieri et al., 2016).

We present data of the ongoing long-term air mercury monitoring that began in 2011 at Listvyanka station, located on the shore of Lake Baikal in Siberia. Air mercury measurements were conducted using a fully automated RA-915AM mercury monitor based on differential atomic absorption spectroscopy with Zeeman background correction. The average concentration of gaseous elemental mercury (GEM) during the 2011-2024 observation period was 1.59 ng/m<sup>3</sup>. Particulate bound mercury (PBM) accounted for approximately 0.7% of GEM.

The data obtained indicate a clear seasonal variation in the background mercury concentration in air. The concentration increases during the cold seasons (November-February) with an average GEM of 1.74 (1.56-1.95) ng/m<sup>3</sup>, and decreases during the warm seasons (June-September) with an average of 1.43 (1.12-1.63) ng/m<sup>3</sup>. Short-term anomalies (lasting from minutes to hours), up to 5-7 ng/m<sup>3</sup>, are associated with winds carrying air from industrial areas and forest fires.

The short-term variations and monthly average levels show a positive correlation between the concentrations of mercury, SO<sub>2</sub>, and NO<sub>2</sub>. The areas and sources of mercury emissions are revealed by the HYSPLIT trajectories and concentration-weighted trajectory (CWT) modeling.

178

## SI traceable calibration methods for mercury gas generators

De Krom I<sup>1</sup>

<sup>1</sup>VS

To underpin global efforts to control and reduce the mercury concentrations in the environment robust and defensible measurement results of mercury concentrations, traceable to the International System of Units (SI), are essential. Therefore, primary mercury gas standards and SI traceable calibration methods for mercury concentrations in air have been developed in the past decade. Notwithstanding these efforts there are no standardized procedures that ensure the dissemination of the metrological traceability from primary to working standards among calibration and testing laboratories and in emission sources. Scientifically sound calibration protocols, to assess the performance of elemental and oxidised mercury gas generators in the form of formally accepted documentary standards, are of fundamental importance to guarantee the accuracy and comparability of the mercury measurement results in gas emission sources in Europe and globally. Within the EMPIR (European Metrology Programme for Innovation and Research) SI-Hg project (Metrology for traceable protocols for elemental and oxidised mercury concentrations - 19NRM03) such metrological calibration protocols were developed and validated. The calibration protocols contribute to establishing a traceability chain from a primary mercury gas standards to measurement data obtained in gas emission sources and the atmosphere.

During validation of the calibration protocols, mercury gas generators available on the market were tested using the protocol to assess their performance. Among others, repeatability, reproducibility and uncertainty of the calibration procedure were determined. The developed calibration protocols and validation results will be presented.

The validation data are key for the incorporation of the protocols into new and existing documentary standards. As a documentary standard, the protocol replaces other references currently used in mercury concentration measurement. This is of fundamental importance to guarantee the accuracy and comparability of the mercury measurement results in gas emission sources and the atmosphere in Europe and globally.

## Comparability of calibration strategies for measuring mercury concentrations in gas emission sources and the atmosphere

De Krom I<sup>1</sup>, McGhee E<sup>2</sup>, Brown R<sup>2</sup>, Živković I<sup>3</sup>, Gačnik J<sup>3</sup>, Fajon V<sup>3</sup>, Kotnik J<sup>3</sup>, Horvat M<sup>3</sup>, Ent H<sup>1</sup>  
<sup>1</sup>VSL, <sup>2</sup>NPL, <sup>3</sup>JSI

A primary mercury gas standard was developed at the Van Swinden Laboratory (VSL), the National Metrology Institute in the Netherlands, to establish an SI-traceable reference point for mercury concentrations at emission and background levels in the atmosphere. The primary mercury gas standard can be used for the accurate and precise calibration of analytical systems used for measuring mercury concentrations in air. It has been especially developed to support measurements related to ambient air monitoring (1 ng/m<sup>3</sup> – 2 ng/m<sup>3</sup>), indoor and workplace related mercury concentration levels according to health standards (from 50 ng/m<sup>3</sup> upwards) as well as to stationary source emissions (from 1 µg/m<sup>3</sup> upwards).

The primary mercury gas standard is based on diffusion according to ISO 6154-8. Calibration gas mixtures are obtained by combining calibrated mass flows of nitrogen and air through a generator holding diffusion cells, containing elemental mercury. In this poster, we present the results of comparisons between the primary gas standard and mercury calibration methods maintained by NPL, a National Metrology Institute (NMI), and JSI, a Designated Institute (DI). The calibration methods currently used at NPL and JSI are based on the bell-jar calibration apparatus in combination with the Dumarey equation and a NIST reference material, respectively. For the comparisons, mercury was sampled on sorbent traps to obtain transfer standards with levels between 2 ng and 1000 ng with an expanded uncertainty not exceeding 3 % (k = 2). The comparisons performed show that the results for the primary gas standard and the NIST reference material are comparable, whereas a difference of -8 % exists between results traceable to the primary gas standard and the Dumarey equation. These results pave the way to set up the first proficiency testing scheme for mercury on sorbent traps.

180

## Role of photoperiod and reactive oxygen species (ROS) on methylmercury production and degradation in the rhizosphere of wetland soils

Sagisaka Mendez S<sup>1</sup>, Mitchell C<sup>1</sup>, Dittrich M<sup>1</sup>, Kokilathanan N<sup>1</sup>

<sup>1</sup>University Of Toronto Scarborough

Wetlands are an important source of methylmercury (MeHg) to hydrologically connected streams and lakes, leading to bioaccumulation and biomagnification of mercury in aquatic food webs. Net MeHg production depends on the balance of demethylation and methylation processes, though demethylation processes are less studied than methylation. New degradation pathways of MeHg are emerging, such as demethylation via reactive oxygen species (ROS). ROS can be found in the rhizosphere of vegetation and ROS production can vary according to photoperiod conditions. In addition to seasonality, photoperiods can be affected by landscape disturbances like deforestation, where canopy removal alters shading patterns. To examine how ROS production during different photoperiod durations affects MeHg production and degradation processes in wetland soils, a laboratory-controlled experiment was conducted using boreal wetlands soils and applying photoperiod treatments (0, 6, 9, 12, 15 hrs) in growth chambers at a consistent photosynthetically active light intensity. Enriched stable mercury isotope incubations were used to determine methylation and demethylation rate constants and in situ characterization of ROS species were assessed using H<sub>2</sub>DCFDA as a fluorescence probe. Results from this study will help broaden our understanding of how landscape disturbances affect the balance between demethylation and methylation processes in wetland ecosystems.

## Bottom sediment as a potential source of mercury to benthic organisms

Zarzczańska A<sup>1</sup>, Popławska A<sup>1</sup>, Płońska P<sup>1</sup>, Hetko D<sup>1</sup>, Witak M<sup>1</sup>, Zgrundo A<sup>2</sup>, Złoch I<sup>3</sup>, Beldowska M<sup>1</sup>  
<sup>1</sup>Department of Chemical Oceanography and Marine Geology, University of Gdańsk, <sup>2</sup>Department of the Functioning of Marine Ecosystems, University of Gdańsk, <sup>3</sup>Department of Marine Biology and Biotechnology, University of Gdańsk

The Baltic Sea, characterized as a shallow, and semi-closed reservoir with an average depth of 52 meters, experiences limited water exchange. Over time, it has been subjected to various pollutants, emitted from untreated industrial and municipal sewage discharge, and surface runoff. The toxic substances introduced into the Baltic Sea have predominantly been accumulated in its sediments. With a global rise in temperature and an extended vegetation season, shallow estuaries are increasingly covered by underwater meadows. This scenario raises concerns about a potential escalation in mercury levels, by its remobilization from sediments to benthic organisms and subsequently enter higher trophic levels of the food web. The aim of this research was to assess the mercury re-entry potential into the food web in the estuaries of the southern Baltic Sea. Between 2019 and 2021, 67 sediment samples were collected from the Bay of Puck —underwater meadow. The sediment collection employed a manual Van Veen sampler. The concentration of total mercury was analysed through thermodesorption on a mercury analyser DMA-80 (Milestone, Italy). Notably, the highest mercury concentrations in sediment were identified in proximity to the sewage treatment plant and the deepest region in the inner Puck Bay (approximately 9 meters deep). These regions also exhibited elevated concentrations of labile mercury compounds, predominantly associated with halides and organic matter. Conversely, the southern part of the inner Puck Bay showed the highest concentrations of stable mercury sulfide due to the presence of peats in the area. Mostly surface sediments in the examined area were characterized by a higher proportion of stable mercury compounds (HgS), which are not prone to recirculation. The research was financially supported by National Science Center, project no. 2022/45/B/ST10/00368.

## The impact of 20th century conflicts on mercury contamination of sediments from the southern Baltic Sea

Zarzeczńska A<sup>1</sup>, Popławska A<sup>1</sup>, Płońska P<sup>1</sup>, Narwojsz D<sup>3</sup>, Łęczyński L<sup>2</sup>, Bełdowski J<sup>3</sup>, Bełdowska M<sup>1</sup>

<sup>1</sup>The impact of 20th century conflicts on mercury contamination of sediments from the southern Baltic Sea, <sup>2</sup>2. Department of Geophysics, University of Gdańsk, <sup>3</sup>3. Department of Marine Chemistry and Biochemistry, Institute of Oceanology, National Academy of Sciences

Armed conflicts in the 20th century in Europe still have a negative impact on the Baltic Sea environment. Military operations that have taken place in this area left many sunken wreck at the bottom of the sediments, often along with ammunition and supplies. Currently, it is estimated that there are about 10 000 shipwrecks at the bottom of the Baltic Sea, most of which were sunken during World Wars I and II. Over the years, the sunken units began to corrode, which caused and continues to cause the release of many hazardous substances, including mercury, into the marine environment. Therefore, the aim of the study was to estimate the mercury contamination of surface sediments near the wrecks of S/S Stuttgart, T/S Franken, Abille, Munin and UJ 1102.

Sediment samples were collected using a Van Veen sampler in 2019-2021. A total of 78 samples were collected near the S/S Stuttgart wreck, the T/S Franken, the Abille, the Munin and UJ 1102. The mercury concentration in the samples were determined using thermodesorption method on a DMA-80 analyzer (Milestone, Italy).

The concentration of total mercury in surface sediments was the highest at stations near the S/S Stuttgart wreck than any other station in this study. Very high concentrations were observed near the slope behind the S/S Stuttgart wreck. Based on the available literature, it can be concluded that this was the highest Hg concentration measured in Baltic Sea sediments. It was almost 14 times higher than the maximum concentration of this metal previously measured in this area. Additionally near T/S Franken hotspots of high concentration of mercury was observed. Moreover, Hg is transported by sea currents along with sediment to places far from the wrecks. Statistical analyzes indicate that wrecks are a potential, significant source of Hg to surface sediments and nearby environment.

## Characterizing mercury dynamics in a flood control reservoir downstream of a historical mercury mine

Silvertooth J<sup>1</sup>, Dent S<sup>1</sup>, Crawford J<sup>2</sup>, Eckley C<sup>2</sup>

<sup>1</sup>CDM Smith, <sup>2</sup>United States Environmental Protection Agency

Cottage Grove Reservoir (CGR) is a flood control reservoir downstream of a historical cinnabar mine in Oregon, United States and is part of the Black Butte Mine Superfund site managed by the United States Environmental Protection Agency (USEPA). Sport fish within CGR contain mercury concentrations above the USEPA fish consumption advisory threshold of 0.3 µg/kg and the Oregon Department of Environmental Quality methylmercury fish criterion of 0.04 mg/kg. Recent investigations have been conducted to evaluate the fate and transport of mercury and methylmercury in reservoir surface water, sediment, and porewater, and to assess biogeochemical processes that may be impacting mercury uptake into the food web. Because the reservoir is partially dewatered in the winter, mud flats and wetland areas are oxidized in the upstream portion of the reservoir when water levels drop, exposing sediments to air. Investigations were designed to characterize the distinct sedimentation and biogeochemical conditions in the permanent pool, seasonally inundated mud flats, and wetlands. Study results have demonstrated that methylation occurs in sediments throughout the reservoir but is most pronounced in the seasonally inundated mud flats and wetlands. Methylmercury is present in the water column throughout the reservoir, but the most enrichment of mercury and methylmercury in the water column is seen in the hypoxic zone that develops in the deeper regions of the reservoir. Sediment core analysis has shown that deeper sediments contain higher mercury concentrations than shallow sediments in areas with current or historical sedimentation, indicating that loading of mercury-contaminated particulates from upstream has decreased over time. Study results are being used in conjunction with results of parallel studies of the river system upstream of CGR and biological studies of CGR to inform the assessment of mercury uptake into the food web and to support risk management decisions at the site.

## GMOS-Train uncertainty course – training young scientists in fundamentals of metrology and determination of measurement uncertainty

Zivkovic I<sup>1</sup>, Koenig A<sup>2</sup>, Vijayakumaran Nair S<sup>1</sup>, Malberti L<sup>3</sup>, Torres Rodriguez N<sup>4</sup>, Kleindienst A<sup>5</sup>, García Arévalo I<sup>6</sup>, Gindorf S<sup>7</sup>, Haugk C<sup>7</sup>, Ali S<sup>1</sup>, Andron T<sup>1</sup>, Mages Raj A<sup>8</sup>, Amptmeijer D<sup>9</sup>, Molepo K<sup>9</sup>, Gournia C<sup>10</sup>, Horvat M<sup>1</sup>

<sup>1</sup>Jozef Stefan Institute, <sup>2</sup>UGA, <sup>3</sup>CNRS, <sup>4</sup>AMU, <sup>5</sup>UPPA, <sup>6</sup>IFREMER, <sup>7</sup>Stockholm University, <sup>8</sup>IOS, <sup>9</sup>Hereon, <sup>10</sup>CNR-IIA

The overall objectives of the GMOS-Train network are to provide urgently needed training in mercury (Hg) science within the context of the Minamata Convention, and to fill key knowledge gaps in biogeochemical Hg cycling linking anthropogenic emissions and Hg in marine food webs. The project addresses major uncertainties in the current understanding of global Hg cycling in response to a reduction in anthropogenic emissions, including partitioning between ocean, atmosphere, land and the biosphere, and cost-effective monitoring strategies. To properly address these uncertainties, accurate and precise measurement methods are required, and corresponding measurement uncertainties must be known. However, currently this is not the state. Therefore, within the GMOS-Train project, we determined measurement uncertainty for most commonly used methods in mercury community. Participants of the uncertainty course were given basic knowledge about metrology and were taught principles of measurement uncertainty and its proper calculation and use. Participants calculated the measurement uncertainties of their analytical methods. These included the determination of total mercury concentrations in the atmosphere, seawater, soil, and leaves; methylmercury in water, bacterial media, plankton pellets, and its  $\delta^{13}\text{C}$  values; dissolved gaseous mercury in water; and gaseous oxidized mercury in atmosphere. Methods used for these determinations were based on atomic fluorescence spectrometry, atomic absorbance spectrometry, inductively coupled plasma mass spectrometry, isotope dilution, and isotope ratio mass spectrometry. Measurement uncertainties were determined using a classical bottom-up ISO-GUM approach or in some cases, using a Monte Carlo approach. The expanded relative combined standard uncertainties ( $k = 2$ ) ranged from 3.64% for isotope dilution deconvolution method to 35.5% for total mercury in soils using atomic absorption spectrometry. For all methods, uncertainty sources were determined and quantified. Depending on the method, the largest contribution to the overall measurement uncertainty was commonly attributed to either instrumental calibration or sample repeatability.

## Origin of mercury in soils in the vicinity of emission sources using stable isotope approach

Božič D<sup>1</sup>, Zivkovic I<sup>1</sup>, Kotnik J<sup>1</sup>, Puhar G<sup>1</sup>, Jagodic Hudobivnik M<sup>1</sup>, Štrok M<sup>1</sup>, Ogrinc N<sup>1</sup>, Horvat M<sup>1</sup>  
<sup>1</sup>Jozef Stefan Institute

In this study, we conducted an examination of top soils from two sites in western Slovenia: Idrija and Anhovo. Idrija is renowned as the location of one of the world's largest mercury (Hg) mine, while Anhovo is positioned downstream of Idrija, where a cement production plant is recognized as a source of local Hg contamination. Samples were collected from both locations, and we measured their total mercury concentrations, multi-elemental composition, as well as their Hg isotopic composition. At both Idrija and Anhovo sites, the range of mass-dependent fractionating isotope fingerprints is broad, underscoring the complexity of the mechanisms underpinning our findings. In Idrija, the isotopic fingerprint progressively shifts towards lighter isotopes (more negative  $\delta^{202}\text{Hg}$  values) with increasing distance from the roasting and ore processing sites. To assess the origin of mercury in these top soils, we conducted statistical analyses and performed source appointments using a mercury mixing model. Although the precise mechanisms and sources of mercury remain uncertain, we presume that the heavier isotopic fingerprint is associated with mercury originating from the mine, while the lighter one is attributed to atmospheric mercury deposition on the soil. In the case of Anhovo, Hg concentrations are generally orders of magnitude lower compared to Idrija. However, due to its location downstream of Idrija, the effects of Hg contamination from the mining area are still evident. The floodplains exhibit a heavier isotopic fingerprint, whereas areas situated higher up the valley sides display a relatively uniform and lighter isotopic composition. The observed shift from heavier to lighter isotopes could prove valuable in identifying the most contaminated areas, not only within these two locations but also at similar sites elsewhere.

## Requirements for comparable mercury speciation analyses in seawater

Zivkovic I<sup>1</sup>, Heimbürger-Boavida L<sup>2</sup>, Petrova M<sup>2</sup>, Dufour A<sup>2</sup>, Begu E<sup>1</sup>, Horvat M<sup>1</sup>

<sup>1</sup>Jozef Stefan Institute, <sup>2</sup>Aix Marseille Université

The comparability of measurement results is an important issue in contemporary mercury (Hg) speciation in seawater. Sampling campaigns must be properly designed to determine significant differences on spatial and temporal scales, considering two major parameters: the variability of expected data at a given sampling point/transect and variability in the results due to the intrinsic properties of specific analytical methods. This study assessed the required sample sizes, considering several aspects of data variability. The required sample sizes were calculated using: (1) a single-laboratory measurement of the uncertainty of analytical methods for determining total mercury, dissolved gaseous mercury, and methylated mercury in seawater; (2) international interlaboratory comparison exercise data; and (3) natural sample variability in Hg fractions in a case study in the Central Adriatic Sea. We assessed critical factors influencing required sample sizes in environmental studies, with a focus on mercury concentrations in the Central Adriatic Sea. While measurement uncertainty and interlaboratory variations play a marginal role in overall sample size, their influence was significant only when considering the low natural variability in a selected dataset. Measurement uncertainty was important for the single-sample determination of Hg fractions using two different analytical methods within a single laboratory. Due to the importance of measurement uncertainty, we provide recommendations for properly estimating it and reducing it by making slight modifications to analytical methods. We recommend the use of geometric means and geometric standard deviations for log-normally distributed results and underscore the efficacy of narrowing measurement uncertainty through appropriate calibration curves. This modification proves particularly valuable in scenarios with low natural variability in Hg fraction concentrations.

## Advancing Mercury Detection: A MerB (Organomercurial-lyase)-based Solid-State Voltammetry Sensor for Methylmercury detection

Raj A<sup>1,2,3</sup>, Rijavec T<sup>1</sup>, Sharifi T<sup>1</sup>, Živković I<sup>1,2</sup>, Klemenčič<sup>1</sup>, Alilović A<sup>1</sup>, Begu<sup>1</sup>, Horvat M<sup>1,2</sup>, Lobnik A<sup>3</sup>, Košak A<sup>3,4</sup>, Lapanje A<sup>1</sup>

<sup>1</sup>Department of Environmental Sciences, Josef Stefan Institute, <sup>2</sup>Jožef Stefan International Postgraduate School, <sup>3</sup>IOS, Institute of Environmental Protection and Sensors, Ltd., <sup>4</sup> University of Maribor, Faculty of Mechanical Engineering, Centre of Sensor Technology,

Mercury is a highly toxic and mobile element that has had a pronounced and adverse effect on organisms. Accordingly, bacteria have evolved mer operons to meliorate the toxic action of different chemical forms of mercury. The bacterial mercury detoxification system contains two proteins, organomercurial lyase (MerB) and mercuric ion reductase (MerA). MerB specifically catalyses the protonolysis of the carbon-mercury bond of methylmercury (MeHg), resulting in the formation of a reduced carbon compound and inorganic ionic mercury (Hg<sup>2+</sup>) [1]. We intend to develop a simple solid-state voltammetry sensor for detecting MeHg through changes in the current across gold films caused by the redox potential of Hg-bound-MerB (Organomercurial lyase) after cleaving MeHg. Since MerB is a highly specific organomercurial lyase, we plan to use its Met-Hg-specific binding characteristics as a sensing/receptor component of the sensor. On binding of MeHg onto MerB, the current fluctuation in the conductive paths ultimately percolates the entire gold film [2]. To achieve that, we have prepared an expression system that will enable us to obtain enough highly active MerB enzymes. The expressed MerB enzyme with his-tag was purified and it showed High Hg-bound onto the MerB after cleaving from MeHg for preparing the Met-Hg-specific sensor. For the reporter system, We would prepare an SPE (Screen-printed gold electrode) and functionalize with thiol followed by NTA-Ni<sup>2+</sup> (Nitriloacetic acid with Nickel) for specific Histag MerB proteins binding.

188

## Solubility and Fate of Mercury in Gas Processing Solvents

Corns W<sup>1</sup>, Dexter M<sup>1</sup>, De Feo G<sup>1</sup>, Lancaster S<sup>1</sup>

<sup>1</sup>PS Analytical Ltd

The presence of Hg in oil and gas feedstocks can have a detrimental effect on downstream processing equipment such as the corrosion and embrittlement of brazed aluminium heat exchangers in cryogenic facilities, precious metal catalyst poisoning and equipment contamination due to the surface accumulation of mercury. Mercury is also known to be stripped out and released by various gas processing and purification stages such as acid gas removal and dehydration. These are often located upstream of mercury removal and as such they have a major influence on the fate and transportation of mercury across the plant.

The solubility of elemental mercury in water, methanol, mono-ethylene glycol, tri-ethylene glycol, methyl-diethanolamine and mono-ethanolamine at different concentrations and temperatures between 5 °C and 50 °C was established by determining the dimensionless Henry's law constant (HLC or  $kH'$ ) at different temperatures and concentrations for each solvent. By measuring the rate of release of mercury vapour from the solvent using gold traps installed at the exit of the stripping vessel. In general terms, a slower rate of release corresponds to a higher solubility of mercury in the solvent. A reductant of tin(II) chloride was added to the solvent to prevent oxidation of elemental mercury during the experiments. The solubility of elemental Hg in the solvent was calculated by inputting the saturated gas phase mercury concentration at the temperature of the solvent being tested. A bottom-up expanded uncertainty budget was produced and applied to all the experimental data. In all cases the solubility of Hg increases with temperature and with increasing concentrations of the solvent. The fate of mercury during solvent regeneration was also studied using a classic distillation. These data are of special significance since the reject streams in these units overhead streams from amine or glycol stills are often emitted to the atmosphere.

## Chungara Chronicles: Exploring mercury dynamics in Chile's highest lake

Chiang G<sup>1,2</sup>, Bahamonde P<sup>3,4,5</sup>, Hirmas A<sup>1,2</sup>, Gonzalez K<sup>4,6</sup>, Harrod C<sup>4,6,7</sup>

<sup>1</sup>Centro de Investigacion para la Sudentabilidad, Universidad Andres Bello, <sup>2</sup>Department of Ecology and Biodiversity, Faculty of Life Sciences, Universidad Andres Bello, <sup>3</sup>Center for Resilience, Adaptation and Mitigation, Faculty of Sciences, Universidad Mayor, <sup>4</sup>Millennium Nucleus of Austral Invasive Salmonids (INVASAL), <sup>5</sup>Cape Horn International Center (CHIC), Universidad de Magallanes, <sup>6</sup>Instituto de Ciencias Naturales Alexander Von Humboldt, Universidad de Antofagasta, <sup>7</sup>Universidad de Antofagasta Stable Isotope Facility, Instituto de Antofagasta, Universidad de Antofagasta

The introduction of non-native fishes has been commonly used as a means of diversify available protein for isolated human populations. It is important that once established, these stocks are assessed (e.g. [Hg]) to ensure that they pose no risk for human consumption. In Chile, salmonids have been introduced to almost all watersheds from the north (~18°S) to southern Patagonia (~56°S) for sportfishing and fisheries/aquaculture activities. Chungara Lake is located at 4500 m in the Altiplano above the Atacama Desert of N Chile. Formed ca. 10,000 ybp by the collapse of Parinacota volcano, the catchment has a (pre)history of gold mining since pre-Columbian times. Rainbow trout *Oncorhynchus mykiss* were introduced for human consumption in the 1990s, and pose not only a threat to endemic fish species (*Orestias chungarensis*, *Trichomycterus chungarensis*), but also potentially to human consumption. We analyzed total mercury (THg) in fish muscle and trophic level ( $\delta^{15}\text{N}$ ) of the three fish species in two inflowing rivers (Mal Paso stream, Chungara River), and Chungara lake. THg levels were higher in the lake (>1000 ppb ww), with *O. chungarensis* and *O. mykiss* showing similar concentrations. Rainbow trout THg levels from Chungara River ranged from ~200 to ~800 ppb ww, while *T. chungarensis* from Mal Paso stream had the widest THg distribution (~10 to ~1100 ppb ww). All species showed a significant relationship with size and mass, with bioaccumulation slopes in *O. chungarensis*>*T. chungarensis*>*O. mykiss*. Trout from Chungara Lake showed the highest  $\delta^{15}\text{N}$ , but similar mercury levels to *O. chungarensis*, showing a biomass dilution effect in the trout (known to be cannibalistic and prey on the endemic fish). The Chungara watershed has a story of Hg, that is reflected in fish bioaccumulation in all the sites, and consumption of trout should be limited to fish < 25 cm/1.2 kg.

## From North to South of Australia: A Comprehensive Examination of Atmospheric Mercury Deposition and their Implications for the Southeast Asia Mercury Cycle

Schneider L<sup>1</sup>, Thomas Z<sup>2</sup>, Saunders K<sup>3</sup>, Latimer J<sup>1</sup>, Sean-Fletcher M<sup>4</sup>, Haberle S<sup>1</sup>

<sup>1</sup>Australian National University, <sup>2</sup>University of Southampton, <sup>3</sup>Australian Nuclear Science and Technology Organisation, <sup>4</sup>University of Melbourne

Studies on mercury atmospheric deposition using natural archives, including lake sediments, have been conducted to gain insights into the effects of industrialisation on the natural cycle of mercury. While these studies indicate an increase in mercury since industrialization (1850 AD), there is a discrepancy regarding the magnitude of this rise in various parts of the world. The Southeast Asia and Pacific region, in particular, remains understudied concerning mercury deposition fluxes in natural archives. This study addresses this gap by focusing on ten lakes spanning from North to South in Australia. Sediment cores were collected and analysed to assess both pre- and post-anthropogenic mercury deposition fluxes. The interpretation of mercury profiles in these lake sediments relied on <sup>14</sup>C and <sup>210</sup>Pb dating, pollen, charcoal and carbon-to-nitrogen ratios. The collection comprised ten sediment cores, five from lakes situated above 23° S (Lake Barrine, Girraween, Euramoo, Horse Swamp, and Boggy Swamp) and five lakes below 23° S (Blue Lake, Club Lake, Hidden Lake, White Bull Lagoon, and Lake Wilks). The findings reveal an increase in mercury deposition fluxes in these lakes concurrent with the onset of the anthropogenic period. Lakes above 23° S exhibited an increase in mercury deposition in the 1800s, while those below 23° S experienced a later rise in the 1900s. Notably, lakes above 23° S displayed a decrease in deposition fluxes during the 1900s, likely reflecting atmospheric transport to northernmost lakes from the Northern Hemisphere. This observed decrease aligns with atmospheric measurements in Northern Australia, highlighting the Monsoon as an important driver of mercury transport from the Northern Hemisphere to the region. These results suggest that policy changes and technological advancements in the Northern Hemisphere, designed to reduce mercury emissions since industrialization, have contributed to a decrease in mercury deposition in lakes in the northern region of Australia.

### Abstract Graphics



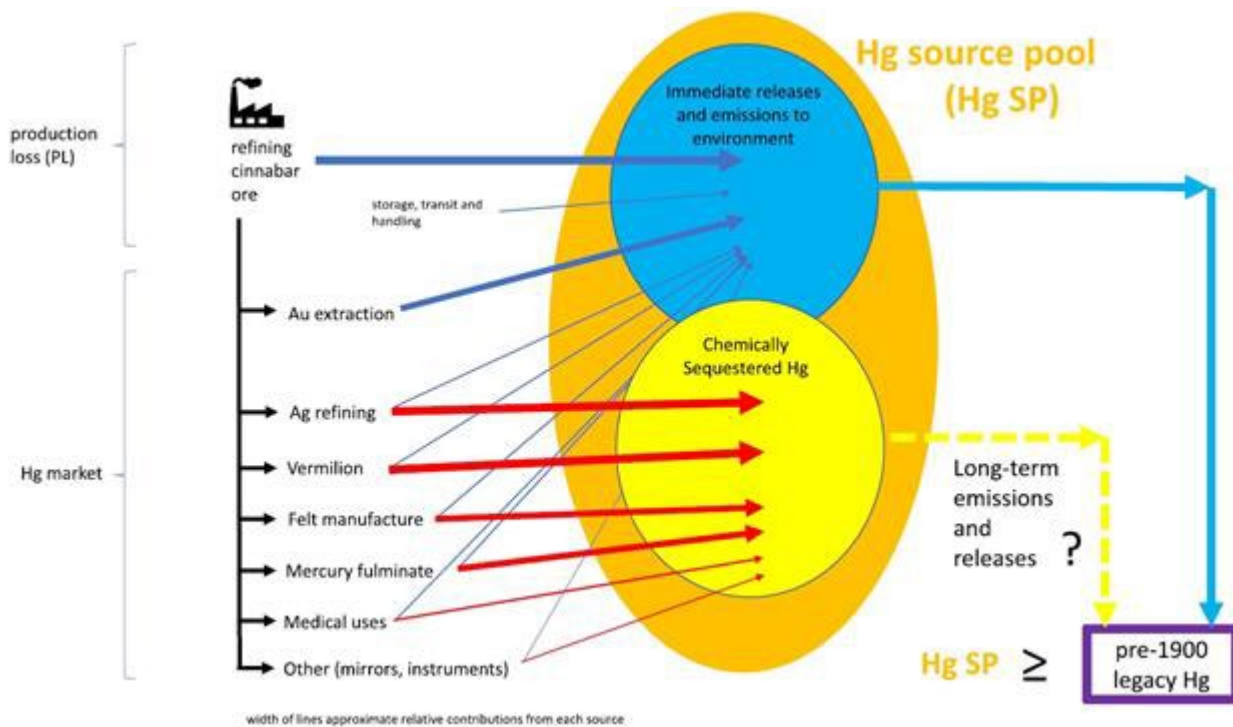
## Global Roots of Pre-1900 Legacy Mercury

Schneider L<sup>1</sup>, Guerrero S<sup>1</sup>

<sup>1</sup>Australian National University

Pre-1900 legacy mercury has multiple global sources that extend well beyond the silver-gold duopoly that prevailed until the early 1800s. Quantitative analysis of historical production and trade archival records reveal a significant expansion of mercury uses, both in terms of industrial consumption and geographical scope. China in the 19C becomes a major destination of mercury supplied from California and European mines, nearly equal to the USA mercury market. The United Kingdom and France show significant consumption of mercury. None of the countries are associated with major silver or gold production. Alternative industrial-scale uses of mercury require more detailed study, such as the production of the pigment vermilion, the manufacture of felt hats, mercury fulminate, and others. The previous picture of substantial mercury emissions to the air from thermal processes in the late 19C, as a result of the refining of silver ores or the extraction of gold, is no longer supported. In the case of silver production with mercury, solid and insoluble calomel ( $\text{Hg}_2\text{Cl}_2$ ) was the main immediate byproduct of the process. Extraction of gold from placer deposits did not necessarily require major consumption of mercury, so observations from the modern application of mercury in Artisanal and Small-Scale Gold Mining cannot be extrapolated to historical mercury emission scenarios. The main source of direct emissions of legacy mercury to the air would have taken place during its production from cinnabar ore. The current environmental impact of pre-1900 legacy mercury from the new data from 19C global trade patterns requires establishing a mass balance of mercury and its byproducts during the dry and wet processes of vermilion production, during the carroting of felt and in the manufacture of mercury fulminate.

### Abstract Graphics



## Identification of methanogens responsible for MeHg demethylation in rice paddy soils

Hu H<sup>1</sup>, Liu X<sup>1</sup>, Wang B<sup>2</sup>, Wu Q<sup>1</sup>, Long Y<sup>1</sup>, Feng X<sup>1</sup>

<sup>1</sup>State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, <sup>2</sup>School of Geography and Environmental Science, Guizhou Normal University

The net concentration of the neurotoxic MeHg in the environment is equally determined by Hg methylation and MeHg demethylation, with the former transforms inorganic Hg to MeHg and the latter does the opposite. In the past decades, Hg methylation has attracted a lot of public attention from worldwide and considerable researches have been conducted in revealing the mechanisms of this process in diverse environmental systems. Compared to Hg methylation, much less attention has been paid to, and consequently knowledge gained on, MeHg demethylation. Previous studies showed that methanogens are crucial to MeHg demethylation in rice paddy soils as Hg concentration increased. However, it remains unclear which methanogen species is responsible for MeHg demethylation in rice paddies. In this study, we aim to estimate MeHg demethylation potential by methanogens consortia and identify the key species driving this process. Results showed that methanogens consortia obtained by enrichment culture from paddy soil demethylated MeHg efficiently, up to 69.6%, 88.4% and 98.3% of MeHg were demethylated in 6, 12 and 24 h, respectively, and the Hg methylation potential was negligible (0.01131%-0.01046%). Furthermore, demethylation activity required it to be in contacted with cells rather than by cellular secretion, suggested by the observation of absent demethylation activity with cell filtrate. 16S rRNA gene diversity and metagenomic analysis showed that *Methanobacterium B*, *Methanomethylophilus* and *Methanosarcina* were the dominant methanogens in the enrichment culture, with the abundance were 38.8%, 31.8% and 9.0%, respectively, from the whole methanogens consortia. Meanwhile, bacteria were also detected in the enrichment culture, with *Terrisporobacter*, *Clostridium\_sensu\_stricto\_7* and *Clostridium\_sensu\_stricto* were the dominant species. Augmentation of the methanogens consortia to the rice paddies decreased MeHg concentration in rice paddies, and the decreasing extent depended on the augmentation method and time.

## Canadas Global Mercury Passive Sampling Network – A Global International Collaboration

Steffen A<sup>1</sup>, MacSween K<sup>1</sup>, Stupple G<sup>1</sup>

<sup>1</sup>Environment And Climate Change Canada

Monitoring mercury in the atmosphere on an ongoing basis is critical for the assessment of concentration changes occurring in response to the implementation of regulatory measures or climatic perturbations. In 2019, Environment and Climate Change Canada (ECCC) initiated a multi-year pilot study to investigate the feasibility of using passive air sampling to collect atmospheric mercury concentration data around the world. A passive sampling technique was developed in Canada as part of a University of Toronto and ECCC collaboration and has since been commercialized as the MerPAS<sup>®</sup> (Tekran Instrument Corporation). To address obligations of monitoring, effectiveness evaluation and capacity building under the Minamata Convention, global monitoring of mercury is required. Unfortunately, there is no mechanism within the Convention to develop and fund a global monitoring network, which creates a divided world of monitoring abilities. Canadas passive mercury network was created to close these gaps and provide an inexpensive and simple method of air sampling anywhere around the world for anyone who needs it. The network aims to combine efforts from currently operational infrastructure and work with international partners to reach a common goal. Currently, the global network combines efforts from 7 different mercury networks and the Global Atmospheric Passive Sampling (GAPS) network run under Stockholm's GMP. The network boasts 102 sites in 42 countries with numerous collaborators. The results from this study show the effectiveness of the technique and the ability of this network of networks to work collaboratively together on the international stage to achieve results that have been missing. Further international collaboration and commitments from Parties of Minamata are still required to fully ensure successful impacts of the treaty on the environment and human health related to mercury.

## Use of environmental reference materials (RMs) for quality control of precise isotopic measurements

Yamakawa A<sup>1</sup>, Nagano K<sup>1</sup>, Onishi K<sup>1</sup>

<sup>1</sup>National Institute For Environmental Studies

Reference Materials (RMs) for the environment are used to evaluate new analytical methods and to control the accuracy of pretreatment and instrumental analysis. Since most environmental samples have complex compositions, it is important to confirm the validity of the analytical method and analytical values by using RMs with compositions similar to those of the sample to be measured. In recent years, accuracy control and reliability assurance in chemical analysis have become important issues in various fields, and RMs are very useful in ensuring traceability of measurements. There is a need to add reference values to environmental RMs to contribute to the recent development of isotope analysis, such as mercury (Hg) isotope analysis. There are seven stable isotopes of mercury, and their abundance varies depending on the biogeochemical processes occurring in the environment. Because of this feature, they have been used as tracers to identify the source of mercury in environmental samples and to infer processes related to the environmental fate of mercury. For example, mass independent fractionation of odd isotopes ( $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$ ) in human hair varies with the type and quantity of the food, particularly seafood consumed, it can be used to estimate the sources of exposure. In addition, absorption of mercury, mostly in the form of methylmercury, by the human organism was shown to induce mass dependent fractionation of  $\sim +2\%$  for  $\delta^{202}\text{Hg}$ , implying that the isotopic composition of Hg in human hair is as expected following its ingestion and distribution in the body. Furthermore, Hg isotopes in atmospheric samples (gaseous and oxidized Hg) are known to be indicators of their emission sources and chemical reactions occurring in the atmosphere. This presentation will report on reference values and their use for mercury and other isotopes assigned to NIES CRMs (Certified Reference Materials) and RM.

196

## Mercury abatement and recycling from non-ferrous smelting flue gas

Xu H<sup>1</sup>

<sup>1</sup>Shanghai Jiao Tong University

Gaseous elemental mercury (Hg<sup>0</sup>) is increasingly concerning in industrial flue gases because of its difficult disposal. Catalysis conversion and adsorption to oxidized species (Hg<sup>2+</sup>) and particle-bonded states (Hg<sub>p</sub>) are two common Hg<sup>0</sup> disposal methods. Here, we selected different methods focusing on Hg<sup>0</sup> capture and recycling from non-ferrous smelting flue gas. The high concentration of mercury and high concentration of SO<sub>2</sub> posed big challenges for mercury disposal. The best technology is to convert Hg<sup>0</sup> to HgS which was not sensitive to SO<sub>2</sub>, compared to HgO, HgCl<sub>2</sub>, and other mercury species. The novel adsorbents were developed for Hg<sup>0</sup> capture, and the results indicated that CuS has the best performance among the metal sulfides. The reaction mechanism was well discussed. In addition, a novel technology that directly converts SO<sub>2</sub> to active S\* species was first put forward. Using this method, it realize unlimited mercury adsorption capacities.

## Monitoring, assessment, and possible remediation in the abandoned Hg-mine of Abbadia San Salvatore (central Italy)

Montegrossi G<sup>1,2</sup>, Meloni F<sup>1,2,3</sup>, Nisi B<sup>1,3</sup>, Cabassi J<sup>1</sup>, Bianchi F<sup>4</sup>, Rappuoli D<sup>5,6</sup>, Vaselli O<sup>1,2,3</sup>

<sup>1</sup>CNR-IGG Institute of Geosciences and Earth Resources, <sup>2</sup>INSTM-National Interuniversity Consortium of Materials Science and Technology, <sup>3</sup>Department of Earth Sciences, <sup>4</sup>S.B.C., Geologi Associati, <sup>5</sup>Unione dei Comuni Amiata Val d'Orcia, Unità di Bonifica, <sup>6</sup>Parco Museo Minerario di Abbadia San Salvatore

In the former Hg-mine of Abbadia San Salvatore (Tuscany, central Italy), the shallow groundwater system is currently monitored due to the strikingly high Hg pollution. The survey consist of shallow piezometers to assess the hydraulic setting and characterize the water chemistry, with particular attention to mercury. In the last 10 years of surveys, large variations of the geochemical facies have been observed, apparently not related to the effects of the rainwaters. The variability of the main composition (Ca(Mg)-SO<sub>4</sub>; Ca(Mg)-HCO<sub>3</sub> and, subordinately, Na-HCO<sub>3</sub>) is intimately associated with the large differences recorded in terms of Hg. This is related to water-rock interaction processes governed by the dissolution of carbonates and gypsum-anhydride (typical minerals recognized in the waste materials found in the SE zone of the mining area). High concentrations of Hg (up to 407 µg/L) were found during the wet period while they abruptly decreased (81.4 µg/L) during the dry period. A first remediation was carried in 2007 in a small sector (about 4500 m<sup>2</sup>) of the mining area by a jet-grouting method. This approach cannot apply to the whole area (ca. 65 ha) and consequently, the gather hydraulic (piezometer monitoring) and geochemical data (from 2013 to 2023) were used to produce a flow and transport model with MODFLOW-MT3D to evaluate the barrier performance and the current state of mercury dispersion. An improvement of the hydraulic barrier and/or other remediation methods can thus be better evaluated. Nevertheless, the installation of a hydraulic barrier is presently the most suitable solution to both minimize water-rock interaction processes, likely responsible for the large chemical variability recorded during the surveys, and reduce the mercury concentration. The target is that to achieve a Hg content of 5 µg/L before discharging the waters into a local stream.

## Enhancing the analytical capabilities of Zeeman AAS in mercury determination in samples with complex matrices

Shashko A<sup>1</sup>, Sholupov S<sup>1</sup>, Pogarev S<sup>1</sup>, Ryzhov V<sup>2</sup>, Mashyanov N<sup>1</sup>

<sup>1</sup>Lumex-marketing LLC, <sup>2</sup>Lumex Analytics GmbH

Mercury (Hg) occurrence in the formidable diversity of samples and wide variation of its concentration are the main challenges for mercury analytics. The thermal decomposition method combined with Zeeman AAS provides a universal approach for analysis of any solids and liquids, including samples with complex matrices such as foodstuff, cosmetics, biological samples, crude oil and products of its distillation.

The advantages of this method are high selectivity, low limit of detection, optimization of sample atomization modes including thermoscanning, the absence of memory effect, an automatic closed-loop temperature control function expanding the range of measurements. Some application examples are listed below.

The EU Directive 1223/2009 specifies the allowable level for mercury compounds as 0.10 mg/kg (100 ppb). In recent years, a new standard method ISO 23674:2022 (thermal decomposition with AA spectrometry) has been developed to meet these requirements. Zeeman AAS allows to omit time-consuming sample preparation procedures required for the classic cold vapour technology. This technique enables to determine mercury in a whole range of its concentration in cosmetics starting from the background level (2 ppb).

Direct analysis of crude oil and naphtha according to ASTM D7622 starts from 5 ppb level. A pre-concentration step using solid-phase extraction on aluminum oxide allows to enhance the sensitivity of the analysis to 0.1 ppb for naphtha and gas condensate.

Zeeman AAS enables the direct analysis of complex matrixes of the passive air samplers (PAS) based on activated carbon impregnated by sulphur. In this case, sodium bicarbonate is used as an additive binding sulphur dioxide formed during sorbent combustion.

## Two-channel system for simultaneous determination of elemental and oxidized mercury in a gas stream

Sholupov S<sup>1</sup>, Pogarev S<sup>1</sup>, Ryzhov V<sup>2</sup>, Rajamäki T<sup>3</sup>

<sup>1</sup>Lumex-marketing LLC, <sup>2</sup>Lumex-Analytics GmbH, <sup>3</sup>National Metrology Institute VTT MIKES

In oxidized mercury (Hg) reference gas generators, unwanted mercury reduction may occur during oxidized mercury flux generation, in which case both oxidized and elemental mercury will be present at the output of such a generator. So, it is important to know the content of both oxidized (Hg<sup>2+</sup>) and elemental (Hg<sup>0</sup>) mercury in the generator output flow. For instrumental analysis methods, it is more convenient to determine the total mercury (Hgtot), which is the sum of the elemental and oxidized mercury, and elemental mercury. For this purpose, an analytical system containing an inlet unit and two gas channels, for the simultaneous determination of Hg<sup>0</sup> and Hgtot concentrations was developed. To avoid water vapor condensation in the inlet, the latter is heated up to 130 °C. The Hg<sup>0</sup> channel consists of a heated cell, an atomic absorption spectrometer using the Zeeman effect (RA-915F) and a pump. The temperature of the cell is maintained at about 130 °C. To avoid catalytic reduction of Hg<sup>2+</sup> in the Hg<sup>0</sup> channel all wetted parts are made of quartz, PTFE or other plastic. The Hgtot channel consists of an atomizer, a heated cell, the spectrometer of the same type (RA-915F) and a pump. The temperature of the atomizer is 700 °C. Two manual valves on the inlet unit can direct ambient air in the channel through a mercury absorption filter before entering the measurement cell for instrument zeroing or directly into the measurement cells for analysis. The design of the Hgtot channel is similar to the LUMEX commercial attachment PYRO-915 This system enables simultaneous real time determination of both mercury species with fast response time of some seconds and without matrix effect caused by changes in test gas composition e.g., its water content. The results of a HovaCAL calibration gas generator testing are shown in the presentation.

## Effect of natural and assisted revegetation of an alluvial gold mine on the reduction of mercury remobilisation from soil and transport to hydrosystems (French Guiana)

Nitschke N<sup>1,2,3,4</sup>, Hellal J<sup>3</sup>, Legout C<sup>5</sup>, Tessier E<sup>2</sup>, Ali A<sup>4</sup>, Taravella S<sup>4</sup>, Amouroux D<sup>2</sup>, Guedron S<sup>1</sup>

<sup>1</sup>Université Grenoble Alpes, CNRS, IRD, ISTERRE, <sup>2</sup>Université de Pau et des Pays de l'Adour, CNRS, IPREM, <sup>3</sup>BRGM DEPA/GME, <sup>4</sup>GAIA SAS, <sup>5</sup>Université Grenoble Alpes, CNRS, IRD, IGE

French Guiana is experiencing a new rush in artisanal and small-scale gold mining (ASGM). Unlike illegal ASGM, legal mines extract gold without mercury (Hg). However, both mining activities have an impact on Hg emissions to rivers as they involve deforestation and soil excavation, remobilising particles from naturally Hg-rich Amazonian soils.

In French Guiana, legal mines are responsible for restoring their sites after exploitation, through landscaping and replanting. However, the impact of legal mines on particle and contaminant fluxes, and the efficiency of their restoration is not fully characterised, as their remote location makes continuous monitoring challenging.

In this study, we monitored particle and Hg fluxes during rain events, comparing two different sites on a small scale legal alluvial gold mine: one replanted site with trees and vegetation cover (>3 years), and a site with bare soil (< 6 month). Fluxes were monitored over three campaigns spanning one year, and indicators related to soil restoration were measured (i.e., root density, enzyme activity and DNA concentration).

Results showed that THg (dissolved + particulate) fluxes were reduced 3-fold over one year in the non-replanted site. Hg fluxes in the replanted site were 100 times below the non-replanted site at the beginning of the study (1.7 ng Hg/m<sup>2</sup>/L rain), and close to zero after one year. These results are explained by the increase in root density due to spontaneous revegetation on both replanted and non-replanted sites (7 and 4.5 fold, respectively). Initial soil restoration with an increase in some enzyme activity (arylsulfatase) was also observed on both replanted (3-fold) and bare soil (4.5-fold) sites.

This indicates that spontaneous revegetation significantly decreases particle and Hg fluxes from the restored mining to the downstream watershed. To reduce completely fluxes and enable soil refunctionalisation, the relevance of assisted revegetation (replanting) is demonstrated here.

## Impact of Artisanal Small-scale Goldmining in West Africa: Assessment of mercury levels and speciation in water and soil of mining sites along the Mouhoun River (Burkina Faso)

Dabre D<sup>1,2</sup>, Guédron S<sup>2</sup>, Maïga Y<sup>1</sup>, Odile B<sup>3</sup>, Gardon J<sup>3</sup>, Ouédraogo O<sup>1</sup>, Mason R<sup>4</sup>

<sup>1</sup>Université Joseph Ki-zerbo, <sup>2</sup>Université Grenoble Alpes, CNRS, IRD, ISTerre, 38000 Grenoble, France ,

<sup>3</sup>HydroSciences Montpellier, University of Montpellier, CNRS, IRD, , <sup>4</sup>University of Connecticut, 1080 Shennecossett Rd, Groton, CT 06340 USA Dept Chemistry, Dept Marine Sciences, UConn, Storrs, CT

Over the past decade, Artisanal Small-scale Gold Mining (ASGM) activities have developed intensively in West Africa due to the rise of gold price. Extraction processes and the chemicals used for gold (Au) recovery (i.e., mercury (Hg) and cyanide (CN)) have a strong impact on soil and water resources.

Given the recent development of these activities and the presence of terrorist groups, very little information is available on the impact of ASGM in Burkina Faso. In this study, we assessed the Hg contamination of soils, surface and ground waters, in mining sites located along the Mouhoun river with regard to the history and density of ASGM activities.

Results show evidence of Hg contamination in soils located close to the Au amalgamation sites with total mercury [THg] in soils up to 14 µg.g<sup>-1</sup> compared to the geochemical background of 0.15 ± 0.10 µg.g<sup>-1</sup>. Selective extraction and thermodesorption experiments indicated that Hg in pristine soils was mainly found as divalent Hg [Hg(II)] associated with organic matter [Hg(II)-OM = 60 ± 19 %], and iron oxides (21 ± 16%). In contrast, a significant proportion of Hg(0) (35 ± 13%) was found in soils of ASGM sites, highlighting the contribution of redeposited Hg(0) by condensation near amalgam burning sites. Unfiltered total Hg (THg) concentration in surface and ground water of ASGM site (121 ± 103 ng.L<sup>-1</sup>) was found mainly associated to suspended particles (94 ± 6%), and largely exceeded the maximum permissible concentration of 70 ng.L<sup>-1</sup>, according to the environmental quality standard.

Our results show evidence of Hg contamination of ground water used by local population in ASGM areas. In addition, we show that fine particles enriched in Hg are the major carrier phases for the Hg transfer to downstream aquatic ecosystems. Human exposure is also expected via the inhalation of fine Hg-rich dust particles.

## Mercury compounds distribution and flux towards the hydrosystem on an alluvial gold mine during the restoration phase (French Guiana)

Nitschke N<sup>1,2,4,5</sup>

<sup>1</sup>Université Grenoble Alpes, CNRS, IRD, ISTERRE, <sup>2</sup>Université de Pau et des Pays de l'Adour, CNRS, IPREM, <sup>3</sup>Université Grenoble Alpes, CNRS, IRD, IGE, <sup>4</sup>BRGM DEPA/GME, <sup>5</sup>GAIA SAS

Alluvial goldmining activities have an impact on mercury (Hg) emissions to rivers as they involve deforestation and soil reworking for gold-extraction, remobilising particles from naturally Hg-rich Amazonian soils.

In French Guiana, legal mines extract gold without Hg, and are responsible for the restoration of their sites after exploitation. However, the added-value of such restoration is not fully characterised, and the erosion of surface particles enriched in geogenic or inherited Hg from former illegal mining activities as well as the internal recycling of Hg between environmental compartments are poorly characterised.

Here, Hg species were monitored in the dissolved and particulate fractions upstream and downstream of a legal alluvial gold-mine during restoration process in discrete sampling campaigns spanning one year. Turbidity and water-flow were monitored continuously ( $\Delta t=1h$ ) over this year. Ecosystem compartments (pristine and mined soils, stream, rain and pore-water, illegal mining-ponds, atmosphere) were monitored to identify and characterise Hg pools and sources.

Methylmercury (MeHg) concentrations were almost constant in the dissolved ( $60\pm 19\text{pg.L}^{-1}$ ) and particulate ( $202\pm 70\text{pg.L}^{-1}$ ) fraction and poorly influenced by rain events.

In contrast, dissolved inorganic Hg (iHg) was significantly correlated to water-flow and particulate iHg to turbidity, allowing the estimation of iHg and MeHg fluxes all year. Specific Hg fluxes upstream and downstream of the restored mine-flat indicate an increase in the particulate iHg export by a factor two due to restored-soil runoff.

Atmospheric Hg concentrations were matching ones found in remote locations ( $1.9\pm 0.4\text{ng.m}^{-3}$ ) and mining surface soils displayed concentrations in the range of pristine surface soils ( $229\pm 19\text{ng.g}^{-1}$ ). However, high concentrations of dissolved gaseous mercury were measured locally in some mining-ponds, exceeding by 100-fold the river concentrations, hinting towards past and isolated contamination sources. These results show Hg concentrations matching background levels in most compartments, the main source of Hg-export to the river being the erosion of the post-mining-flat.

## New gold rush in Guinea Conakry (West Africa): Assessment of mercury levels and speciation in the Artisanal Small-scale Goldmining district along the Niger River.

Dabre D<sup>1,2</sup>, Guédron S<sup>2</sup>, Maïga Y<sup>1</sup>, Odile B<sup>4</sup>, Gardon J<sup>4</sup>, Konaté A<sup>3</sup>, Doumbouya Y<sup>3</sup>

<sup>1</sup>Université Joseph Ki-zerbo, <sup>2</sup>Université Grenoble-alpes, <sup>3</sup>Institut Supérieur des Mines et Géologie de Boké, <sup>4</sup>HydroSciences Montpellier

Artisanal small-scale goldmining (ASGM) activities has a long history in Guinea Conakry (GC). Due to the rising price of gold over the last decades, ASGM in GC has intensified, accompanied with increased mechanisation and increasing production. Current ASGM extraction processes and gold (Au) recovery are performed both with mercury (Hg) and cyanide (CN), contaminating soil and water resources. In this study, we assessed Hg contamination of soil and groundwater at four mining sites, together with surface water, sediment and fish along the Niger River and tributaries in the Kouroussa district.

Results show evidence of intense Hg contamination in soils located close to Au amalgamation sites with total mercury [THg] in soils reaching up to 16 µg.g<sup>-1</sup> compared to the geochemical background (0.46 ± 0.39 µg.g<sup>-1</sup>). The highest levels of Hg contamination were found at large ASGM sites with a long mining history. Thermodesorption experiments indicated that THg was found partly in the elemental form (43±21 %) in ASGM soils, highlighting the significant contribution of redeposited Hg(0) by condensation near amalgam burning sites. In pristine soils, Hg was mainly found as divalent Hg [Hg(II)] associated with organic matter (59± 2 %), and iron oxides (16 ± 13 %).

Unfiltered total Hg (THg) concentration in ground water (well) of ASGM sites were high, up to 347 ng.L<sup>-1</sup>, and mainly associated to suspended particles (98±10 %), with dissolved Hg representing less than 2 %. Similarly, THg concentration in river was mainly associated to suspended solids.

These results show evidence of significant Hg contamination of soils and ground water used as drinking water by local population in ASGM areas. This highlights that particles enriched in Hg are the main sources of contamination for downstream aquatic ecosystems where Hg can be methylated and enter the trophic chains.

## Improve the performance of the RA-915AM mercury monitor in measuring background and high levels of mercury

Ryzhov V<sup>1</sup>, Sholupov S<sup>2</sup>, Pogarev S<sup>2</sup>, Mashyanov N<sup>2</sup>

<sup>1</sup>Lumex-analytics GmbH, <sup>2</sup>Lumex-marketing LLC

Atmospheric mercury monitoring networks require analyzers providing reliable measurements over extended periods of time. The RA-915AM mercury monitor is based on Zeeman Atomic Absorption Spectroscopy (ZAAS) and is designed for the long-term (months) non-attended measurement. ZAAS combined with multipath cell having optical length of 10 m enables direct continuous real-time measurement of the background mercury concentration in ambient air without mercury preconcentration on traps. The limit of detection (LoD) at an averaging time of 5 min is 0.3-0.5 ng/m<sup>3</sup>, which is sufficient for background monitoring. However, LoD can be further reduced to 0.1 ng/m<sup>3</sup> by increasing the averaging interval. The wide dynamic range of more than four orders of magnitude and the variable optical length of the analytical cell allow high mercury concentrations of up to 3 mg/m<sup>3</sup> to be measured. Due to highest selectivity and fast response time (up to 14 readings per second), the RA-915AM monitors can be used to control processes with fast changes of the mercury concentration in air or gas.

For conventional monitors that use mercury preconcentration on sorption traps, the main analytical errors are caused by changes in sorption capacity. For ZAAS monitors that implement direct measurements not requiring accumulation on sorbents, there are specific sources of measurement errors. For example, automatic calibration with a built-in saturated mercury vapor test cell reduces analytical errors for high and intermediate mercury measurements, but has little or no effect on background results. In background measurements, the main source of error is the instrumental drift of the zero line. To minimize its influence, it is important to select the appropriate time for automatic zero control. For measurements of medium to high concentrations of mercury in air, zero line drift can be ignored. The examples of long-term measurements under various conditions illustrate the analytical performance of the RA-915AM monitors.

## Gaseous elemental mercury (GEM) in Florence (central Italy): measurements at point stations and comparison with other gaseous pollutants

Cabassi J<sup>1</sup>, Venturi S<sup>2</sup>, Randazzo A<sup>2</sup>, Santi R<sup>2</sup>, Maioli G<sup>2</sup>, Capecchiacci F<sup>2</sup>, Nisi B<sup>1</sup>, Meloni F<sup>2</sup>, Tassi F<sup>2</sup>, Rappuoli D<sup>3</sup>, Vaselli O<sup>2</sup>

<sup>1</sup>Institute of Geosciences and Earth Resources (IGG), National Research Council of Italy (CNR),

<sup>2</sup>Department of Earth Sciences, University of Florence (DST-UNIFI), <sup>3</sup>Unione dei Comuni Amiata Val d'Orcia, Unità di Bonifica

Mercury is emitted in the atmosphere as elemental vapour ( $\text{Hg}^0$  or GEM, i.e. gaseous elemental mercury) from different sources, including earth's surface natural degassing and re-evaporation of previously deposited mercury, and past and present anthropogenic activities. The urban environment is not an exception, being characterized and affected by local-sourced emissions (e.g. related to municipal waste, motor vehicles, urban surfaces, industrial activities, and biomass combustion) and by non-point sources of Hg, which, although extremely difficult to identify, can be relevant. In this context, quantifying the presence of mercury in urban air and investigating and deciphering its behavior under different environmental conditions is pivotal, especially following the provisions of the Minamata Convention on Mercury concerning increased knowledge and inventory of Hg emissions. For this purpose, GEM measurements through a Lumex<sup>®</sup> RA-915M instrument were for the first time performed in different areas of Florence (central Italy) at selected fixed monitoring points and in combination with the analysis of  $\text{CO}_2$  and  $\text{CH}_4$ . Mercury concentrations ranged from  $<5$  to over  $150 \text{ ng/m}^3$ , the daily averages being characterized by a completely different trend with respect to those of  $\text{CO}_2$  and  $\text{CH}_4$ , implying that their emission source(s) and/or behavior in the atmosphere is/are not the same. Indeed, Hg presented a significant increase in the central hours of the day and showed a direct correlation with temperature and an inverse correlation with relative humidity as a consequence of Hg dependence on solar radiation, which causes photochemical reactions that reduce and mobilize previously deposited  $\text{Hg}^{2+}$ . Nevertheless, vehicular traffic (at its highest during peak hours), i.e. the main factor regulating  $\text{CO}_2$  and  $\text{CH}_4$  dynamics, likely had a minor influence on Hg too, since the measurement stations were characterized by different concentrations in agreement with the traffic intensity.

206

## Historical atmospheric mercury concentration reconstructed from tree rings in the Qinghai-Tibetan Plateau

Liu X<sup>1</sup>, Wang X<sup>2</sup>, Wang D<sup>1</sup>

<sup>1</sup>College of Resources and Environment, Southwest University, <sup>2</sup>State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences

**Abstract:** Tree rings are an emerging high-resolution archive for historical atmospheric mercury (Hg) reconstruction. In this study, tree cores of spruce and fir were collected from 8 high-altitude areas affected by different atmospheric circulation in the Qinghai-Tibetan Plateau (QTP) of China to investigate the chronology of atmospheric Hg concentration. The tree-ring records showed that Hg concentrations were low and stable between 1760s and 1850s, followed by an increase after the Industrial Revolution. The concentrations in sites strongly controlled by the westerlies peaked in the 1970s and subsequently declined, consistent with anthropogenic Hg emission trends in Europe and North America. Sites close to the interior of China displayed continued increase of Hg concentrations, particularly a sharp rise after in the 1980s, reflecting the dramatic increase of industrial activities in China. Regions dominated by the Indian monsoon presented that Hg concentrations reached a peak in 1930s and subsequently remained stable, which likely caused by the combined effects of anthropogenic Hg emissions in South Asia and China. Overall, the distinct Hg emissions from west countries contribute the slight increase of atmospheric Hg concentration in QTP before 1970s, while the dramatic increase of emissions from South Asia and China contribute to the sharp elevation after 1980s.

**Keywords:** Mercury; tree rings; long-term trends; Qinghai-Tibetan Plateau

## Mercury exposure determined by unique oxidation pathways in mid- and high-latitude marine food webs

Kwon S<sup>1</sup>, Lim S<sup>2</sup>, Motta L<sup>3</sup>

<sup>1</sup>Pohang University of Science and Technology, <sup>2</sup>Pohang University of Science and Technology,

<sup>3</sup>Woods Hole Oceanographic Institution

It is well-established that gaseous elemental Hg (Hg<sup>0</sup>) oxidation followed by rain and particulate scavenging supply Hg found in marine waters and biota. To contradict this, a recent modeling study has estimated that Hg<sup>0</sup> invasion into seawater is underestimated by 40%. This raises ecologically relevant questions of: does Hg<sup>0</sup> invasion influence Hg sources bioaccumulated in marine biota? If so, what is the environmental pathway leading to Hg<sup>0</sup> exposure?

Hg stable isotopes have played an instrumental role in deciphering Hg sources and exposure pathways in aquatic ecosystems. In particular,  $\Delta^{200}\text{Hg}$  anomalies, which occur via tropospheric oxidation, has served as a tracer for distinguishing between atmospheric Hg<sup>0</sup> and Hg<sup>2+</sup> depositional pathways. Here, we characterized Hg isotope ratios in zooplankton, fish, and environmental matrices (atmospheric samples, seawater, sediment, snowpack) sampled across mid-latitude oceans (Chinese marginal seas to the Bay of Bengal) and the Arctic Ocean. The results depict a clear  $\Delta^{200}\text{Hg}$  dichotomy, in which the samples of mid-latitude and high-latitude oceans have distinctly positive and near-zero  $\Delta^{200}\text{Hg}$ , respectively. This indicates that, while mid-latitude ocean biota accumulate Hg<sup>2+</sup> that has undergone oxidation in the high troposphere, the Arctic Ocean biota are influenced by Hg<sup>0</sup>. Based on the preferential diffusion of dissolved Hg<sup>2+</sup> by plankton cellular membrane, we hypothesize that Hg<sup>0</sup> is subjected to near surface oxidation, where near-zero  $\Delta^{200}\text{Hg}$  value can be preserved. The similarity of  $\delta^{202}\text{Hg}$  and  $\delta^{199}\text{Hg}$  between our Arctic Ocean plankton and atmospheric samples suggest that Hg<sup>0</sup> is oxidized at the marine boundary layer. Our broad spatial scale observations of Hg isotopes in marine biota shed new light into the specific oxidation pathways leading to Hg exposure in marine biota. The fact that there are no anthropogenic Hg sources in the Arctic highlights the pervasive nature of Hg<sup>0</sup>, explaining the unusually elevated Hg levels previously monitored across the Arctic food web.

## The role of macrophytobentos in mercury remobilization from sediments of the estuary in southern Baltic Sea

Popławska A<sup>1</sup>, Płońska P<sup>1</sup>, Bełdowska M<sup>1</sup>, Zgrundo A<sup>2</sup>, Złoch I<sup>3</sup>

<sup>1</sup>Department of Chemical Oceanography and Marine Geology, Faculty of Oceanography and Geography, University of Gdańsk, <sup>2</sup>Department of Functioning of Marine Ecosystems, Faculty of Oceanography and Geography, University of Gdańsk, <sup>3</sup>Department of Marine Biology and Biotechnology, Faculty of Oceanography and Geography, University of Gdańsk

In the previous century, untreated industrial and municipal sewage found were delivered into the Baltic Sea, a semi-closed reservoir with an average depth of approximately 52m. The Baltic Sea, subject to a warming climate and prolonged vegetation seasons, has experienced an expansion of shallow estuaries covered by macrophytobentos. These plants, comprising vascular plants and macroalgae, have the ability to accumulate toxic mercury from water or sediments, potentially leading to the larger-scale remobilization of mercury in the area.

As macrophytobentos are the initial link in the marine trophic web, understanding the concentration of mercury in these plants is crucial due to the biomagnification process, wherein mercury ascends through the trophic levels. This is especially significant in underwater meadows, vital habitats and food sources for zoobentos organisms and small fish. The research sought to estimate the mercury enter into macrophytobentos, the foundational element of the Baltic food web, particularly in the estuaries of the southern Baltic Sea.

Between 2019 and 2021, approximately 400 macrophytobentos samples were collected from 94 stations by divers. The samples were categorized into vascular plants and macroalgae, followed by species identification. The concentration analysis of total mercury (THg) and mercury fractions utilized the thermodesorption method with an automatic analyzer DMA-80 (Milestone, Italy). The distribution of mercury fractions in both groups was similar, with vascular plants being less contaminated than macroalgae—a notable departure from observations made two or four decades earlier. These findings suggest the effectiveness of environmental regulations implemented in the late 90s, particularly in reducing the emission of toxic metal wastes. It is hypothesized that mercury deposited in the last century may now reside in deeper sediment layers, beyond the reach of vascular plants, a trend observed in 2010. The research received financial support from the National Science Center, project no.2022/45/B/ST10/00368.

## Mercury in permafrost soils from the South Shetland Islands, Antarctica

Zilhão H<sup>1,2</sup>, Louro C<sup>1</sup>, Cesário R<sup>1</sup>, Vieira G<sup>2</sup>, Canário J<sup>1</sup>

<sup>1</sup>Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, <sup>2</sup>Centro de Estudos Geográficos, Instituto de Geografia e Ordenamento do Território, Universidade de Lisboa

Permafrost soils of the northern hemisphere are characterized by high content of organic matter and store significant amounts of mercury, with the potential of having a global impact. On the opposite, the less studied Antarctic soils are essentially mineral, with very low organic matter content, and less is known about the consequences of permafrost degradation. For that reason, Antarctic soil characterization is essential for contamination monitoring and to understand Hg dynamics in austral permafrost ecosystems.

The South Shetland Islands archipelago is located approximately 120 km of the Antarctic peninsula in an area of discontinuous permafrost and where the increase of temperatures may lead to rapid permafrost thaw, possibly meaning Hg remobilization. Its ice-free areas are home to scientific research stations and are the most accessible places for Antarctic tourism.

We intend to evaluate Hg concentrations in soils of different islands of the archipelago with distinctive characteristics. Total Hg concentrations were determined in soil samples collected in discontinuous permafrost areas of King George (KGI) and Deception Islands (DI). In Barton Peninsula, KGI, values ranged between 2.6 – 35.3 ng/g and, in DI, between 8.0 and 221.8 ng/g. DI high values are attributed to its volcanism with the highest concentrations being found in areas close to where the last volcanic eruption occurred. In Barton Peninsula, reported values are lower than those proposed for the continental crust and may set a baseline for monitoring contamination.

Deception's porous and insulating soils give rise to a thin active layer, meaning that frozen soil is, sometimes, very close to the surface. At two areas, close to the most recent volcanic eruption, different trends appear to exist. While in one, unfrozen surface soils present higher values, in the other, frozen soils present higher concentrations, possible indicating mobilization and accumulation susceptible of mercury release in climate change scenarios.

## Overview of the Asia Pacific Mercury Monitoring Network (APMMN)

Sheu G<sup>1</sup>, Lin D<sup>1</sup>, Schmeltz D<sup>2</sup>, Gay D<sup>3</sup>

<sup>1</sup>National Central University, <sup>2</sup>U.S. Environmental Protection Agency, <sup>3</sup>National Atmospheric Deposition Program

The Asia Pacific Mercury Monitoring Network (APMMN) cooperatively measures mercury in precipitation in a network of sites operating in Asia and the Western Pacific region. The network addresses significant data gaps in a region where mercury emission estimates are the highest globally, but available measurement data are limited. The reduction of mercury emissions under the Minamata Convention on Mercury also justifies the need for continent-wide and consistent observations that can help determine the magnitude of the problem and assess the efficacy of reductions over time. The APMMN's primary objectives are to monitor wet deposition and atmospheric concentrations of mercury and assist partners in developing their own monitoring capabilities. Network planning began in 2012 with pilot wet deposition sampling starting in 2014. The APMMN started operation in 2016. Currently, 15 sites in the region measure mercury in precipitation following standardized procedures adapted from the National Atmospheric Deposition Program (NADP). The network has a common regional analytical laboratory in Taiwan, and quality assurance procedures, which ensure the network makes scientifically valid and consistent measurements. Results from our ongoing analytical quality assurance measurements show accurate analytical analyses. We have partnered with the National Institute for Minamata Disease (NIMD) to concurrently conduct an inter-comparison study at National Central University (NCU) and NIMD to assess the variability of wet Hg deposition measurements using different types of wet deposition samplers (KASC-02, MIC-B and N-CON). Moreover, a pilot passive air sampler study is currently underway. Future APMMN plans are to (1) foster new network partnerships, (2) continue to collect, quality assure, and distribute results on the APMMN website, (3) provide training and share best monitoring practices, and (4) establish a gaseous concentration network for estimating dry deposition.

## Climatic regulation of atmospheric mercury concentrations at a mountain-top site in Taiwan

Sheu G<sup>1</sup>, Nguyen L<sup>2</sup>, Hsiao P<sup>1</sup>, Yen M<sup>1</sup>

<sup>1</sup>National Central University, <sup>2</sup>University of Science, Vietnam National University

Atmospheric mercury (Hg) cycling is sensitive to climate-driven changes, but links with various teleconnections are not well studied due to the scarcity of long-term monitoring dataset.

Concentrations of atmospheric mercury Hg have been monitored since April 2006 at the Lulin Atmospheric Background Station (LABS; 120.87°E, 23.47°N, 2862 m a.s.l.), a high mountain forest site in central Taiwan, and the monitoring is still ongoing. Multiscale temporal variations of gaseous elemental Hg (GEM) concentrations at LABS in 2007-2019 were studied and distinguished by the application of the Hilbert-Huang transformation (HHT). Diurnal, monthly, annual, and inter-annual GEM cycles were identified. Daily GEM variability at the LABS is controlled by the local upslope movement of boundary layer air, whereas seasonal variability is driven by regional air mass origins and transport paths. The amplitude of the GEM concentration inter-annual variability (IAV) is greater than those of diurnal and seasonal variabilities, highlighting the importance of GEM IAV and the associated driving factors. The IAV cycles for the SOI were similar in frequency to the GEM IAV cycles but negatively correlated, revealing the dependency of GEM IAV on large-scale climatology variations (e.g., ENSO). Large-scale atmospheric circulation likely plays an important role in modulating GEM IAV. Furthermore, the relationship between ENSO and GEM is sensitive to extreme events (e.g., 2015–2016 El Niño), resulting in perturbation of the long-term trend and atmospheric Hg cycling. Future climate change will likely increase the number of extreme El Niño events and, hence, could alter atmospheric Hg cycling and influence the effectiveness evaluation of the Minamata Convention on Mercury. Further research on this topic using only the March GEM data is still underway and results will be presented in the ICMGP.

212

## An interhemispheric difference in atmospheric gaseous elemental mercury isotopes suggests an overestimation of oceanic mercury emissions

Zhang H<sup>1</sup><sup>1</sup>Institute of Geochemistry, Chinese Academy of Sciences

Interhemispheric gradient in atmospheric gaseous elemental mercury (GEM) with higher concentrations in the Northern Hemisphere is typically observed in the global atmosphere, the causes of which, however, is not well understood. In this study, a year of continuous observations of atmospheric GEM concentrations and isotopic composition at two coastal sites in the tropical Terengganu, Malaysia showed lower mean (+1sd) concentration ( $1.28 \pm 0.20 \text{ ng m}^{-3}$ ),  $\Delta^{199}\text{Hg}$  ( $-0.23 \pm 0.03\text{‰}$ ), and  $\Delta^{200}\text{Hg}$  ( $-0.07 \pm 0.02\text{‰}$ ) and higher  $\delta^{202}\text{Hg}$  ( $0.43 \pm 0.12\text{‰}$ ) during wet seasons (May to October) than during dry seasons (November to April; mean (+1sd) concentrations,  $\Delta^{199}\text{Hg}$ ,  $\Delta^{200}\text{Hg}$ , and  $\delta^{202}\text{Hg}$  of  $1.77 \pm 0.09 \text{ ng m}^{-3}$ ,  $-0.17 \pm 0.03\text{‰}$ ,  $-0.05 \pm 0.02\text{‰}$ , and  $0.25 \pm 0.11\text{‰}$ , respectively). Backward trajectory analysis suggests that the seasonal variations in GEM concentration and isotopic compositions were mainly caused by the transitions of air masses, which were predominantly from the Southern Hemisphere during wet seasons and from the Northern Hemisphere during dry seasons. Our observations therefore suggest an interhemispheric difference in both GEM concentrations and isotopic compositions. Based on an atmospheric  $\Delta^{200}\text{Hg}$  mass balance model, we estimate that the global oceanic GEM emissions should be less than  $1283 \pm 605 \text{ Mg yr}^{-1}$  (1sd), which is at the low end of the range of previous global modelling results. We conduct a global three-dimensional  $\Delta^{200}\text{Hg}$  GEOS-Chem simulation and find that a global oceanic GEM emission of  $1283 \text{ Mg yr}^{-1}$  could better reproduce the global distributions and interhemispheric gradient of atmospheric GEM  $\Delta^{200}\text{Hg}$  than higher emissions scenarios, indicating current knowledge of oceanic GEM emissions is likely overestimated.

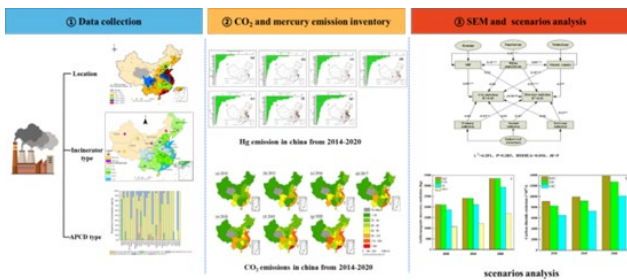
## Temporal and Spatial Analysis of Anthropogenic Mercury and CO<sub>2</sub> Emissions from Municipal Solid Waste Incineration in China: Implications for Mercury and Climate Change Mitigation

Liu L<sup>1</sup>, Guo J<sup>1</sup>, Feng Q<sup>1</sup>, Chen Y<sup>1</sup>

<sup>1</sup>University of Chinese Academy of Sciences

The contribution of municipal solid waste incineration (MSWI) to anthropogenic mercury and CO<sub>2</sub> emissions have become increasingly important over the past decade. This study developed an inventory of anthropogenic mercury emissions and CO<sub>2</sub> emissions during the period of 2014-2020, of MSWI process in China using a bottom-up inventory at the plant level. Overall, national MSWI anthropogenic mercury emissions increased from 2014 to 2020 by province. It was estimated that total 8321.09 kg of anthropogenic mercury emissions from 548 MSWI plants were scattered in 31 provinces of mainland China in 2020. The average intensity of mercury emission in China was 0.06 g-t<sup>-1</sup> in 2020, which was much lower than the pre-2010 level. Furthermore, the increased CO<sub>2</sub> emission generated by MSWI from 2014 to 2020 is 1.97 times. Anthropogenic mercury emissions and CO<sub>2</sub> emissions were concentrated mainly in developed coastal provinces and cities. The general uncertainty of national mercury emissions and CO<sub>2</sub> emissions was estimated to be -123% to 323% and -130% to 335%, respectively. Furthermore, future emissions were predicted from 2030 to 2060 based on different scenarios of the independent and collaborative effects of control proposals, the results indicate that the enhancement of advanced air pollution control technologies and effective management of MSWI represent pivotal factors in realizing future reductions in CO<sub>2</sub> and mercury emissions. The findings will supplement those for mercury and CO<sub>2</sub> emissions, and be useful for relevant policy-making and to improve urban air quality, as well as human health.

### Abstract Graphics



215

## A database for seawater mercury observations

Soerensen A<sup>1</sup>, Bieser J<sup>2</sup>, Dastoor A<sup>3</sup>, He Y<sup>4</sup>, Zhang Y<sup>5</sup>

<sup>1</sup>Department of Environmental Monitoring and Research, Swedish Museum Of Natural History,

<sup>2</sup>Institute of Coastal Research, Helmholtz-Zentrum hereon, <sup>3</sup>Air Quality Research Division, Environment and Climate Change Canada, <sup>4</sup>Applied Research Center, Florida International University,

<sup>5</sup>School of atmospheric sciences

The ocean links atmospheric concentrations with those of the food web. Currently, there is no systematic monitoring of Hg seawater concentrations but an increasing number of cruises analyze for speciated seawater Hg. Synthesizing these data will provide an observational based overview of large-scale spatial Hg variability in the ocean that can be used in the Minamata Effectiveness Evaluation and play an important role for biogeochemical model evaluation. There is therefore a need for the development of a seawater Hg database. We have created a simple offline database, which currently include ~35 datasets from the last two decades containing a mix of coastal and offshore datasets from published papers (that include or exclude the raw data) and published datasets. We would like to discuss the support and format needed to create an open online database where the mercury community can share their speciated seawater Hg data and where data contributors can feel confident that they get the required credit when their data is used.

## Mercury and methylmercury monitoring in the Brazilian water reservoir Billings-Guarapiranga from 2020 to 2023

Barbosa Ferreira G<sup>1</sup>, Soares W<sup>1</sup>, Tominaga M<sup>1</sup>

<sup>1</sup>Cetesb

The Rio Grande Reservoir (RGR) is a crucial component of the Billings-Guarapiranga complex (BGC), the largest water reservoir in São Paulo's Metropolitan Region, Brazil. Monitoring by the 'Companhia Ambiental do Estado de São Paulo' (Cetesb) since 1974 has consistently indicated elevated mercury levels in RGR water, surpassing Brazilian legal limits (0.2 µg/L). This study, conducted from 2019 to 2023, analyzed total mercury (Hg) and methylmercury (meHg) concentrations in water, sediment (CVAFS), and fish (LC-ICP-MS) samples from the BGC. Among 139 water samples analyzed for Hg, almost all concentrations were below the limit of quantification (LQ = 0.02 µg/L), with only three exceptions. However, for the 77 water samples analyzed for meHg, levels frequently exceeded the LQ (0.125ng/L), particularly at two RGR sites: its entrance and the lacustrine zone (up to 2.06 ng/L and 4.69 ng/L, respectively). The latter result surpasses Canadian water quality guideline for the protection of aquatic life (4 ng/L). Sediment analysis of 50 samples for Hg and 25 for meHg showed more elevated concentrations near the reservoir entrance (up to 85.8 µg Hg/kg and 1.9 µg meHg/kg). Sediment profile investigation revealed higher Hg and meHg concentrations at depths of 25 to 30 cm, suggesting non-recent contamination. Fish samples, obtained from the reservoir entrance and near its end, exhibited relatively high Hg and meHg concentrations in both muscle and viscera, reaching up to 775 µg Hg/kg wet weight. However, even the peak Hg concentrations found in sediment and fish remain below international standards for environmental protection – 0.17 mg/kg in sediment (Canada) and 1.0 mg/kg in carnivore fish muscle (European Union). In summary, while two RGR sites exhibit noteworthy Hg and meHg concentrations, the overall contamination appears contained, due to pollution control actions, which led to decreased mercury releases and minimal spread within the reservoir system.

## Combining Hg stable isotopes and sea ice biomarker to provide new insights into the role of sea ice as a source of Hg contamination in Arctic seabirds

Charrier J<sup>1</sup>, Amouroux D<sup>2</sup>, Massé G<sup>3</sup>, Asensio O<sup>2</sup>, Gilchrist H<sup>10</sup>, Guillou G<sup>1</sup>, Grémillet D<sup>4,5</sup>, Hanssen S<sup>6</sup>, Klein V<sup>7</sup>, Lacoue-Labarthe T<sup>1</sup>, Love O<sup>8</sup>, Moe B<sup>6</sup>, Dupuis-Smith R<sup>8</sup>, Tertitski G<sup>9</sup>, Tessier E<sup>2</sup>, Fort J<sup>1</sup>  
<sup>1</sup>Littoral Environnement et Sociétés (LIENSs), UMR 7266 CNRS - La Rochelle Université, <sup>2</sup>Université de Pau et des Pays de l'Adour, E2S UPPA - CNRS, Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et la Matériaux (IPREM), <sup>3</sup>Station Marine de Concarneau, CNRS, UMR7159 LOCEAN, <sup>4</sup>Centre d'Ecologie Fonctionnelle & Evolutive (CEFE), Université de Montpellier, CNRS, EPHE, IRD, <sup>5</sup>FitzPatrick Institute of African Ornithology, Department of Biological Sciences, University of Cape Town, <sup>6</sup>Norwegian Institute for Nature Research, <sup>7</sup>LOCEAN, UMR7159, CNRS, UPMC, IRD, MNHN, <sup>8</sup>University of Windsor, <sup>9</sup>Institute of Geography of the Russian Academy of Sciences, <sup>10</sup>Environment and Climate Change Canada (ECCC)

Mercury (Hg) contamination in Arctic ecosystems has wide impacts on wildlife, with amplified effects on top-predators such as seabirds, exhibiting highest concentrations due to Hg biomagnification along the trophic chain. The cycling circulation of Hg in the environment is still an issue despite international regulations, raising the question of the source of contamination for Arctic species, notably through melting sea ice influenced by global changes. Hg stable isotopes have been recently used to provide key evidence about the complex biogeochemical pathways that Hg undergoes before reaching the food web. But isotopic information alone is insufficient to clearly demonstrate the role of sea ice on Hg bioaccumulation and trophic transfer. Highly branched isoprenoids (HBIs) are biomarker tools which allow to evaluate the importance of sea ice-associated preys into the diet of predator species. We therefore combined for the first time the use of Hg stable isotopes and HBIs to provide new insights into the role of sea ice as a source of Hg in seabirds. We analysed blood samples collected on common eiders (*Somateria mollissima*) in four Arctic regions influenced by contrasting sea ice conditions. Our first results show that birds' diet partially explains their Hg contamination, which also seems influenced by the presence of sea ice. Sources and levels of Hg contamination also depend on whether Hg inputs were terrestrial or oceanic, in association with sea ice. These results underscore the importance of integrating diverse analytical tools to advance fundamental knowledge and support conservation policies in a global change context.

## Stability of common preconcentration methods for gaseous oxidized mercury in air

Vijayakumaran Nair S<sup>1,2</sup>, Gačnik J<sup>1,2</sup>, Živković I<sup>1,2</sup>, Andron T<sup>1,2</sup>, Ali S<sup>1,2</sup>, Horvat M<sup>1,2</sup>

<sup>1</sup>Department of Environmental Sciences, Jožef Stefan Institute, <sup>2</sup>Jožef Stefan International Postgraduate School

Due to low atmospheric concentrations, the sampling of gaseous oxidized mercury (GOM, HgII) requires a preconcentration step. Denuders and cation exchange membranes (CEM) are widely used as preconcentration methods in atmospheric mercury (Hg) speciation studies. Sampling losses during the pre-concentration step could result in biases, leading to an underestimation of HgII. In this study, we evaluated the performance of denuders and CEM for HgII sampling to evaluate the biases arising from sampling losses. Laboratory experiments were performed at trace level HgII concentrations using highly specific <sup>197</sup>Hg radiotracer, and the production of HgII was based on nonthermal plasma oxidation of Hg<sup>0</sup> with reactant gases O<sub>2</sub>, Cl<sub>2</sub>, and Br<sub>2</sub>. Exposing denuders loaded with known amount of HgII to ambient air for 2 hours (at 1 L min<sup>-1</sup>) resulted in higher losses. Meanwhile, CEM loaded with known concentrations of HgII (HgO, HgCl<sub>2</sub>, and HgBr<sub>2</sub>) were exposed to ambient air flow at 1 L min<sup>-1</sup> for 72 hours; with losses captured on a gold cartridge and measured every 24 hours throughout this period. To obtain mass balance, filter packs were subjected to acid washing, and CEM were digested overnight in BrCl solution. The residual content of HgII remaining on CEM post-digestion was also quantified. Results showed a varied distribution of HgII in the digestate, with a substantial fraction of HgII retained on the inner Teflon parts of the CEM cartridge. HgII losses from CEM were quantified to be higher for HgO when compared to HgCl<sub>2</sub> (HgBr<sub>2</sub> under investigation). The BrCl digestion of HgII on CEM was not fully quantitative, resulting in retention of considerable amounts of HgII content on CEM as leftover. Both sampling losses and the digestion procedure contribute to biased HgII measurements by the CEM method. Further work is needed to characterize these losses in real-time atmospheric Hg sampling.

## Pre-concentration method for Hg isotope analysis in low-concentration foliar samples: Optimization and validation

Ali S<sup>1,2</sup>, Božič D<sup>1,2</sup>, Vijayakumaran Nair S<sup>1,2</sup>, Živković I<sup>1,2</sup>, Gačnik J<sup>1,2</sup>, Andron T<sup>1,2</sup>, Jagodic Hudobivnik M<sup>1</sup>, Kocman D<sup>1</sup>, Horvat M<sup>1,2</sup>

<sup>1</sup>Jožef Stefan Institute, <sup>2</sup>Jožef Stefan International Postgraduate School

The analysis of Hg isotopes in foliage samples with low Hg concentration presents a challenge and is constrained by the sensitivity of the analytical method. Currently, available Hg pre-concentration methods involve complex sample processing steps and limit higher sample mass loading. We present an optimized Hg pre-concentration method that involves a pre-digestion step followed by microwave-assisted sample digestion. Foliar samples along with CRMs digested in the microwave-digestion system were transferred to a purging unit and Hg was reduced with SnCl<sub>2</sub>. The solution was purged for 30 min with Hg-free N<sub>2</sub> and produced Hg(0) was captured in a trapping solution of 2.25 mL concentrated inverse aqua regia (3:1 HNO<sub>3</sub>:HCl, v/v). The trapping solution was diluted to 15 mL corresponding to 15% (v/v) final acid concentration to enable the analysis on MC-ICP-MS. The robustness of the preconcentration efficiency was evaluated through experiments performed with <sup>197</sup>Hg radiotracer, CRMs, and foliar samples. Tests with pure reagents and matrix of foliar samples spiked with <sup>197</sup>Hg radiotracer resulted in a mean recovery of 99 ± 1.7% and 100 ± 3.0% respectively. Foliar samples having Hg concentrations between 1-2 ng g<sup>-1</sup> were pre-concentrated by combining several aliquots of samples digested in multiple vessels, and yielded an average pre-concentration recovery of 99 ± 6.0%. Recoveries of NIST SRM 1575a (pine needle) and reagents spiked with NIST SRM 3133 were on average 95 ± 4.7% and 95 ± 2.5%, respectively. Hg isotope analysis on MC-ICP-MS revealed low δ<sup>202</sup>Hg fractionation with no significant mass-independent fractionation thus, indicating the robustness of the Hg pre-concentration method. The proposed method offers a simple setup suitable for Hg pre-concentration in complex biological matrices.

## Investigating mercury dynamics during litter decomposition: Insights from a mesocosm study

Ali S<sup>1,2</sup>, Živković I<sup>1,2</sup>, Vijayakumaran Nair S<sup>1,2</sup>, Gačnik J<sup>1</sup>, Kocman D<sup>1</sup>, Horvat M<sup>1,2</sup>

<sup>1</sup>Jožef Stefan Institute, <sup>2</sup>Jožef Stefan International Postgraduate School

Several processes related to the fate of mercury (Hg) during the process of litterfall degradation and its complex interaction within forest soil remain understudied. In particular, the understanding of temporal variations in Hg fractions during the process of litterfall degradation and their association with soil organic matter needs further research. Though, litterfall Hg composition varies during the entire process of litterfall decomposition, factors such as soil carbon (C) and nitrogen (N) potentially control Hg retention in forest soil, in addition to the influence of seasonal meteorological conditions. Additionally, the impact of soil properties of distinct forest sites on the retention and mobility of Hg warrants further investigation under controlled environmental conditions.

In this work, the Hg dynamics during litterfall degradation was studied under mesocosm setup representing four forest sites having distinct Hg presence. The aim was to study the changes in soil and litterfall Hg composition driven by the process of litterfall degradation. Additionally, the study of controls including soil properties, organic matter presence, and seasonal meteorological conditions on Hg fractionation during litterfall degradation are investigated. Freshly fallen litterfall along with underneath soil samples from the Oi (uppermost) layer was collected and placed in individual mesocosms. Litterfall degradation was studied for seven months. For each mesocosm, composite samples of litterfall and soil samples were sampled on a bimonthly basis for the analysis of Hg fractions and associated organic matter content.

The implications of this work on improving our understanding of the changes and controls on Hg dynamics of the litterfall-soil interface will be presented in this work. The results will contribute to improving modeling approaches for predicting Hg mobility, bioavailability, and potential risks for human health and the environment.

## Thermal desorption: an experimental technique to assess liquid Hg in different soil matrices

Meloni F<sup>1,2,4</sup>, Higuera P<sup>3</sup>, Cabassi J<sup>2</sup>, Nisi B<sup>2</sup>, Vaselli O<sup>1,2,4</sup>, Montegrossi G<sup>2,4</sup>

<sup>1</sup>University Of Florence, <sup>2</sup>CNR-IGG Institute of Geosciences and Earth Resources, <sup>3</sup>University of Castilla La Mancha y Almadén, <sup>4</sup>INSTM-National Interuniversity Consortium of Materials Science and Technology

Mercury speciation in soils is challenging, mostly because they can be characterized by different (carbonate-, silicate, or organic-rich) matrices. The pedological cover may host mercury in different forms (Hg(0), Hg(I), and Hg(II)) depending on different factors such as pH, redox potential, and organic matter contents. Moreover, the presence of clay minerals, iron, sulfur, and phosphorus, can impact the distribution of Hg in solid matrices. Determining whether Hg(0) (gaseous elemental Hg and/or liquid Hg) is significantly present in soil has a critical role during remediation operations of mercury-contaminated soils located in or close to mining and industrial areas. Numerous analytical techniques, such as thermal desorption and sequential or selective extractions, have been developed to identify distinct mercury species in solid matrices over time. However, thermal desorption appears to be the most suitable, and less costly, method for identifying and measuring the speciated Hg phases at low concentrations. The amount of Hg(0) in solid geological and anthropic matrices was also measured by comparing the Hg concentration between heated (usually at 80 °C) and non-heated samples. In this work, experiments on different soil matrices were carried out by coupling two Lumex instrumentations for Hg speciation via thermal desorption: RA-915M and Pyro-915+. During the experimental runs, significant differences were recorded in terms of breakdown temperatures of the Hg compounds when carbonate and silicate soils were analyzed. Similar variations were also observed when the soil matrices were doped with liquid Hg since the latter oxidises as a function of the soil matrix and the reaction time. In fact, Hg(0) tends to form Hg(I) and then Hg(II), the latter being adsorbed by organic matter and/or Fe-Mn-Al oxides. It was computed that the oxidation of half of the initial value of Hg(0) (%) occurs in about 42 days.

## Electrochemical Alloy Formation for Mercury Decontamination of Aqueous Solutions

Roth V<sup>1</sup>, Järlebark J<sup>1</sup>, Wickman B<sup>1</sup>

<sup>1</sup>Chalmers University Of Technology

Mercury pollution in water presents a critical threat to both environmental and public health, necessitating the development of efficient and effective decontamination methods. Current methods for mercury removal from aqueous solutions, such as water, waste streams, and acids, while in some cases functional, are far from optimal. Notably, as of today, there is no viable method for aqueous solutions at high acidic conditions, like concentrated acids [1]. In this presentation we will show results from our recent studies on a novel method based on electrochemical alloy formation for mercury removal from aqueous solutions. The method involves electrochemical reduction of mercury ions in solution, followed by a formation of a stable amalgam on an electrode surface such as platinum [2]. Our results demonstrate the ability of this method to remove over 99% of mercury from a range of different aqueous solutions, achieving concentrations significantly below recommended limits for mercury in drinking water [3]. Further, we show that the method's performance is consistent across a wide pH range and remains effective in the presence of various other compounds and impurities. The process does not require consumables or additional chemicals and is reversible, allowing for safe recovery of mercury and the regeneration and reuse of the platinum electrodes. By using this method, we have successfully demonstrated, for the first time, the removal of mercury from contaminated concentrated sulfuric acid from a zinc smelting plant [4]. More than 98% of mercury was removed from the acid, at both laboratory scale (50 mL) and in a medium scaled demonstrator (20 L), resulting in mercury content that falls below established commercial and regulated limits. This method demonstrates high effectiveness in removing mercury from various aqueous solutions and shows potential for widespread decontamination applications, presenting a versatile and promising method for mercury remediation on a global scale.

223

## Tricks of the Trade: Building Instrumentation for Atmospheric Mercury

O'Neil T<sup>1</sup>, Lyman S<sup>1,2</sup>, Zager K<sup>1</sup>

<sup>1</sup>Bingham Research Center, Utah State University, <sup>2</sup>Department of Chemistry and Biochemistry, Utah State University

Most mercury pollution is emitted to the atmosphere where atmospheric transport and chemistry determine the location and timing of deposition into terrestrial and aquatic systems. Oxidized mercury compounds are especially important as they are quick to deposit into ecosystems, but they are uniquely challenging to sample and analyze. They exist in the ppq range and are semi volatile, chemically labile and are retained by every surface. Also, when they contact surfaces, they tend to reduce to elemental mercury and re-volatilize back to the atmosphere.

For some time, we have been investigating and developing methods to identify and quantify atmospheric oxidized mercury compounds and calibration methods because commercial instrumentation is known to have a strong low bias due to these unique characteristics. This presentation will discuss several key elements of oxidized mercury instrumentation that have proven successful in our laboratory.

First, all tested materials and coatings retain some oxidized mercury and result in some reduction to elemental form. Heated, Sulfinert-coated (a deactivated fused silica) stainless steel appears to perform best, but it still requires 1-2 hours for mercury compounds to equilibrate with tubing walls. Second, system temperatures between 1200 and 1800C appear to best balance the competing needs to keep mercury compounds in the gas phase while avoiding thermal decomposition. Third, short tubing lengths with high pass-through rates, and carrier gas choice improve mercury compound recovery. Fourth, instrument analytics (real time tracking and recording of system components) is essential. Fifth, keeping systems similar in design is important for comparability, as slight differences often precipitate substantial changes in Hg transmission and transformation.

## Particle-bound mercury dynamics in the Gulf of Maine

Taylor V<sup>1</sup>, Mason R, Janssen S, Tate M, Armstrong G, Smith S, Inman H

<sup>1</sup>Dartmouth College

The Gulf of Maine is an important ecosystem for understanding coastal mercury dynamics. The productive waters of the Gulf support the largest coastal fishery in the U.S. and Canada, and are the mixing site of cold, Labrador current waters, and warm Atlantic slope waters, and also receive substantial inputs of freshwater from rivers along the eastern U.S. coast. Over the past 30 years, increasing levels of riverine organic matter have been observed in the Gulf, attributed to increases in watershed land disturbance and storm frequency and intensity. Modeling of mercury inputs to the Gulf suggests marine sources are dominant, although increases in terrestrially-sourced mercury are substantial and likely to increase with higher riverine loading. To date, measurements of mercury in the water column of this system are scant. In this study, we collected large samples of marine particles using high volume pumps at multiple stations and depths across the Gulf of Maine, and from the estuary of the Penobscot River, a major tributary. Samples were collected from a research vessel on four cruises over the course of a year, to capture contrasting conditions of river runoff and plankton bloom density. Particles were analyzed for mercury concentrations and mercury isotope ratios, which can broadly distinguish watershed-derived mercury from atmospheric and marine sourced mercury, as well as mercury from point sources of contamination. Ancillary measures of particle character (major elements, POC) and source (<sup>7</sup>Be, <sup>210</sup>Pb, <sup>234</sup>Th) are also taken to inform particle origin. Together, these measures will inform the sources and cycling of mercury in a coastal ecosystem under climate change-related increases in river discharge.

225

## Mercury bioaccumulation in zooplankton and fish from the deep and shallow basins of Lake Champlain

Taylor V<sup>1</sup>, Chen C, Schroth A, Stepenuck K

<sup>1</sup>Dartmouth College

Lake Champlain is an important freshwater ecosystem bordered by Vermont, New York, and Quebec, and supports a large population of recreational and subsistence anglers. It is also a sensitive ecosystem to mercury bioaccumulation, where concentrations of mercury (Hg) in game fish frequently exceed the EPA criterion calculated to protect human health. The lake consists of seven adjoining basins having different depths and trophic statuses, which influence methylmercury bioaccumulation at the base of the food web. Fish Hg surveys have been conducted on Lake Champlain since the early 1980's, with the most recent in 2022-23, and have assembled a valuable record of Hg concentrations in five commonly caught fish species. In the past decade, regional atmospheric inputs of Hg have decreased based on data from the Mercury Deposition Network site in Underhill, VT. However, between 2011 and 2017, fish Hg levels increased substantially (50% in yellow perch) across four of the five species monitored, but Hg concentrations in 2022 have returned to levels found in 2011. The increase in Hg concentrations in 2017 was largely driven by fish in the three deep, main basins of the lake, whereas fish Hg in the four shallower basins did not change significantly. Examination of mercury in the water column, seston and zooplankton found up to 3 times higher concentrations of methylmercury in zooplankton from the hypolimnia of the deep lake basins relative to concentrations in the epilimnia and in the shallow basins. Differences in zooplankton taxonomy between the surface and bottom waters are thought to be the primary drivers of this vertical trend in Hg. This novel finding of elevated Hg in zooplankton from deep waters is important to understanding sources of Hg to cold deep waters of large lakes, which are inhabited by several of the most widely consumed fish species.

## Mercury emissions from Icelandic volcanism

Edwards B<sup>1,2</sup>, Outridge P<sup>1,2</sup>, Wang F<sup>1</sup>

<sup>1</sup>University of Manitoba, <sup>2</sup>Geological Survey of Canada, Natural Resources Canada

Volcanism is a natural source of mercury to surface environments, but its contributions to the global mercury budget are poorly constrained. Of major uncertainties are mercury emissions from closed-conduit geothermal systems and effusive eruptions. Here we report the results of four field campaigns from 2019 to 2022 on the highly active volcanic island country of Iceland. During the 2021 and 2022 effusive eruptions of the Fagradalsfjall volcanic system, we measured mercury in the volcanic plume by drone directly above the active vent as well as at more distant downwind locations. Based on coincident mercury and sulfur dioxide measurements, we estimated a relatively low time-averaged mercury flux of  $84 \pm 62$  kg/yr for these eruptions. To assess the role of continuous geothermal degassing in Iceland's natural mercury emissions, we measured soil gaseous elemental mercury (GEM) concentrations at six high-temperature geothermal fields using an adapted gradient method with a Lumex mercury analyzer. The results suggest similarly low GEM emissions to the atmosphere, with an estimated Icelandic geothermal flux of 1.8 kg/yr and a total Icelandic flux (including non-geothermal areas) of  $\sim 18$  kg/yr, comparable to the country's total anthropogenic emissions ( $\sim 25$  kg/yr). Despite the minor geothermal flux, soil gas GEM concentrations at 10 cm depth were often hundreds and in some cases thousands of times higher than surface air concentrations, and geothermal soils showed major enrichments in mercury, similar to soils heavily contaminated by anthropogenic activity. This work shows that Icelandic geothermal activity can generate extreme gas and soil mercury enrichment in the local environment, but its contribution to global mercury cycling appears to be minor. Additional background measurements of air, soil and water bodies around the country further suggest that Iceland is a relatively low-mercury environment.

## Migratory Birds Methylmercury Exposure in Eastern China :

### Risk and Challenge

Wang Z<sup>1</sup>, Zhang X<sup>1</sup>, Liu X<sup>1</sup>

<sup>1</sup>Research Center For Eco-environmental Sciences, Chinese Academy Of Sciences

Mercury (Hg), especially methylmercury (MeHg), which is highly neurotoxic, is a global pollutant that can affect human and wildlife health because of its bioaccumulation and biomagnification in food webs. Birds, as top predators with wide distribution and large populations, have been great concerned in the world. Elevated MeHg in birds negatively affects and can cause oxidative damage to organs, change the foraging and reproductive behavior, and damage the ability of migrate and navigate. East Asia has been considered a mercury pollution hotspot, but little information about bird mercury exposure is available in this area, especially in Eastern China, and thus significant knowledge gaps of ecological risks of mercury exposure on birds exist in this region. In our investigations of Eastern China, MeHg concentrations in breast feathers and habitat (sediments, plants, and aquatic organisms) of wintering birds (n=434 from 43 species 9 orders) in Poyang Lake and of breeding bird (n=200 from 15 species 4 orders) in Zhalong National Nature Reserve were obtained. In general, MeHg concentrations in breast feathers varied greatly by species, foraging guilds and taxonomic orders, with the highest concentration in great egret and the lowest in swan goose. Comparing the worldwide, high MeHg concentrations in feathers of Ardeidae from Pelecaniformes were found in Eastern China. Based on our dataset, the optimization of assessment approaches and revealing risk of migration bird was performed in this study. Carnivorous birds from Pelecaniformes had the highest risk levels with 11.1% moderate risk (1.0~3.0  $\mu\text{g g}^{-1}$  ww), 1.1% high risk (3.0~4.0  $\mu\text{g g}^{-1}$  ww) and 1.7% severe risk (> 4.0  $\mu\text{g g}^{-1}$  ww). Considering the large-scale ecological engineering and restoration in China, the big challenge of Mercury exposure risk for the migration bird is worthy of great attention in the future.

## Development of a novel graphene-based passive air sampler to bridge gaps in atmospheric mercury data in South Africa

Kempkes G<sup>1</sup>

<sup>1</sup>University Of Pretoria, <sup>2</sup>The South African Weather Service

South Africa has slowly begun to increase its monitoring efforts with respect to mercury in the environment, but there are challenges associated with achieving compliance with the Minamata Convention. Available monitoring efforts are comprised of both active (with Lumex®/ Tekran®) and passive sampling (with MerPAS®) from air. Although a long-standing temporal active data set at the Global Atmosphere Watch Station (GAW) at Cape Point is available, temporally resolved measurements for the other regions of the country are needed, as the Cape Point Hg data set is not representative of the current ambient concentrations found throughout the country. This has led to a reliance on inventory estimations which are becoming progressively outdated.

Herein, a passive sampling approach was developed, making use of a novel graphene foam which was synthesized to sample ambient TGM mercury. The sorbent was chemically doped using different techniques to provide sulfur-derivatized foams. Their performance in sampling Hg was tested at both an impacted and a less impacted site after extensive material characterization. Surface chemistry effects and sorbent surface area were found to affect the Hg uptake rates upon deployment. The accuracy of this novel passive air sampler (PAS) was compared to that of the commercially available MerPAS® after the analysis method had been optimized and validated for the sorbent and performed well at the ng.kg<sup>-1</sup> Hg level with ~6 %RSD found for a selected standard reference material (SRM). Although mercury concentrations calculated for deployed samplers were somewhat underestimated, when considering the lack of Hg monitoring across South Africa, the use of this sampler may provide a base estimate of concentrations of Hg in air. These can then be corrected when the sampling rate and other parameters regarding mercury capture by this graphene foam passive sampler are further optimized.

## Mercury dynamics in heavily polluted Idrijca and Soča Rivers

Kotnik J, Živković I, Begu E, Klemenčič P, Waqar Ali S, Kerševan T, Horvat M

<sup>1</sup>Jozef Stefan Institute

Historical Hg mining and smelting activities in Idrija (W Slovenia) left severe Hg contamination in the Idrijca and Soča rivers. Long term study includes seasonal sampling during low and high-water flow regimes, measuring Hg fractionation, speciation, stable isotopes, and various water quality parameters, including dissolved organic carbon (DOC), particulate organic carbon (POC), anions, cations, and other water quality parameters. One aspect of the study involves the examination of bacterial diversity across different size fractions and its correlation with mercury content. Genetic material isolated from each sample (fraction) was sequenced to assess the diversity and abundance of bacteria. This microbial perspective contributes to a more holistic understanding of the ecological impacts of mercury contamination in aquatic environments.

Measurement reveals huge differences during low or high-water regimes and different seasons showing different mercury transport and cycling in these rivers depending on hydrological and seasonal conditions. Microbiological analyses and analyses of Hg on suspended particles of different sizes show different concentrations and distribution of microorganisms on different sized particles as well as dependence of water regimes and seasons.

More than 30 years after the end of Hg production in Idrija, the concentrations of various Hg species in the Idrijca and Soča river water remains extremely high and indicates that the natural recovery of rivers will take very long time.

230

## Endogenous methylmercury production: implications for biomagnification in pelagic food webs

Motue Ngou J<sup>1</sup>

<sup>1</sup>Stockholm University

Mercury (Hg) is a contaminant of global concern due to its bioaccumulation capacity. The bioavailability of Hg is increased dramatically by converting inorganic Hg to methylmercury (MeHg) by anaerobic microbes carrying the *hgcAB* gene pair. Today, Hg and MeHg concentrations in the Baltic fish exceed safe levels; moreover, no direct links are seen between the inputs and biota concentrations. The complexity of MeHg dynamics – influenced by various factors, including microbial processes in sediments and, potentially, endogenous methylation within animals – can lead to a lack of straightforward correlations between mercury inputs and biota concentrations.

We hypothesise that Hg-methylating bacteria in the microbiome of primary consumers is an ecologically plausible source of their MeHg body burden. If true, the variability in the Hg-methylating gut bacteria in lower consumers can explain (at least partly) the variability in MeHg load in consumers higher in the food web. Preliminary results show that the *hgcA* gene is present in the gut microbiome of pelagic copepods and benthic amphipods in the Baltic Sea, with significant variability in the gene abundance across the species. However, the functionality of these genes and the extent of MeHg production in the gut remain uncertain.

The aim of this study is to evaluate endogenous MeHg production by microbiomes of these primary consumers using a combination of (1) quantitative PCR and RNAseq analyses to identify the *hgcAB* genes and their carriers in the animal guts, (2) experiments with isotopically enriched Hg to measure its methylation in the consumers, and (3) spatio-temporal modelling to link endogenous Hg methylation in prey to Hg/MeHg concentrations in the Baltic herring. If endogenous methylation is proven to be an additional MeHg source in primary consumers, this would reshape our global understanding of MeHg dynamics and bioaccumulation in food webs.

## Mercury Pollution and Health Risks in Chinese Fish and Rice

Zhang H, Feng X<sup>1</sup>

<sup>1</sup>Institute Of Geochemistry, Chinese Academy Of Sciences

China is the world's largest producer, consumer, and emitter of mercury, as well as the world's largest commercial fish producer and consumer. Although mercury pollution in fish in China is currently receiving much attention worldwide, its status remains largely unknown. Here, it is found that, opposite to the increasing emission and documented mercury contamination events, mercury levels in fish have gradually decreased in China over the past 30 years. The results were in sharp contrast to those found in North America and Europe. The mercury concentrations in fish were significantly anticorrelated with the fish catch and fish aquaculture and were inverse to trophic levels. Overfishing and the short lifecycle of aquaculture fish, both reducing the trophic level and the duration of mercury accumulation, were the most likely causes leading to the decline of mercury concentrations found in fish in China. Similar to fish, China is also the largest rice producer and consumer in the world. The main human exposure to Me-Hg via food consumption is not restricted to fish, but in some cases in mining areas of China to frequent rice meals. Although the mercury content in the main rice producing areas is generally low, 90% of inland residents in China are exposed to methyl-Hg through rice, which because rice is the most toxic methylmercury enriched plant. In conclusion, fish and rice samples shown very low Hg concentrations in China. Thus, the overall exposure level of methyl-Hg among residents in China is relatively low, and residents in coastal and inland areas (mining areas) may have a higher risk.

## Hg stable isotope composition and compounds in the different compartments of seabird eggs: the case of three species breeding in East Greenland

Charrier J<sup>1</sup>, Fort J<sup>1</sup>, Tessier E<sup>2</sup>, Asensio O<sup>2</sup>, Guillou G<sup>1</sup>, Grémillet D<sup>3,4</sup>, Gentès S<sup>1</sup>, Marsaudon V<sup>3</sup>, Amouroux D<sup>2</sup>

<sup>1</sup>Littoral Environnement et Sociétés (LIENSs), UMR 7266 CNRS - La Rochelle Université, <sup>2</sup>Université de Pau et des Pays de l'Adour, E2S UPPA - CNRS, Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et la Matériaux (IPREM), <sup>3</sup>Centre d'Ecologie Fonctionnelle & Evolutive (CEFE), Université de Montpellier, CNRS, EPHE, IRD, <sup>4</sup>FitzPatrick Institute of African Ornithology, Department of Biological Sciences, University of Cape Town

Mercury (Hg) is a toxic contaminant of global concern. The impact on Arctic ecosystems, particularly in seabirds, is critical due to large-scale Hg transport towards polar regions and its biomagnification in marine trophic systems. While the adverse effects on reproductive processes in aquatic birds are well-documented, the understanding of physico-chemical mechanisms occurring during Hg maternal transfer is limited, which is unfortunate as these mechanisms could condition Hg reproductive toxicity. The combination of Hg stable isotope composition and Hg compounds (inorganic Hg and methylmercury MeHg) in the different egg compartments (yolk, albumen, membrane, and shell) before embryo development could provide information on (i) Hg maternal transfer mechanisms, (ii) influence of egg biochemical composition on Hg organotropism and (iii) the source of Hg contamination. We measured Hg stable isotopes and Hg compounds in the different egg compartments of three seabird species (common eider, black-legged kittiwake, little auk) breeding in East Greenland. For all species, albumen and membrane, the most protein-rich compartments, were the most contaminated. In these two compartments, more than 82% of this contamination was in the form of MeHg. According to our results, mass-dependent fractionation (MDF) values ( $\delta^{202}\text{Hg}$ ) were higher in albumen and membrane. Protein-rich egg compartments received most of the Hg maternal transfer probably due to affinity of Hg for their biochemical composition. Among the different egg compartments/individuals/species, odd-isotopes mass-independent fractionation (MIF) values were identical. We conclude that Hg measured in the three species originates from the same source and undergone similar photodemethylation pathways. Low quantities of MeHg were photodemethylated, suggesting an influence of sea ice cover.

## Mercury dynamics in thermokarst lakes in continuous permafrost areas: Zackenberg Valley, Northeast Greenland

Canário J<sup>1</sup>, Martins B<sup>1,2,3</sup>, Folhas Ferreira D<sup>1,4</sup>, Hintelmann H<sup>2</sup>, Pilote M<sup>3</sup>, Couture R<sup>4</sup>, R. Christensen T<sup>5,6</sup>

<sup>1</sup>Centro De Química Estrutural - Instituto Superior Técnico - Universidade De Lisboa, <sup>2</sup>Water Quality Centre, Trent University, <sup>3</sup>Environment and Climate Change Canada, Water Science and Technology Directorate Aquatic Contaminant Research Division, <sup>4</sup>Department of Chemistry, Université Laval, <sup>5</sup>Department of Ecoscience, Aarhus University, <sup>6</sup>University of Oulu

Recently special attention was given to the study of contaminant processes in permafrost. This was the case of Hg where studies have been focused on other Arctic environmental compartments rather than in permafrost.

Mercury studies in Greenland are scarce compared to other Arctic regions, and in permafrost are practically nonexistent. Zackenberg Valley, located in the high Arctic, is an area of stable continuous permafrost. Recently, signs of permafrost degradation are being observed with thermokarst features appearing in the landscape. The area is well documented in terms of greenhouse gas fluxes but information on Hg biogeochemistry is absent.

In July/August 2023, fieldwork was conducted in the Zackenberg area and two thermokarst lakes (ZAC1 and ZAC2) were studied. Water profiles and sediment cores were sampled. Total Hg and methylmercury (MMHg) concentrations were measured and Hg methylation and MMHg demethylation rates were determined using Hg stable isotopes techniques. A benthic flux chamber (BFC) was deployed and Hg and MMHg benthic fluxes were also determined.

Results showed that, in spite of lower concentrations that are typical for such environments (water: Hg up to 5.9 ng/L; MMHg up to 0.37 ng/L - sediments: Hg up to 32 ng/g; MMHg up to 2.1 ng/g), the proportions of MMHg to total Hg were higher than expected, particularly in sediments and in the most recent ZAC2 lake (water: up to 13%; sediment: 6.6%). These results were confirmed by the high methylation rates observed, particularly in sediments (up to 11% in 6 hours). Incubations with methylation enhancers or inhibitors suggest that sulfate reducing bacteria are the main methylators. Data from the BFC not only showed solute fluxes in the sediment/water interface, but also other biogeochemical processes in the water column. These preliminary results point to a higher Hg dynamic in thermokarst lakes even in recently thawed systems

## Mercury speciation in cement plant emissions and impact on ambient air quality and Hg distribution

Kotnik J<sup>1</sup>, Živković I<sup>1</sup>, Gačnik J<sup>1</sup>, Vijayakumaran Nair S<sup>1</sup>, Ljubič Mlakar T<sup>2</sup>, Horvat M<sup>1</sup>

<sup>1</sup>Jozef Stefan Institute, <sup>2</sup>Salonit Anhovo

Samples from the stack gas were collected from the cement clinker production facility using different types of commercial sorbent traps for the determination of total Hg, mercury speciation, and stable isotope ratio analysis. The results of analyses using sorbent traps were in good agreement with the results measured by continuous emission monitor. To evaluate the mercury removal efficiency of the flue-gas three modes of operation were employed during the sampling, depending on the number of mills operating. The results showed a clear trend in concentrations of different mercury fractions that depend on the plant operation mode. Total Hg and oxidized Hg were the lowest during two-mills operation while greatest during no-mill operation of the plant. The inverse trend was observed for the elemental mercury.

The influence of Hg emissions from the cement plant on Hg levels was measured in the ambient air, kilometer downwind from the plant chimney. Atmospheric Hg speciation, coupled with plant emissions and wind data, has revealed that the total gaseous mercury emitted from the cement plant is clearly related to all Hg species measured. Wind blowing from the north-eastern quadrant (mostly NE, ENE) is responsible for the elevated Hg levels, where gaseous oxidized mercury levels are highly linked to the cement plant emissions. However, elevated levels of Hg species in the absence of north-eastern winds indicate potential inputs from other unknown local sources as well as inputs from regional and global transport mechanisms.

Within study, method validation was completed for sorbent traps in line with the analytical test requirements for CEN TS 17286 and the US EPA 30B sorbent trap standard methods.

## Minamata Convention Guidance on best available techniques and best environmental practices to control mercury releases

Toda E<sup>1</sup>, H.Dlamini B<sup>2</sup>, Efros N<sup>3</sup>

<sup>1</sup>Secretariat of the Minamata Convention, <sup>2</sup>Eswatini Environment Authority, <sup>3</sup>Public Association Experts Association Pro-Mediu

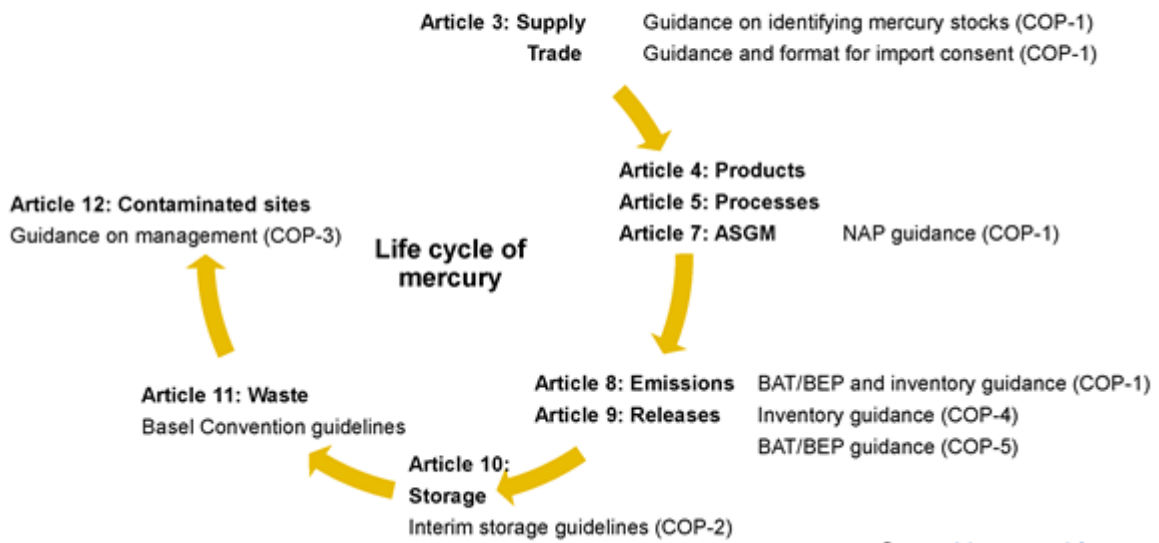
The Minamata Convention on Mercury provides for the use of best available techniques (BAT) and best environmental practices (BEP) to control mercury emission to air and mercury release to land and water. The Convention provides that the Conference of the Parties (COP) is to adopt guidance on BAT/BEP.

Article 8 of the Minamata Convention addresses five types of point sources of mercury emissions such as coal-fired power plants, which add up to about half of total anthropogenic mercury emission. As required by the Convention text, COP-1 in 2017 adopted BAT/BEP guidance describing technologies and practices to reduce mercury emissions from five source categories.

Article 9 of the Convention addresses mercury releases to land and water from relevant point sources to be identified by Parties and not covered in other provisions of the Convention. In the periodic national reports in 2021, 38% of the Parties responded that there were relevant point sources of releases in their territory. COP-2 in 2018 established a group of technical experts to first work on draft a list of potentially relevant point sources and draft guidance on preparing inventories of mercury releases for the consideration at COP-4. The expert group started working on BAT/BEP guidance after COP-4 adopted the guidance on inventories in 2022. The group reviewed BAT documents and other information submitted by Parties and stakeholders. OECD supported the work of the expert group with a cross-country comparison study of BAT. Based on the report of the expert group, COP-5 in 2023 adopted guidance describing considerations in selecting BAT/BEP and specific techniques to control mercury releases, as the last piece of technical documents for COP to adopt. A technical reference document to supplement the guidance was also submitted to COP. Parties are to exchange information on the use of guidance through the Convention website.

### Abstract Graphics

## Mercury life cycle – control measures and guidance



## Establishment of mercury waste thresholds under the Minamata Convention

Toda E<sup>1</sup>, Vasiliu-Isac G<sup>2</sup>, Olabanji O<sup>3</sup>, Gössnitzer A<sup>4</sup>

<sup>1</sup>Secretariat of the Minamata Convention, <sup>2</sup>Ministry of Environment, Romania, <sup>3</sup>Federal Ministry of Environment, Nigeria, <sup>4</sup>Federal Office for the Environment, Switzerland

Article 11 of the Minamata Convention requires Parties to manage mercury waste in an environmentally sound manner. Mercury waste is defined as waste consisting of, containing or contaminated with mercury or mercury compounds in a quantity above the relevant thresholds defined by the Conference of the Parties (COP). The COP has been considering these thresholds since its first meeting (COP-1) in 2017, supported by a group of technical experts nominated by Parties. COP-3 in 2019 agreed that no thresholds needed to be established for waste consisting of mercury (category A) and containing mercury (category B), presented a list of waste that should be regarded as category A mercury waste, and established that end-of-life mercury-added products should be regarded as category B waste. COP-4 in 2022 agreed on two-tier thresholds for mine tailings to be regarded as mercury waste. COP-5 in 2023 established the threshold for waste contaminated with mercury (category C), which concluded the COP consideration of mercury waste thresholds. The expert group worked through two in-person meetings, held in 2019 and 2023, and frequent online meetings. The group considered two specific proposals of a threshold value for category C waste - 25 mg/kg, proposed by a Party based on ecotoxicity of mercury used for the globally harmonized system for classification and labelling (GHS), and 1 mg/kg proposed by an NGO. The group reviewed the existing thresholds and approaches used by Parties to manage waste contaminated with mercury. Based on the report of the expert group, COP established 15 mg/kg total mercury concentration as the thresholds for category C waste, allowing Parties to use alternative definitions. The Secretariat is to collect and disseminate information on such alternative approaches, and develop a document for COP-7 in 2027 for the review of the thresholds.

### Abstract Graphics

#### Recap: COP-5 consideration of mercury waste thresholds



##### Minamata Convention Article 11

2. For the purposes of this Convention, mercury wastes means substances or objects:  
(a) Consisting of mercury or mercury compounds;  
(b) Containing mercury or mercury compounds; or  
(c) Contaminated with mercury or mercury compounds, in a quantity above the relevant thresholds defined by the COP, in collaboration with the relevant bodies of the Basel Convention in a harmonized manner, that are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law or this Convention.

##### COP Decisions 3/5 and 5/10

No threshold needs to be established for waste consisting of mercury, and waste listed in Table 1 shall be regarded as such mercury waste.

No threshold needs to be established for waste containing mercury, and mercury-added products that are disposed of, are intended to be disposed of or are required to be disposed of, including those listed in Table 2, will be regarded as such mercury waste;

COP established 15 mg/kg total concentration of mercury as the threshold for waste contaminated with mercury, allowing Parties to use alternative approaches to define such waste.

Table 1: List of mercury waste consisting of mercury or mercury compounds

- Recovered elemental mercury
- Elemental mercury
- Mercury (II) chloride and mercury (II) chloride
- Mercury (II) oxide (mercuric oxide)
- Mercury (II) sulfate (mercuric sulfate)
- Mercury (II) nitrate (mercuric nitrate)
- Cinnabar concentrate
- Mercury sulfide

Table 2: Non-exhaustive list of waste containing mercury or mercury compounds

- Non-electronic measuring devices containing mercury (barometers, hygrometers, manometers, thermometers, sphygmomanometers)
- Electrical and electronic switches, contacts, relays and rotating electrical connectors with mercury
- Fluorescent bulbs, high intensity discharge (HID) bulbs (mercury vapour bulbs, metal halide and high-pressure sodium bulbs), neon/argon lamps
- Batteries/accumulators containing mercury
- Biocides and pesticides containing mercury and their formulations and products
- Paints and varnishes containing mercury
- Pharmaceuticals containing mercury for human and veterinary uses, including vaccines
- Cosmetics and related products containing mercury
- Dental amalgam
- Scientific instrument used for the calibration of medical or scientific devices containing mercury



## Distribution in dissolved gaseous mercury and air-sea gas exchange of mercury in Yatsushiro Sea and Minamata Bay

Kondo F<sup>1</sup>, Maruo Y<sup>2</sup>, Marumoto K<sup>2</sup>

<sup>1</sup>Japan Coast Guard Academy, <sup>2</sup>National Institute for Minamata Disease

Human activity has substantially increased the amount of mercury (Hg) in the biosphere. Air-sea exchange of gaseous Hg is a critical component of the global Hg cycle and its estimation is associated with high uncertainty. One of the causes of this uncertainty is the lack of observation data of dissolved gaseous Hg (DGM) concentrations in surface seawater. In this study, we presented the results of shipborne continuous measurements of atmospheric Hg and DGM concentrations in Yatsushiro Sea and Minamata Bay in Japan during the four research cruises. Four cruise campaigns of Dolphin Super Challenger of Kumamoto University were conducted in May 2022, November 2022, February 2023, and May 2023. For DGM concentration measurements with surface temperature and salinity, seawater from the ship's intake at 0.5 – 1 m depth was sampled with our uniquely developed on-board automatic continuous equilibrium system. The seawaters in Yatsushiro Sea and Minamata Bay were typically supersaturated with DGM compared to the atmosphere Hg, and the DGM concentrations were higher in May than in other seasons. DGM concentrations observed around Minamata bay were greater than surrounding areas. Higher DGM concentration areas also present in Yatsushiro Sea, and DGM enters the sea via runoff of Kuma River. This result indicates that both river runoff and input from the seafloor may play important roles in controlling the DGM distribution in these observation area. This work was supported by JSPS KAKENHI Grants 21H04935 of Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

## A review on the findings of South Africa's the UNEP Level 1 Report, and the SA-MIA Report 2021 in the countries effort to ratify the Minamata Convention

Resane T<sup>1</sup>, Martin L<sup>2</sup>, Sibali L<sup>3</sup>

<sup>1</sup>University Of South Africa, <sup>2</sup>S.A. Weather Service, <sup>3</sup>Unisa

The present paper is a review on the findings of the South African Department of Environmental Affairs (DEA) (now the South African Department of Forestry, Fisheries, and the Environmental (DFFE) UNEP Level 1 Report 2011 on mercury, and the SA-MIA Report 2021. The UNEP Level 1 Report of 2011, presented the situation analysis of mercury (Hg) as a pollutant, and further developed the inventory of mercury use, sources, the availability of safer, effective, and affordable alternatives where applicable in South Africa. The report further identified vulnerable populations requiring awareness raising about the mercury issues, and mitigation measures to protect human health and the environment. The calculations of mercury release used the UNEP Toolkit Level 1, which are based on the mass balance principle. Mass balance is an arbitrary calculation used for screening purposes, which cannot precisely be used for decision making processes. Studies conducted by SA researchers through the South African Mercury Assessment initiative (SAMA) from 2006 – 2009, formed the basis of this study. Though SAMA the first SA Hg assessment was conducted and the 2011 study builds on this work. Both the emission factor and the real emission measurements were used to generate results from two coal power plants. However, there were some degree of ambiguity with those results as most of the emissions were estimated using emission factors.

The Minamata Initial Assessments (MIA) is a set of pre-ratification activities funded by the Global Environmental Facility (GEF) to prepare countries for treaty ratification and implementation. The South Africa Minamata Initial Assessments (SA-MIA) project was undertaken during the period 2016 to 2020. This MIA report provided a more up to date and realistic summary of South Africa's mercury emission and its capacity to implement the Minamata Convention precepts. The report further suggested the needs for South Africa.

239

## Mercury over southern Africa and the Southern Ocean

Mugabe V<sup>1</sup>, Fietz S<sup>1</sup>, Martin L<sup>2</sup>

<sup>1</sup>Stellenbosch University, <sup>2</sup>South African Weather Service (SAWS)

Sources, distribution and speciation of mercury remain to be explored in many areas of the world, especially in the Southern Hemisphere. The aim of the project presented here is to better understand factors driving the distribution of mercury over and in the Southern Ocean. Here we will present atmospheric mercury observations from three recent (2022-2023) research expeditions into the oceans south of South Africa in winter (June/July/August). We will link these observations with atmospheric mercury data from ground-based monitoring sites in southern Africa, other Southern Hemisphere marine observations, as well as concentrations in the surface ocean along the transects. We will discuss future plans and extend our invitation for collaboration.

## Assessment and modelling of the impact of climate change on Hg concentrations in contaminated sites – the Idrijca and Isonzo (Soča) rivers and the Gulf of Trieste

Žagar D<sup>1</sup>, Novak G<sup>1</sup>, Četina M<sup>1</sup>, Lebar K<sup>1</sup>, Bezak N<sup>1</sup>, Atanasova N<sup>1</sup>, Škerjanec M<sup>1</sup>, Kotnik J<sup>2</sup>, Horvat M<sup>2</sup>  
<sup>1</sup>University of Ljubljana, Faculty of Civil and Geodetic Engineering, <sup>2</sup>Jožef Stefan Institute

The consequences of climate change in the Mediterranean region are reflected in rising temperatures and an intensification of extreme meteorological and hydrological events. From the former Hg mining area in Idrija, the Hg-rich soils and sediments are transported by the rivers into the Gulf of Trieste. Methylation takes place both in the river and in the marine sediment and facilitates remobilisation of MeHg into the water column and the food chain.

We analysed historical data on river discharge, sediment transport, seawater temperature, salinity and wind conditions. In the catchment we conducted a rainfall-runoff analysis and applied general and regional climate models to three RCP scenarios. Hydrological models were created and the relationship between runoff and suspended sediment concentration was determined. The number of flood events and their peak discharges show an increasing trend. The calculated amount of Hg transported along the rivers increases by 50 % and 66 % in the periods 2021-2060 and 2061-2100, respectively. The analysis of parameters in the Gulf for the period 2003 – 2023 shows an increase in temperature throughout the water column in autumn and winter and a decrease in strong wind events; both the higher temperature and lower winds reduce volatilisation.

Climate change-induced conditions will be significant and pronounced along the river system over the next 80 years and more Hg will be transported to the Gulf, while loss to the atmosphere will tend to decrease. Therefore, more Hg could be available for biogeochemical transformations in the Gulf, and for uptake into the food chain, more Hg could be carried into the Adriatic Sea and through deep water formation to the Eastern Mediterranean. The obtained results can serve as input data for the multi-box models in the river basin and the models of Hg processes in the Gulf.

## Microbial mercury methylation in rice paddy soils

Meng B<sup>1</sup>, Pu Q<sup>1</sup>, Liu J<sup>1,2</sup>, Hu H<sup>1</sup>, Feng X<sup>1</sup>

<sup>1</sup>Institute Of Geochemistry, Chinese Academy Of Sciences, <sup>2</sup>Sichuan Agricultural University

The organic form of mercury (Hg), methylmercury (MeHg), is the most toxic compound of this element, which can be bioaccumulated and biomagnified along the food chains posing potential threat to human health. Fish eating has long been recognized as the predominant pathway of human exposure to MeHg. However, this consensus was recently updated in Hg contaminated areas, where rice is the dominant produce and rice consumption is suggested as the dominant exposure route of MeHg for local residents. Rice as a potential bio-accumulator plant of MeHg, is the staple food for half of the global population; therefore, research concerning Hg cycling in the paddy ecosystem has received considerable attention in past decades. Inorganic Hg can be transformed into MeHg in anaerobic conditions. Rice paddy soil, as a typical ephemeral wetland, was considered to be a significant setting for Hg methylation, which results to the accumulation of MeHg in rice grain. On the basis of the previous studies from our group, we systematically summarized the current understanding of Hg methylation in rice paddy ecosystem and its primary controlling factors, including 1) the relative importance of different microbial groups on MeHg production and degradation in paddy soils, 2) the relative importance of geochemically relevant Hg(II) species on Hg methylation in paddy soils, 4) mercury, sulfur, and, nitrogen redox cycling affect MeHg production in paddy soils, 5) the key role of dissolved organic matter in microbial mercury methylation in paddy soils. Finally, we further identify various research gaps in previous studies and proposes commented recommendations for future research.

## The role of primary producers in the transfer of mercury into the primary consumers of the estuarine trophic web (southern Baltic Sea)

Bełdowska M<sup>1</sup>, Bełdowski J<sup>2</sup>, Dziubińska A<sup>1</sup>, Korejwo E<sup>2</sup>, Kornijów R<sup>3</sup>, Panasiuk A<sup>1</sup>, Sapota M<sup>1</sup>, Wilman B<sup>1</sup>, Wojdasiewicz A<sup>1</sup>, Woźniczka A<sup>3</sup>, Popławska A<sup>1</sup>, Zarzeczańska A<sup>1</sup>, Złoch I<sup>1</sup>, Zgrundo A<sup>1</sup>

<sup>1</sup>Faculty Of Oceanography And Geography, University Of Gdańsk, <sup>2</sup>Institute of Oceanology, National Academy of Sciences, <sup>3</sup>National Marine Fisheries Research Institute

The mercury level at the base of the aquatic food web is the main factor influencing the Hg level at the higher trophic level. The transfer of the metal from the water into primary producers determines the subsequent bioaccumulation of Hg in pelagic and benthic primary consumers and the biomagnification of Hg from primary consumers to secondary consumers. In the temperate zone, the cold season is warming, leading to a lack of ice cover or a reduction in its thickness and duration. An elongated vegetation season, together with an improvement in water quality, can affect the growth and development of primary producers. Vegetated habitats are known not only for the higher biomass of benthic organisms but also for an elevated number of species, both plants and animals. As a result, the number of organisms that effectively accumulate mercury from surrounding water (present day Hg) and sediments (historical Hg) is increasing.

Taking into account the current state of knowledge, we hypothesize that climate-induced ecosystem changes, including warming and elongation of the growing season will increase the load of neurotoxic Hg introduced to the initial links of the food web and affect the exposure to Hg of organisms from the higher trophic levels, such as fish, seabirds and humans.

In the studies we present: determination of the influence of benthic primary producers, , on the Hg level in the surface sediments of the coastal areas; Recognition of the transfer of Hg from water and sediments into primary producers; Estimation of the concentration of total Hg and the share of individual Hg forms in marine primary producers and in primary and secondary consumers like zooplankton and small planktivorous fish.

The study was funded by a research project National Science Centre 2022/45/B/ST10/00368.

243

## Knowledge and technology transfer to investigate marine mercury contamination in SA: An SA-France collaboration

Fietz S<sup>1</sup>, Martin L<sup>2</sup>, Heimbueger Boavida L<sup>3</sup>

<sup>1</sup>Stellenbosch University, <sup>2</sup>South African Weather Service (SAWS), <sup>3</sup>MIO - CRNS

This short presentation will introduce our recent bilateral collaboration between SA and France on mercury in the Southern Ocean. We briefly report on joint expedition and some outcomes.

## Use of MercLok™ P-640 to reduce elemental mercury beads and remediate highly contaminated building materials to non-hazardous waste classification.

Fontenot C<sup>1</sup>, Miller J<sup>1</sup>, Pingree K<sup>1</sup>

<sup>1</sup>Albemarle Corporation

MercLok™ P-640, a mercury treatment technology, has been developed by Albemarle to address environmental impacts from mercury contamination. MercLok is designed to capture and sequester multiple species of mercury, including elemental mercury. MercLok has been demonstrated to provide robust performance and long-term stability in the environment through both bench and field studies in a wide range of soil conditions.

To evaluate capture and sequestration of elemental mercury, mercury beads were placed into sealed bottle reactors containing a deionized water/MercLok slurry and agitated over several days. The solid and liquid fractions of the samples were separated by filtration and analyzed separately to arrive at a mass-balance calculation. Analysis by USEPA method 7473 indicated that the solid portion of the sample contained most of the mass of mercury added to each reactor, though elemental mercury was no longer visible within the filter cake matrix. Additionally, the TCLP (Toxicity Characteristic Leaching Procedure) analysis of the filter cakes from each reactor was only able to extract 0.002% of the total mercury mass at the lowest dosage of MercLok.

These findings were validated at bench scale using soil and forge cinders from an industrial site. The study demonstrated a reduction in leachable mercury from the material by over 99% to an order of magnitude below the TCLP hazardous limit of 0.2 mg/l. Additionally, following the study, elemental mercury was no longer visible within the MercLok-treated materials.

After pilot scale amendment of these materials, mercury concentrations of TCLP leachates from the treated cinders were reduced to 0.004 mg/l, which was a reduction of 99.98% compared to untreated materials. Additionally, elemental mercury was no longer visible within the treated material. As a result of the treatment with MercLok, the forge cinders were reclassified to a non-hazardous waste profile, which allowed for economically attractive disposal options.

245

## Use of the remediation product MercLok™ P-640 to reduce mercury concentrations in effluent from wastewater treatment systems.

Pingree K<sup>1</sup>, Miller J<sup>1</sup>, Fontenot C<sup>1</sup>

<sup>1</sup>Albemarle Corporation

MercLok P-640 is a product developed by Albemarle to rapidly capture and sequester multiple species of mercury. The fast kinetics that facilitate the capture and sequestration allow the use of P-640 in wastewater treatment systems. P-640's efficiency to effectively reduce the concentration of mercury in effluent has been validated through both bench and field studies.

A field bench study was conducted at a chlor-alkali manufacturing facility that utilizes a sodium sulfide treatment to remove mercury from water entering its wastewater system. The study tested the ability of P-640 to reduce mercury concentrations in water to below the discharge criteria of 42 ng/L. A dosage of 0.01 weight percentage of P-640 to the mass of water treated in a stirred tank batch reactor was effective in reducing the mercury concentration by 99%, attaining the discharge criteria. A dosage of 0.07 weight percent was successful in reducing mercury concentration to below the background concentration of the receiving waterbody.

The use of P-640 as fixed bed media was further tested at field-scale for a facility utilizing a recovery well network for landfill leachate management. The pilot system employed PVC pipe columns configured in three-column series sets. P-640 reduced the average influent mercury concentration of 336 ng/L to below the discharge limit of 50 ng/L with a 5% P-640/sand mixture. At the conclusion of this test, the pilot system was upscaled to use a single drum containing a 3% P-640/sand mixture. The upscaled system was able attain over 99% reduction in the concentration of mercury from an average influent concentration of 834 ng/L to below the detection limit of 2.5 ng/L.

The use of P-640 in water treatment applications has been demonstrated to provide compliant effluent concentrations in a cost-effective fashion.

246

## In-situ remediation of mercury-contaminated mining calcines using a novel amendment product known as MercLok™ P-640

Miller J<sup>1</sup>, Pingree K<sup>1</sup>, Griffin D<sup>1</sup>

<sup>1</sup>Albemarle Corporation

MercLok™ P-640 has been developed by Albemarle to address environmental impacts from mercury contamination. MercLok is designed to capture multiple species of mercury, preventing it from leaching or diffusing into groundwater and surface water.

Albemarle conducted a pilot study for in-situ mercury stabilization using MercLok at an abandoned mercury mine site in California, referred to here as Mine A. Layers of unamended (controls) and MercLok amended calcines were arranged in open-top container “reactors” representing two alternative application techniques and various dosages. Analytical results from rainwater leachate collected from the reactors and acid-based leaching tests demonstrate MercLok reduced total mercury leaching by up to 99% and reduced methylmercury in leachate by 75%.

Based on the pilot study at Mine A, MercLok was identified as a potential solution for in-situ remediation of calcines at the Elgin Mine in California. Results from treatability testing of samples from Elgin Mine were acquired using several standard leachability test procedures including STLC (soluble threshold limit concentration), DI WET (deionized waste extraction test), and SPLP (synthetic precipitation leaching procedure). Results for treated samples showed a reduction in mercury leachability from calcines of greater than 99%, which was also significantly lower than the leachability of background soil.

The contaminated calcines and furnace bricks at Elgin Mine were combined into a single pile over which a cap of MercLok was applied. Hydrologic controls to minimize run-on and manage runoff as well as a trenched permeable reactive barrier of MercLok were installed surrounding the pile. Confirmation sampling and subsequent observations indicate that the treatment effectively stabilized the site. This application demonstrates the efficacy of MercLok used with hydrologic controls for treating mercury-contaminated solids at remote sites with light duty equipment to achieve long-term mine site remediation and closure for reduced remediation project costs.

## Uncovering mercury methylation potential and microbial communities involved in Subarctic thermokarst lakes

Malcata Martins B<sup>1,2</sup>, Costa J<sup>3</sup>, Hintelmann H<sup>4</sup>, Pilote M<sup>5</sup>, Cesário R<sup>1</sup>, Magalhães C<sup>3</sup>, Canário J<sup>1</sup>

<sup>1</sup>Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, <sup>2</sup>Center for Northern Studies (CEN), Université Laval, <sup>3</sup>CIIMAR/CIMAR Interdisciplinary Centre of Marine and Environmental Research, University of Porto, <sup>4</sup>Water Quality Centre, Trent University, <sup>5</sup>Environment and Climate Change Canada, Aquatic Contaminants Research Division

The Arctic is characterized by large permafrost areas that may store various contaminants, including mercury (Hg). Moreover, anthropogenic activities release substantial amounts of Hg into the atmosphere and long-range atmospheric transport and deposition are important sources of Hg in Subarctic and Arctic regions. Temperature increase and permafrost thawing releases previously stored carbon and can lead to the formation of thermokarst lakes. These ecosystems are rich in organic matter and therefore ideal for bacterial activity. As the formation of methylmercury (MMHg), the most stable toxic Hg form that has the capacity to bioaccumulate and biomagnify, is mainly carried out by bacteria, thermokarst lakes can be hotspots of MMHg formation. The concentration of MMHg in the environment is determined on the Hg pool and the equilibrium between the methylation and demethylation processes. Methylating bacteria have specific genes (*hgcA* and *hgcB*) that encode the proteins used in the methylation of Hg.

In this work, two thermokarst lakes (SAS 1A and SAS 2A) located in a Canadian Subarctic permafrost region were sampled in the winter and summer of 2022. Using isotope enriched Hg it was possible to track the methylation and demethylation processes. In addition, the relative abundance of the genes involved in those processes has been identified through metagenomic shotgun sequencing of the eDNA isolated from the sediments. Although the lakes have a similar Hg pool, SAS 1A has higher methylation rates, which is in line with the different microbial communities involved in the mercury cycle in each lake. Higher methylation rates in the winter, ranging between 1.78-7.94% after 24h, compared to the summer, ranging between 0.13-0.60%, are also confirmed by a dominant pool of Hg methylation genes in the winter.

## Insights into patterns and trends of atmospheric mercury variability in the GMOS network based on a decade of measurements

Bencardino M<sup>1</sup>, Skov H<sup>2</sup>, Norstrom C<sup>2</sup>, Ebinghaus R<sup>3</sup>, Mashyanov N<sup>4</sup>, Vítková G<sup>5</sup>, Komínková K<sup>5</sup>, Cairns W<sup>6,7</sup>, Angiuli L<sup>8</sup>, Read K<sup>9</sup>, Neves L<sup>10</sup>, Nelson P<sup>11</sup>, Dommergue A<sup>12</sup>, Angot H<sup>12</sup>, Magand O<sup>12,13</sup>, Martin L<sup>14</sup>, Labuschagne C<sup>14</sup>, Esposito G<sup>15</sup>, Diéguez M<sup>16</sup>, García P<sup>16</sup>, Amico D<sup>1</sup>, Martino M<sup>1</sup>, Tassone A<sup>1</sup>, Mannarino V<sup>1</sup>, D'Amore F<sup>1</sup>, Cinnirella S<sup>1</sup>, Sprovieri F<sup>1</sup>, Pirrone N<sup>1</sup>

<sup>1</sup>Institute of Atmospheric Pollution Research of CNR, <sup>2</sup>Aarhus University, <sup>3</sup>Helmholtz-Zentrum, <sup>4</sup>Lumex-marketing LLC, <sup>5</sup>Global Change Research Institute, <sup>6</sup>CNR-Institute of Polar Sciences, <sup>7</sup>Ca' Foscari University, <sup>8</sup>Apulia Region Environmental Protection Agency, <sup>9</sup>National Centre for Atmospheric Science, University of York, <sup>10</sup>Cape Verde Observatory, Instituto Nacional de Meteorologia e Geofísica, <sup>11</sup>Macquarie University, <sup>12</sup>Université Grenoble Alpes, <sup>13</sup>Université de La Réunion, <sup>14</sup>South African Weather Service, <sup>15</sup>CNR-Institute of Atmospheric Pollution Research, <sup>16</sup>INIBIOMA-CONICET

The recent guidance on monitoring of mercury and mercury compound of the Minamata Convention on Mercury (MCM) highlights the essential need to have available comparable monitoring data for evaluating the effectiveness of regulatory measures on a global scale (UNEP/MC/COP.4/INF/12). The Global Mercury Observation System (GMOS) network, initially a five-year (2010-2015) project funded by the European Commission (<http://www.gmos.eu>), continued as a GEO Flagship programme aiming to support the Global Observation System for Mercury (GOS4M). GMOS was intended as a coordinated global observing system to monitor mercury (Hg) on a global scale, in support and to evaluate the effective MCM implementation. To date, twenty-eight ground-based stations have been involved in the monitoring activities, adhering to the GMOS sampling protocols and to its data quality control management. This global network enables a representative coverage of all latitudes, from within the Arctic Circle to the Antarctic continent, passing from the Northern to the Southern Hemispheres, also including the Tropical Zone. This work presents atmospheric elemental Hg data, available as both Total Gaseous Mercury (TGM) or Gaseous Elemental Mercury (GEM) concentrations, recorded worldwide in the framework of the GMOS network and with reference to the 2011–2020 timespan. TGM/GEM concentrations were analysed in terms of their variability along latitudinal belts, considering temporal trends, seasonality, and their comparability. Major findings confirmed a clear gradient of TGM/GEM concentrations between the Northern (1.57 ng/m<sup>3</sup>) and Southern (1.00 ng/m<sup>3</sup>) Hemispheres. The Arctic and Antarctic regions, as well as the Tropical Zone were found to be highly influenced by seasonal variations. Decreasing trends in TGM/GEM levels, were found to be significant for regions at high/mid latitudes, where it is reasonable that reduction in TGM/GEM levels have been affected by regional Hg reduction policies.

## Deciphering mercury and selenium interactions in fish: a kinetic comprehensive speciation and isotopic study in rainbow trout with tuna-based diets

Pedrero Zayas Z<sup>1</sup>, Marchán-Moreno C<sup>1</sup>, El Hanafi K<sup>1</sup>, Queipo-Abad S<sup>1</sup>, Bueno M<sup>1</sup>, Ouerdane L<sup>1</sup>, Corns W<sup>2</sup>, Louvat P<sup>1</sup>, Pannier F<sup>1</sup>, Amouroux D<sup>1</sup>, Fontagné-Dicharry S<sup>3</sup>

<sup>1</sup>French National Centre for Scientific Research (CNRS), <sup>2</sup>PS Analytical, <sup>3</sup>INRAE

The tuna canning industry discards approximately 65% of its byproducts, constituting a valuable protein source for sustainable aquafeed production. However, the primary drawback of using tuna byproduct-based diets is the potential high content of heavy metals, such as mercury (Hg), due to biomagnification in the trophic chain. Interestingly, tuna byproducts contain relatively high concentrations of selenium (Se), which may influence Hg bioaccumulation. Despite suggestions of Se's role against Hg bioaccumulation/toxicity, it remains poorly understood. This study aims to contribute to comprehending the dietary fate of Hg and Se in fish.

In a controlled setting, rainbow trout (*Oncorhynchus mykiss*), a model aquaculture fish, was exposed to Hg and Se species through their diet over a 6-month trial. The study monitored the impact of dietary Se on Hg bioaccumulation in fish tissues, including flesh, brain, and liver. Twelve dietary conditions were tested, incorporating plant-based and tuna byproduct diets (0.25 µgHg g<sup>-1</sup>, 8.0 µgSe g<sup>-1</sup> ww) enriched with methylmercury and/or Se as selenite or selenomethionine. Tuna byproduct diet resulted in lower Hg levels than the European Commission's safe threshold (0.3 µgHg g<sup>-1</sup> ww). This investigation evidenced the significant influence of specific Se compounds, particularly from tuna-based aquafeed, on Hg bioaccumulation. Furthermore, a battery of analytical approaches, including biomolecular speciation and (Hg) isotopic analyses, provided new insights into Hg and Se pathways in trout. The hepatic kinetic transfer of methylmercury binding to hemoglobin was explored. This work reports for the first time the presence of selenoneine in freshwater fish, evidencing a trophic transfer and discussing its potential role in Hg detoxification. This study enhances the current limited understanding of the interaction between Hg and Se species in biota, particularly in fish and constitutes a solid basis on the evaluation of tuna byproducts for their potential use as a sustainable alternative to wild fish-based aquafeeds.

250

## Microbial and photochemical processes controlling mercury speciation in an athalassic sulfate-rich saline lake, NE Spain

Xue J<sup>1</sup>, Tessier E<sup>1</sup>, Margalef-Marti R<sup>1,2</sup>, Guyoneaud R<sup>1</sup>, Thibault De Chanvalon A<sup>1</sup>, Sebilo M<sup>1,3</sup>, Pedrero Z<sup>1</sup>, Amouroux D<sup>1</sup>

<sup>1</sup>Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, Institut des Sciences Analytiques et des Physico-Chimie pour l'Environnement et les Matériaux (IPREM), <sup>2</sup>Universitat de Barcelona, <sup>3</sup>Sorbonne Université, CNRS, Institut d'Ecologie et des Sciences de l'Environnement de Paris (IEES Paris)

Aquatic cycling of mercury (Hg) species, like methylmercury (MeHg), is driven by both microbial and abiotic pathways. Understanding their relative contributions is crucial to understand Hg fate and contamination. Gallocanta Lake, a sulfate-rich saline lake, was chosen as a model ecosystem to investigate microbial and geochemical Hg-sulfur interactions under environmental levels of Hg. Seasonal Hg speciation data and water/sediment isotope tracer experiments (i.e., inorganic Hg as <sup>199</sup>iHgII, <sup>201</sup>MeHg) tracked pathways like iHg methylation and reduction as well as MeHg degradation. Sediment MeHg levels varied seasonally, peaking in fall with maximal %MeHg (~10%) in surface sediment (< 5 cm). Porewaters of surface sediment had comparable iHg (6.3–20.7 ng L<sup>-1</sup>) and MeHg levels (6.1–14.0 ng L<sup>-1</sup>), with %MeHg up to 60%, positively correlated with porewater H<sub>2</sub>S interpreted as the activity of sulfate reducers at elevated sulfide levels (> 13.6 mg L<sup>-1</sup>). The calculated positive sediment-water fluxes of iHg (0.8 ng m<sup>-2</sup> h<sup>-1</sup>) and MeHg (6.3 ng m<sup>-2</sup> h<sup>-1</sup>) indicate the diffusion of these species into overlying water. Sediment incubations confirmed sulfate reducers mediated iHg methylation at a maximal rate of 0.014% h<sup>-1</sup> in fall. Water incubation experiments showed significant photo-iHg reduction (up to 2% h<sup>-1</sup>) and MeHg demethylation (~1% h<sup>-1</sup>), while reductive MeHg demethylation into DGM (up to 0.42% h<sup>-1</sup>) was lower. These patterns collectively suggest a greater influence of photochemical processes over microbial activity in sulfate-rich saline water. Overall, this study confirms MeHg production in sulfidic sediments by sulfate reducers in a saline lake, and MeHg then diffuses and degrades in the water column, shedding light on biotic and abiotic drivers in Hg transformations in sulfate-rich conditions.

251

## Unraveling Mercury Species Dynamics and Potential Interactions with Selenium: A Study in Amazonian Riverine Communities

Esplugas J<sup>1</sup>, Tessier E<sup>1</sup>, Neves Cezarette G<sup>2</sup>, Amouroux D<sup>1</sup>, Barbosa Jr. F<sup>2</sup>, Bueno M<sup>1</sup>, Pedrero Zayas Z<sup>1</sup>  
<sup>1</sup>CNRS, <sup>2</sup>USP

Amazonian riverine inhabitants exhibit a worldwide singular mercury (Hg) and selenium (Se) status, much higher than values referred by international health authorities. However, the fate of both elements in humans and their interactions remains unknown. Dietary exposure, through the consumption of local fish, is unequivocally correlated with the levels of Hg in blood. Nevertheless, specific trends regarding dietary sources of Se are yet to be fully identified, with local Brazil nuts and fish being suggested. Understanding the fate of Hg and its interaction with Se, considered a potential antagonist to Hg toxicity, claim for speciation studies in human samples.

The main objective of this study is to investigate the distribution of Hg species (i.e., iHg and MeHg) in blood, plasma, urine, and hair from a large Amazonian population (comprising more than 200 adults from different villages) and assess the influence of Se status. The work provides a comprehensive overview of Hg species within different human matrices and their correlation with the Se:Hg molar ratio. Special attention is given to the unique distribution of Hg in plasma. Notably, in this specific fluid, Hg is primarily found as MeHg (more than 60%), in contrast to findings from previous human studies. Interestingly, MeHg levels in plasma decrease with the Se:Hg molar ratio. Although Hg in urine is dominantly excreted as iHg, a fraction of MeHg, up to 8%, is found in some individuals. The impact of Se levels in blood on the excretion of Hg species (in urine and hair) is addressed. This work provides new insights into the fate and interaction of Hg species and Se in humans.

## Considerations for Including the Impacts of Climate Change on the Human Health Risk Assessment for Mercury Exposure – A Canadian Perspective

Wallace E<sup>1</sup>, Hu X<sup>1</sup>, Chan L<sup>1</sup>

<sup>1</sup>University Of Ottawa

Climate change is a major confounding factor for managing environmental contaminants across the globe. The alterations to biogeochemical processes and ecosystem functions caused by climate change have been documented to affect the sources, transport, fate, and effects of many contaminants, including mercury. Studies reporting climate change-related events, including permafrost thaw, forest fires, flooding, and warming water temperatures, among others, can release naturally occurring mercury stored in environmental compartments, change methylation rates, affect bioaccumulation and biomagnification in animals, and alter environmental transport. These environmental changes potentiate changes in human exposure to mercury, particularly through fish consumption. In Canada, where global warming is occurring at approximately twice the global average rate, there is a need to understand how climate change may impact the movement of mercury through the environment and downstream implications for human health risk. We present findings from a systematic review to characterize the impacts of climate change on mercury sources, transport, and fate in the Canadian environment and subsequent considerations for conducting human health risk assessments (HHRA) in Canada. We searched Scopus and Web of Science databases and found 65 relevant papers published from 1993 to 2023. Impacts of climate change on mercury vary by region within Canada based on the most commonly occurring climate change events, such as permafrost thaw in the north and forest fires in the west. In the context of HHRA, the reported climate change impacts can affect exposure, given the changes to the sources, transport, and fate of mercury and the dose-response relationship with potential interactive effects of multiple stressors. Based on the results, we propose a conceptual framework to include the impacts of climate change on the HHRA for mercury.

## Critical assessment of sample preparation methods for the study of HgSe nanoparticles in fish tissues by SP-ICP-MS

Rodríguez Martín-Doimeadios R<sup>1</sup>, Jiménez-Moreno M<sup>1</sup>, Hernández-Postigo M<sup>1</sup>

<sup>1</sup>Institute of Environmental Sciences, Department of Analytical Chemistry and Food Technology

Understanding the interaction between mercury species and selenium in living organisms is crucial due to their environmental and health implications. In recent years, the importance of mercury in its particulate form in biota has greatly increased since the formation of mercury selenide nanoparticles (HgSeNPs) can be considered an efficient end-product of Hg detoxification mechanisms. There is a need of reliable information about this new Hg species, but this is a current challenge for analytical chemistry. Not only information about shape and size is required, but also about the concentrations both in particle and mass-based terms. Novel analytical methodologies are required. In this sense, inductively coupled plasma mass spectrometry in its single particle mode (SP-ICP-MS) becomes an interesting alternative which offers a simultaneous NP sizing and counting. However, its application in complex biological matrices presents several limitations mainly related to the sample preparation step (i.e., risk of non-quantitative recoveries or possible dissolution of NPs), so new procedures allowing a proper extraction without compromising the NP stability must be developed.

In this work different extraction procedures have been tested for an efficient isolation and separation of HgSeNPs from biological samples prior to SP-ICP-MS analyses. The effect of the sample preparation methodologies in the amount of HgSeNPs extracted, the NP size distribution and the potential dissolution of those NPs has been evaluated. Fish real samples and reference materials certified for classical Hg species have been analyzed. This study supports and critically discuss the need of standardized and validated methods for the analysis of HgSeNPs in fish tissues to ensure reliable and comparable results across different laboratories and their implementation in ongoing monitoring programs for the analysis of NPs in complex biological matrices.

## LARGE-SCALE PROJECTS (HYDROELECTRIC POWER PLANTS) IN THE AMAZON AREA ASSOCIATED TO HIGHER HUMAN EXPOSURE THAN THAT FOUND IN ASGM AREAS

Rodríguez Martín-Doimeadios R<sup>1</sup>, Jiménez-Moreno M<sup>1</sup>, Fernández-Trujillo S<sup>1</sup>, Arrifano G<sup>2</sup>, Augusto-Oliveira M<sup>2</sup>, Santos-Sacramento L<sup>2</sup>, Lopes-Araújo A<sup>2</sup>, Macchi B<sup>3</sup>, do Nascimento J<sup>3</sup>, Crespo-Lopez M<sup>2</sup>  
<sup>1</sup>Environmental Sciences Institute (ICAM), Department of Analytical Chemistry and Food Technology, <sup>2</sup>Laboratory of Molecular Pharmacology, Institute of Biological Sciences, <sup>3</sup>Laboratory of Molecular and Cellular Neurochemistry

The Amazon is a significant contributor to global mercury emissions due to artisanal and small-scale gold mining (ASGM), deforestation, and forest fires. The construction of hydroelectric power plants (HPP) and numerous dams further compounds the issue. These activities create conditions favoring the conversion of mercury to methylmercury, potentially posing global human health risks.

Therefore, the biomonitoring of mercury in Amazonian populations, especially those more vulnerable such as women and traditional communities, get an especially relevant meaning. Although this risk can be evaluated in different matrices, hair is one of the best biomarkers to monitor chronically exposed populations.

This study aims to conduct the largest epidemiological investigation in vulnerable populations of the Amazon (around 900 hair samples), focusing on two representative areas: one of the main and oldest gold mining regions (the Tapajós River basin), and a region under the influence of one of the world's largest HPP Tucuruí). This work demonstrated, for the first time, that human populations in the Amazon are dangerously exposed to mercury, regardless of proximity to ASGM regions. In fact, the populations under the HPP influence and without ASGM influence (Tucuruí) showed a median level of mercury in hair more than twice the exposure found in the Tapajós region. These results support that public health and environmental strategies to combat the mercury contamination in the Amazon must not be limited to the ASGM-influence areas, and that there is an urgent need of biomonitoring Amazonian populations, regardless they live. The influence on mercury exposure of environmental (i.e., seasonal changes) or physiological factors, such as sex and age, were evaluated. The relationship between mercury and selenium levels was also explored. Hence, this research seeks to contribute crucial data for Brazil's National Action Plan under the Minamata Convention and aid in formulating strategies to control global mercury emissions.

## Mercury-related dyslipidemia and cardiovascular risk: apolipoproteins can be useful? An anthropometric, biochemical and genetic study in the Amazon

Lopes-Araújo A<sup>1</sup>, Arrifano G<sup>1</sup>, Macchi B<sup>2</sup>, Augusto-Oliveira M<sup>1</sup>, Santos-Sacramento L<sup>1</sup>, Rodríguez Martín-Doimeadios R<sup>3</sup>, Jiménez-Moreno M<sup>3</sup>, Martins Filho A<sup>4</sup>, Alvarez-Leite J<sup>5</sup>, Oriá R<sup>6</sup>, do Nascimento J<sup>2</sup>, Crespo-Lopez M<sup>1</sup>

<sup>1</sup>Laboratory of Molecular Pharmacology, Institute of Biological Sciences, <sup>2</sup>Laboratory of Molecular and Cellular Neurochemistry, Institute of Biological Sciences, <sup>3</sup>Environmental Sciences Institute (ICAM), Department of Analytical Chemistry and Food Technology, <sup>4</sup>Seção de Patologia, <sup>5</sup>Departamento de Bioquímica e Imunologia, <sup>6</sup>Laboratório da Biologia da Cicatrização, Ontogenia e Nutrição de Tecidos. Departamento de Morfologia e Instituto de Biomedicina, Escola de Medicina

Everyone in the world is exposed to some level of mercury, and, even in small amounts, exposure to the metal can cause health problems. Meta-analyses have previously shown cardiovascular outcomes associated with mercury, but the possible association with apolipoproteins is unknown. This work evaluated human exposure to mercury and cardiovascular risk using lipid (including apolipoproteins) and genetic profiles in an Amazonian riverine population without influence of anthropogenic activities using mercury. After ethical approval (CONEP/Brazil, CAAE nº 43927115.4.0000.0018), anthropometric data (sex, age, height, weight, blood pressure and neck and waist circumferences) were recorded. Hair mercury (total, THg, and methylmercury, MeHg) was quantified by ICP-MS and/or GC-pyro-AFS systems. The polymorphisms rs662799, rs693, rs429358 and rs7412 (of the ApoA-V, ApoB, and ApoE genes at positions 112 and 158, respectively) were genotyped by qPCR. The Amazonian population presented a dyslipidemia profile significantly correlated with mercury levels, without any significant genetic influence. Allelic distributions were similar to those described in other populations, without any significant influence on the lipid profile of exposed individuals, supporting exposure to the metal as the main responsible for dyslipidemia. Surprisingly, median (and interquartile ranges) of hair mercury was 7,991 (3,711–14,691) ng/g, demonstrating that, in the Amazonian environment, human exposure to mercury can be found very far from anthropogenic mercury emissions. Interestingly, multiple regression analyses showed the ApoB/ApoA-I index positively correlated with THg, supporting a probable causal relationship. This study demonstrated for the first time the relationship between mercury exposure and apolipoproteins related to cardiovascular risk in humans. Furthermore, the ApoB/ApoA-I index was associated with mercury-related dyslipidemia, proving to be good biomarker to be used in public health strategies for the prevention and early detection of cardiovascular changes caused by mercury in Amazonian vulnerable populations.

## Evaluation of the accumulation and translocation of mercury species in hydroponic crops of *Lactuca sativa*

Veneciano R<sup>1</sup>, Jiménez-Moreno M<sup>2</sup>, Bravo M<sup>1</sup>, Rodríguez Martín-Doimeadios R<sup>2</sup>

<sup>1</sup>Laboratory of analytical and environmental chemistry, Institute of Chemistry, <sup>2</sup>Institute of Environmental Sciences, Department of Analytical Chemistry and Food Technology

Vegetables such as lettuce can serve as a pathway for mercury to enter the human food chain since plants can accumulate this metal from the surrounding soil or water and then translocate to their edible parts. Agricultural soils close to mercury source exhibit higher concentrations of mercury. However, there is a lack of studies addressing the translocation and distribution of mercury species in highly consumed vegetables grown in contaminated environments.

Thus, this study focuses on the translocation and accumulation of monomethylmercury (MeHg<sup>+</sup>) and inorganic mercury (Hg<sup>2+</sup>) in different *Lactuca Sativa* varieties. For this purpose, hydroponic cultures were conducted in nutritive solutions (pH=7, conductivity=1400  $\mu\text{s cm}^{-1}$ ) contaminated with Hg<sup>2+</sup> (500 to 1000  $\mu\text{g L}^{-1}$ ) or MeHg<sup>+</sup> (50 to 100  $\mu\text{g L}^{-1}$ ). The cultures grew for 45 days, with 16 h of light exposure. Mercury species were determined using a previous optimized methodology for plant tissues based on an acidic extraction and a further analysis via GC-pyro-AFS.

Effective translocation from hydroponic system to the entire plant was observed reaching translocation factors up to 29 in Hg<sup>2+</sup> contaminated crops and 45 in MeHg<sup>+</sup> polluted ones. Regarding species distribution, higher concentrations of MeHg<sup>+</sup> and Hg<sup>2+</sup> were found in the roots. Speciation analysis revealed that varieties exposed to Hg<sup>2+</sup> could accumulate a 99.9% of Hg<sup>2+</sup> in the entire plant. In contrast, in environments contaminated with MeHg<sup>+</sup>, a maximum of 32% MeHg<sup>+</sup> was recovered in the plant, and the remaining 68% corresponds to Hg<sup>2+</sup>. This suggests a potential transformation of MeHg<sup>+</sup> in the plant as a defense mechanism against stress during its growth. In summary, this research supports the effective translocation and accumulation of mercury species in lettuce grown in contaminated environments. Furthermore, it suggests the existence of a defensive mechanism in the plant that involves the transformation of MeHg<sup>+</sup> to a less harmful form.

## Drivers of mercury contamination, methylmercury formation and mercury sources within lake sediments across the contiguous United States

Lepak R<sup>1</sup>, Janssen S<sup>1</sup>, Vitense K<sup>1</sup>, Hollenhorst T<sup>1</sup>, Geyman B<sup>1</sup>, Krumwiede B<sup>1</sup>, Tate M<sup>1</sup>, Krabbenhoft D<sup>1</sup>  
<sup>1</sup>Us Environmental Protection Agency

Atmospheric deposition is the predominant source of mercury (Hg) to food webs across the United States and is dictated by both international and domestic emissions. This study's objectives are to identify ecosystem drivers of sensitivity to Hg inputs and Hg sources to provide the framework to predict how changes in Hg emissions will impact aquatic ecosystems. This will be accomplished through spatial analyses of existing data, including over 1000 sites measured for speciated Hg concentrations in sediment, and through recent Hg-isotope analyses of a subset of over 400 sites from the USEPA 2012 National Lakes Assessment (NLA). Identifying the spatial drivers for ecosystem sensitivity to Hg inputs and responsiveness throughout the U.S. will rely upon many existing federal datasets sediment chemistry (NLA metadata), atmospheric Hg measurements (e.g., National Atmospheric Deposition Program), emission inventories (National Emissions Inventory), and landscape physical lake characteristics (LakeCat and others). Stemming from a Random Forest model, top predictors of Hg concentrations in sediments were catchment characteristics and the GEOS-Chem modeled Hg deposition. Relatively less predictive ability was found for lake trophic status, productivity, or proximity to urban areas. When evaluating Hg isotope heterogeneity across the U.S., we observed isotope clustering within ecoregions to form regional isoscapes. Largely the isotope heterogeneity was driven by differences in precipitation, erosion, and water residency rather than trophic condition or proximity to urban areas. While this work seeks to understand drivers of Hg contamination and Hg sources, it also marks our only known effort to constrain the range of Hg isotope values that may be measured in lake sediment. In that sense, this study serves as a platform for cross evaluation for studies that are comparatively less spatially robust or for ecosystems that lack the wealth of metadata presented here.

## Effects of Habitat on Mercury Exposure in Breeding Songbirds in Southern Massachusetts

Benoit J<sup>1</sup>, Jernakoff M<sup>2</sup>, Knowlton J<sup>1</sup>

<sup>1</sup>Wheaton College, <sup>2</sup>US Department of the Interior, Land Management Division

The objective of this study was to compare mercury exposure between song birds living near cranberry bogs to those living at a distance from them. We set up mist nets on powerline cuts that were adjacent to cranberry bogs or within suburban developments in Bristol and Plymouth counties in Massachusetts during June and August 2018. Blood samples were drawn from the brachial veins of captured birds. We measured HgT in the blood by acid digestion and CVAFS. Four species were analyzed: American Robin (*Turdus migratorius*), Gray Catbird (*Dumetella carolinensis*), Song Sparrow (*Melospiza melodia*), and Yellow Warbler (*Setophaga petechia*). Blood HgT levels ranged between 0.02 – 0.5 ug/gww. Twelve individuals had blood Hg  $\geq$  0.2  $\mu$ g/gww, the lowest observed effects level, and four individuals from the cranberry bog site had blood Hg  $\geq$  0.3 ug/gww, a level that has been associated with adverse reproductive impacts in birds.

Analysis of the whole data set (n=53) showed that HgT was not significantly different in birds from the two sites ( $p \geq 0.05$ ) but was greater in blood collected in June as compared to August ( $p < 0.001$ ). In a subset of the birds in which sex was determined (n=39), males (n=24) showed significantly higher HgT concentrations than females (n=15), and the difference between sites was significant for males but not for females. In contrast, only females showed significantly higher HgT levels in June compared to August, which suggests that transfer of Hg into eggs was an important mechanism lowering blood Hg concentrations. Overall, results indicate that: 1) cranberry bogs contribute Hg to terrestrial food webs, 2) Hg bioaccumulation in birds differs between sexes, and 3) Hg bioaccumulation varies temporally across suburban/agricultural landscapes. This study also shows that Hg exposure in song birds can reach concerning levels in areas receiving only long-range atmospheric deposition.

259

## Drivers of mercury biomagnification by freshwater predatory invertebrates in the field and the laboratory

Sinclair C<sup>1</sup>, Garcia T<sup>1</sup>, Eagles-Smith C<sup>2</sup>

<sup>1</sup>Oregon State University, <sup>2</sup>United States Geological Survey

Mercury cycling in aquatic communities is driven by many complex and interactive factors that change mercury bioavailability and trophic transfer, making tissue data the most representative estimate of risk. Freshwater food webs in general biomagnify organic methylmercury (MeHg) by a factor of about 8 from one trophic level to the next, with high variability within and across landscapes. Biomagnification rates for wider aquatic communities may not accurately characterize dynamics for sub-communities like invertebrates. Dragonfly larvae and other predatory invertebrates are increasingly being used to monitor MeHg impairment, yet their mercury uptake is poorly understood. We sought to estimate predatory invertebrate biomagnification of MeHg from field and experimental data. To synthesize field observations, we conducted a meta-analysis of relevant literature to estimate mercury biomagnification by predatory invertebrates using multiple methods. We also ran a series of laboratory experiments measuring dietary mercury accumulation by larval dragonflies. Preliminary meta-analytic results suggest that freshwater predatory invertebrates do not biomagnify MeHg as efficiently as previously thought, with overall biomagnification estimates ranging from 2.1 to 4.3, with 95% credible intervals from 1.6 to 5.3. Experimental biomagnification by larval dragonflies was also unexpectedly low, with preliminary biomagnification factors under 3 for all dosed treatments. More refined understanding of how biomagnification rates vary and what drives variability in larval dragonflies and other predatory invertebrates is critical to better estimate and manage risk to wildlife and human health.

260

## New insights in Hg and Se speciation in the rainbow trout, an aquaculture model

Ouerdane L<sup>1</sup>, El Hanafi K<sup>1</sup>, Fernández Bautista T<sup>2</sup>, Corns W<sup>3</sup>, Bueno M<sup>1</sup>, Pannier F<sup>1</sup>, Fontagné S<sup>4</sup>, Amouroux D<sup>1</sup>, Pedrero Zayas Z<sup>1</sup>

<sup>1</sup>Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, <sup>2</sup>Departamento de Química Analítica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, <sup>3</sup>PS Analytical,

<sup>4</sup>Université de Pau et des Pays de l'Adour, E2S UPPA, INRAE, NUMEA

Fish bioaccumulate methylmercury (MeHg), which leads to a potential risk for higher trophic levels including humans. The fate of mercury (Hg) in fish as well as its potential interaction with selenium (Se), considered a potential toxicity antagonist, is not known so far and may contribute answering unresolved questions of socioeconomic and health interest. The current study aims to provide novel information about dietary fate of Hg and Se species in an aquaculture fish model, the rainbow trout (*Oncorhynchus mykiss*). Juvenile fishes were dietary exposed individually and simultaneously to MeHg and Se species (precisely selenomethionine and selenite) through the fortification of two different diets based either on fish byproducts or on plants. Internal tissues (blood, brain, liver, kidneys and muscle) were collected during the 6 months feeding trials.

In fish tissue collected at different time of exposure during feeding trials, low molecular weight biomolecules containing Hg or Se were characterized. It was made possible by the coupling of either size exclusion chromatography (SEC) or hydrophilic interaction chromatography (HILIC) to a combination of mass spectrometry (MS) instrument to look for elemental (ICP MS) and molecular (ESI MS) information. In particular, the use of high-resolution molecular MS (orbitrap) gave the opportunity to identify molecules involved in Hg binding. This study brings new insight about the fate of Hg and Se in key fish tissues.

261

## Mapping China's Mercury Emission (1978-2021) Based on Point Sources

Wu Q<sup>1</sup>, Cui Y<sup>1</sup>, Wang S<sup>1</sup>

<sup>1</sup>Tsinghua University

Anthropogenic mercury (Hg) emissions persist in various environmental mediums and subsequently enter the food chain, posing a risk to human health. Time-continuous gridded emission datasets are critical and urgent to understand the effectiveness of mercury pollution control at both global and national scale. Here we compile a new comprehensive point source database covering 1978-2021 by using multiple data source fusion, which includes nearly 190,000 industrial facilities in 2021. We integrate it with our China Atmospheric Mercury Emission Model (CAME) to create an annual gridded emission dataset. Consequently, the percentages of point source emissions in total reached over 80% in 2021. The new point source-based emission maps significantly reduce the modeled biases of atmospheric mercury concentrations at urban sites, generally polluted and populated areas, up to a maximum of 34%, thus improving the assessment of population exposure. The new accurate and annual high-resolution emission map indicated that approximately 20% of cumulative emissions are located in 0.3% of grides, providing an opportunity to identify the hotspots of cumulative emissions and cross-media impacts.

## Drivers of global mercury emissions during 2017 - 2022

Wang S<sup>1</sup>, Wu Q<sup>1</sup>

<sup>1</sup>Tsinghua University

The Minamata Convention is concerned with anthropogenic mercury emissions and requested the signed parties to control five specific source categories that are listed in Annex D according to Article 8. These five sources include coal-fired power plants, coal-fired industrial boilers, non-ferrous metals production, waste incineration and cement clinker production. This study calculates the global emissions in these five sources from 2017 to 2022 in order to assess the implementation of the Minamata Convention. Results show that global mercury emissions decrease from 821 t in 2017 to 717 t in 2022, suffering a rapid decline of 46 t in 2020 caused by pandemic and a slide growth of 9 t in 2011 due to economic recovery. Non-ferrous metals production contributes most, decreasing 83 t in total, followed by cement clinker production with 29 t. Waste incineration, however, increases 27 t of emissions in six-year period. Regional contribution to global mercury emissions has changed little, with Asia reducing its mercury emissions by 55 t in six years. We use driver analysis and find that the implementation of BAT/BEP measures in five sources helps decrease 180 t of mercury emissions in total and efficiency improvement help decrease 110 t of emissions. Sustainability development only brings a reduction of 33 t from 2017 to 2020 then drives an increase of 60 t from 2021 to 2022 since strong demand of economic recovery in post-pandemic period curtailed to the circularity development of the economy. The Minamata Convention has been best implemented in non-ferrous metals production and coal-fired power plants, resulting in 78 t and 56 t of emissions reduction, respectively. The driver analysis developed in this study could also evaluate the implementation result in other countries or industries, helping government better achieve national mercury control.

## Long-Term Changes in Contributions of Anthropogenic and Natural Perturbations to Atmospheric Mercury in the United States

Zhang L<sup>1</sup>, Liu X<sup>1</sup>, Zhang J<sup>1</sup>, Jaffe D<sup>2</sup>, Zhang G<sup>1</sup>, Zhang W<sup>1</sup>, Zhou P<sup>1</sup>

<sup>1</sup>Nanjing University, <sup>2</sup>University of Washington Bothell

There has been a substantial reduction of anthropogenic Hg emissions to the atmosphere in the US since 1990s. However, observations from the Atmosphere Mercury Network (AMNet) and the Mercury Deposition Network (MDN) showed insignificant overall decreasing trends in the gaseous elemental mercury (GEM) concentration and the Hg wet deposition flux in the recent decade. Some sites even exhibited ascending trends. To explore changes in the contributions of anthropogenic and natural perturbations to atmospheric Hg, an eXtreme Gradient Boosting (XGBoost) model combined with the SHapley Additive exPlanations (SHAP) interpretable algorithm and a generalized additive model (GAM) were developed in this study for qualifying their impacts on GEM and Hg wet deposition, respectively. The two types of statistical/machine learning models are useful tools for deciphering key drivers of the spatiotemporal patterns.

Location plays the most important role in the change of the GEM concentration. Longitude, latitude and elevation, which mainly represent anthropogenic activities, climatic condition and atmospheric chemical condition, respectively, contribute 40% to the variance of GEM. The contributions of intra- and inter-regional transport to GEM have been fading in the recent decade, indicating the effectiveness of anthropogenic emission reduction in North America. The increasing contributions of temperature and solar radiation to GEM imply the decelerating effect of climate change on the declining of GEM. The two meteorological factors have much higher impacts on the Hg wet deposition flux than on GEM. The influencing patterns of temperature and solar radiation on Hg wet deposition are quite similar as those on GEM, reflecting the three-step cycle of atmospheric Hg. The residuals of GAM in the western US peaked in 2012–2013 which was consistent with the anthropogenic Hg emissions in East Asia. Our findings suggest that natural perturbations have been gradually taking over the crucial role of anthropogenic emissions on atmospheric Hg.

264

## Illuminating microbial taxa responsible for methylmercury degradation by tracking carbon consumption

Liu Y<sup>1</sup>

<sup>1</sup>Huazhong Agricultural University

Methylmercury (CH<sub>3</sub>Hg<sup>+</sup>) is a potent neurotoxin that threatens human health and wildlife due to its ability to bioaccumulate significantly through the food chain. While microbial demethylation has been recognized as a crucial pathway of CH<sub>3</sub>Hg<sup>+</sup> degradation, the microbial communities accountable for CH<sub>3</sub>Hg<sup>+</sup> degradation in environments have remained elusive. Using <sup>13</sup>C-labeled CH<sub>3</sub>Hg<sup>+</sup> and combined analyses of <sup>13</sup>C-enriched DNA and shotgun metagenomics, here we explored microbial taxa and associated biochemical processes involved in CH<sub>3</sub>Hg<sup>+</sup> degradation in the soils with distinct background mercury levels. The qPCR analysis of <sup>13</sup>C-derived 16S rRNA genes revealed that soil microorganisms assimilated <sup>13</sup>CH<sub>3</sub>Hg<sup>+</sup> after 14 days of incubation. We identified *Arenimonas*, *MM2*, and *Dechloromonas* as the most significant genera potentially engaged in the consumption of <sup>13</sup>CH<sub>3</sub>Hg<sup>+</sup> in the paddy soil characterized by high Hg contamination. We further validated considerable ability of putative taxa (e.g., *Dechloromonas denitrificans* and *Methylovorus mentalis*) to degrade CH<sub>3</sub>Hg<sup>+</sup> by pure culture assays. Furthermore, reconstructed metagenome-assembled genomes from the <sup>13</sup>C-labeled DNA unveiled functional genes associated with processes including Hg reduction, Wood-Ljungdahl pathway, dicarboxylate-hydroxybutyrate cycle, methanogenesis, denitrification, and nitrate reduction. Collectively, these findings provide unprecedented new insights into the soil microorganisms responsible for CH<sub>3</sub>Hg<sup>+</sup> degradation and offer a novel avenue for the development of bioremediation strategies targeting CH<sub>3</sub>Hg<sup>+</sup> contamination.

## Mercury in shallow and deep lakes within a Hg hotspot of the southeastern Patagonian Andes: insights into seasonal and spatial patterns

Diéguez M<sup>1</sup>, Fernandez Z<sup>1</sup>, Soto-Cárdenas C<sup>1</sup>, Arcagni M<sup>2</sup>, Pérez Catán S<sup>2</sup>, Rizzo A<sup>2</sup>

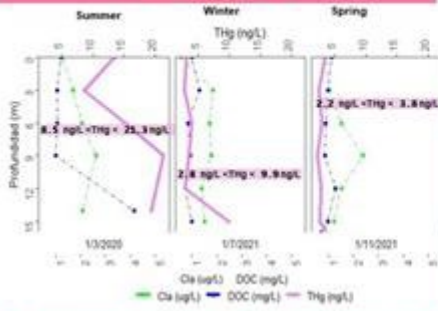
<sup>1</sup>Laboratorio GESAP, INIBIOMA National Scientific and Technical Research Council of Argentina (CONICET), <sup>2</sup>Laboratorio LAAN, Centro Atómico Bariloche, Comisión Nacional de Energía Atómica AB-CNEA

On the eastern side of the Patagonian Andes (Argentina), deposition of mercury (Hg) from volcanic sources and reemission from the Pacific Ocean, favored by atmospheric transport by the westerly winds and orographic precipitation, create Hg hotspots in headwater catchments. We studied the seasonal dynamics of Hg in two connected lakes, the shallow lake Pire and the deep lake Brazo Rincón, within a natural Hg hotspot inside Nahuel Huapi National Park. Hg<sub>2+</sub> was found as the dominant species in lake water (>98%) and in-lake THg dynamics were related to seasonal hydrologic inputs and terrestrial dissolved organic matter (DOM) fluxes. In both lakes, THg concentrations in water were related directly to allochthonous DOM signatures, particularly in the wet season, indicating terrestrial origin and hydrologic mobilization. In the shallow lake, the highest THg concentration (21.30 ng/L) and the lowest (2.22 ng/L) were found in summer and spring, respectively. In contrast in the deep lake the highest concentration (1344.58 ng/L) was recorded in winter and the lowest (1.73 ng/L) in summer. In both lakes, deeper strata displayed higher THg in winter and summer while more even concentrations across depths were found in spring. Overall, the high values recorded of THg:DOC (due to extremely low DOC) and of THg:chlorophyll a, and the positive correlation between THg and chl a in both lakes, indicate the high Hg availability and uptake by phytoplankton. These results suggest that, independent of lake depth, Hg inputs from the catchment determine THg levels in the water column, while DOC levels and MOD quality collectively control Hg availability and uptake at the base of pelagic food webs. Temporal overlap of high Hg availability and high phytoplankton primary production would favor Hg entry into pelagic food webs in ultraoligotrophic Andean-Patagonian lakes.

Keywords: Andean-Patagonian lakes, Hg hotspot, Hg availability, Hg uptake

### Abstract Graphics

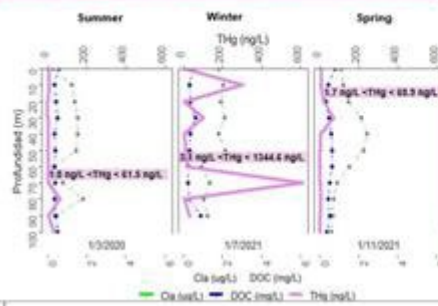
### Shallow lake Pire



2.22 ng/L < THg < 21.30 ng/L

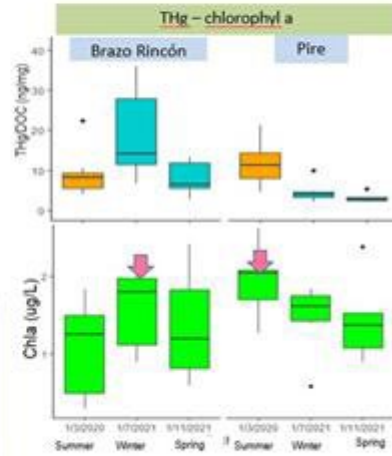
- >THg summer (March)
- <THg en spring (November)
- >THg in deep strata in summer and winter
- THg homogeneous across depth in spring

### Deep lake Brazo Rincón (Nahuel Huapi)



1.73 ng/L < THg < 1344.58 ng/L

- <THg in summer (March)
- >THg winter (July)
- >THg in deep strata in summer and winter
- THg homogeneous across depth in spring



## Characterising summertime atmospheric mercury in the Southern Ocean and Antarctic Coast marine boundary layer during the 2024 MISO Voyage

Powell J<sup>1</sup>, Humphries R<sup>1</sup>, Dunne E<sup>1</sup>, Franklin E<sup>1</sup>, Harnwell J<sup>1</sup>, Molloy S<sup>1</sup>, Somerville N<sup>2</sup>, Alroe J<sup>3</sup>, Mallet M<sup>4</sup>

<sup>1</sup>Commonwealth and Scientific Research Organisation (CSIRO Environment), <sup>2</sup>Bureau of Meteorology, <sup>3</sup>International Laboratory for Air Quality and Health, Queensland University of Technology, <sup>4</sup>Institute for Marine and Antarctic Studies (IMAS), University of Tasmania

The role of atmospheric processes in mercury cycling in the pristine Southern Ocean and Antarctic regions is important but incompletely understood, with limited observations relative to other global regions. The Multidisciplinary Investigations of the Southern Ocean (MISO) voyage, traversing 10,000 km over 60 days in early 2024, provided a unique opportunity to quantify spatial variations in mercury concentrations in the Southern Ocean and along the Antarctic coastline. Throughout MISO, ambient concentrations of gaseous elemental mercury (GEM) were continuously measured onboard the Australian research vessel RV Investigator, along with a suite of complementary atmospheric and meteorological measurements. During the voyage, air-sea interactions were additionally studied using ship-board mesocosm studies of natural seawaters collected at 3 process stations along the Antarctic coast transect and incubated for ~5 days each. These experiments are a novel approach to characterising air-sea interactions of trace gases (including GEM) with seawater biota, biogeochemistry and environmental conditions.

Preliminary results show little temporal or spatial variation in ambient concentrations in the open ocean segments of the voyage, with GEM similar to that observed at Australia's baseline station at Kennaook/Cape Grim, where observations of air masses from the Southern Ocean have been made for a decade. Along the Antarctic coastline however, concentrations of GEM are much more variable over time, with periods of enrichment and depletion observed. Of particular note was a depletion event observed in the D'Urville Sea. This event lasted 48 hours and coincided with elevated ozone and winds likely originating from the Antarctic plateau, which has a high capacity in summer to oxidise Hg(0) to Hg(2+).

Overall, these ambient measurements, along with small scale process studies, contribute to our understanding of sources, sinks and drivers of mercury over the pristine Southern Ocean and Antarctic regions which remain some of the most under sampled regions in the world.

## Temporal dynamics and internal variations of mercury isotopes in a marine fish (Starry flounder, *Platichthys stellatus*) during bioaccumulation and excretion

Jung S<sup>1</sup>, Kwon S<sup>1</sup>

<sup>1</sup>Pohang University Of Science And Technology

Mercury (Hg) isotope ratios in fish tissues have been used to infer the sources and biogeochemical processes of mercury in aquatic ecosystems. Unfortunately, limited experimental studies have been performed to understand the internal dynamics of mercury isotopes and to further assess the feasibility of using fish mercury isotope ratios as a monitoring tool. In particular, our understanding of the potential variations in Hg isotopes over time caused by excretion, a vital detoxification mechanism in fish, remains incomplete. In this study, we exposed Starry flounder (*Platichthys stellatus*) to the pellets spiked with varying concentrations of inorganic Hg (IHg; 2  $\mu\text{g/g}$ , 25  $\mu\text{g/g}$ ) and methylmercury (MeHg; 1  $\mu\text{g/g}$ ) for 4 weeks and then switched to control pellets to observe tissue-specific Hg isotope variations during the 16-weeks excretion period. All tissues except for muscle exhibited complete equilibration of  $\delta^{202}\text{Hg}$  and  $\Delta^{199}\text{Hg}$ , regardless of the speciation and concentration of the exposed Hg. While the equilibration in  $\Delta^{199}\text{Hg}$  maintained throughout the excretion period,  $\delta^{202}\text{Hg}$  varied depending on the exposed Hg speciation and tissue type. Notably, substantial negative shifts in  $\delta^{202}\text{Hg}$  were observed in the liver and kidney during excretion. For fish fed MeHg pellets, the negative  $\delta^{202}\text{Hg}$  shifts in the liver were attributed to MeHg demethylation and the redistribution of isotopically heavier MeHg to other tissues. In contrast, IHg-fed fish exhibit negative  $\delta^{202}\text{Hg}$  shifts during excretion, which is expected to be resulted from the elimination of isotopically lighter glutathione-bound IHg with decreasing Hg concentration. The absence of  $\Delta^{199}\text{Hg}$  changes during excretion ensures the applicability of fish Hg isotopes as Hg source tracers. Furthermore, temporal variations in Hg concentration and isotope ratios in fish tissues provide comprehensive insights for establishing time-dependent Hg remediation guidelines and evaluating the effectiveness of Hg regulations, both locally and globally.

## Does Wetland Act as a Source or a Sink of Atmospheric Mercury

Zhang L<sup>1</sup>, Zhou H<sup>1</sup>, Zhou H<sup>1</sup>, Chang J<sup>1</sup>, Yu Q<sup>1</sup>, Zhao Y<sup>1</sup>

<sup>1</sup>Nanjing University

Wetland is among the most sensitive and complex ecosystems. The source–sink relationships of atmospheric Hg in wetlands are poorly defined. To better understand the characteristics and key drivers of surface–air Hg exchange in wetland, in-situ measurements were conducted in the Baguazhou wetland (BWL) in eastern China. A dynamic flux chamber (DFC) attached to an automatic Hg vapor analyzer was adopted to measure gaseous elemental mercury (GEM) exchange fluxes over two landcover types from September 2022 to July 2023.

The surface–air fluxes of GEM were  $-0.12$  (mudflat) and  $-0.08$  (waterfront)  $\text{ng m}^{-2} \text{h}^{-1}$  in spring,  $0.39$  (mudflat) and  $0.42$  (waterfront)  $\text{ng m}^{-2} \text{h}^{-1}$  in summer, and  $1.72$  (mudflat) and  $0.81$  (waterfront)  $\text{ng m}^{-2} \text{h}^{-1}$  in fall. The mean ambient GEM concentrations were  $1.04$ ,  $2.94$  and  $2.63$   $\text{ng m}^{-3}$  in spring, summer and fall, respectively. The diurnal pattern of GEM flux is characterized by high daytime level and low nighttime level with a peak in the midday. GEM fluxes were found to be positively correlated with solar radiation and air or soil temperatures. Soil Hg reduction driven by solar radiation and soil moisture and Hg re-emission driven by soil temperature could be the most likely sources of GEM fluxes. Plants play a comprehensive role in wetland surface–air Hg exchange. Emergent macrophytes have been found to promote GEM emissions through evaporation from vascular tissues in previous studies. However, the dwarf aquatic plants at BWL in this study acted more as a sink of Hg through stoma uptake, which highly compromised soil Hg emission in spring and summer with lush vegetation. Fall, with strong solar radiation and withered plants, exhibited strong Hg emission fluxes. Overall, a typical wetland in eastern China acts as a strong source of atmospheric Hg in summer and fall, while as a weak sink in spring.

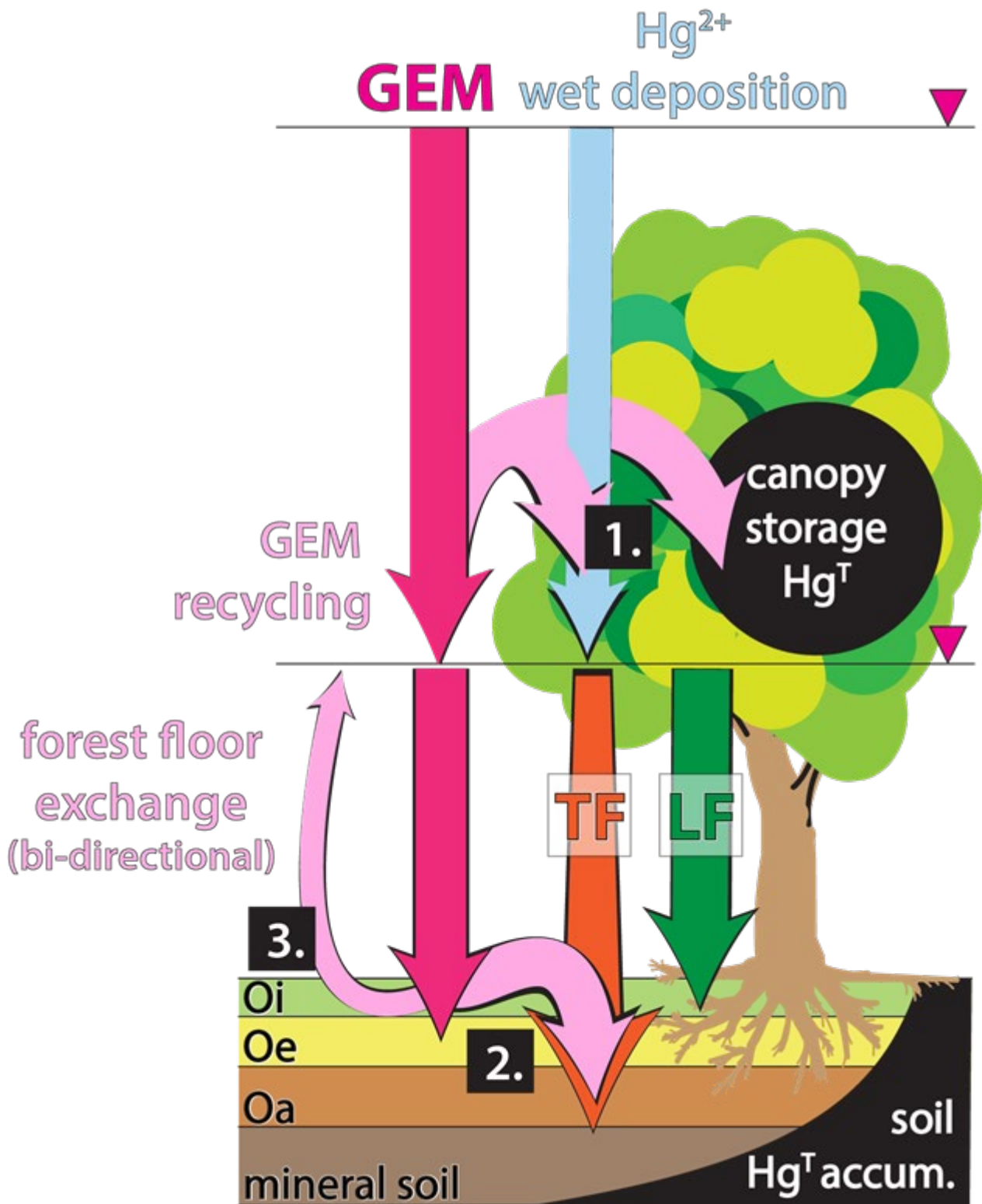
## Latitudinal gradients and quantitative accumulation of atmospheric Hg in forest soils

Landis J<sup>1</sup>, Obrist D<sup>2</sup>, Zhou J<sup>3</sup>, Renshaw C<sup>1</sup>, Palucis M<sup>1</sup>, Del Vecchio J<sup>4</sup>, McDowell W<sup>5</sup>, Nytch C<sup>6</sup>, Montano F<sup>1</sup>, Taylor V<sup>1</sup>

<sup>1</sup>Dartmouth College, <sup>2</sup>University of Massachusetts, <sup>3</sup>Institute of Soil Science, Chinese Academy of Sciences, <sup>4</sup>College of William and Mary, <sup>5</sup>University of New Hampshire, <sup>6</sup>University of Puerto Rico

Soils are a principal global reservoir of mercury (Hg), a neurotoxic pollutant accumulated through a history of anthropogenic emissions to the atmosphere and subsequent deposition to terrestrial ecosystems. The fate of Hg deposition in soils remains fundamentally uncertain, however, particularly to what degree Hg is quantitatively retained or re-emitted back to the atmosphere as gaseous elemental mercury (GEM). Here we introduce a new bottom-up soil mass balance based on fallout radionuclide (FRN) chronometry that allows comparison of Hg soil accumulation rates with independent measures of total atmospheric Hg deposition to ecosystems. We show that soils spanning Arctic, temperate, and tropical ecosystems are unambiguously strong net sinks for atmospheric Hg, and that the soil sink strength decreases with latitude. Peak deposition in years 1950-2000 strongly exceeded contemporary fluxes by factors of approximately two. In the northeastern USA, soil-derived Hg accumulation rates are confirmed in timing and magnitude with records derived from lake sediments and direct atmospheric measurements. We further show that typical soils are quantitatively efficient at retaining atmospheric Hg deposition, with exception of a subset of soils (about 20%, all temperate coniferous), where approximately 10% of Hg deposition is unaccounted for. The observation that Hg in soils is effectively sequestered long-term calls into question global model and mass balance studies that assume a continued re-cycling of legacy Hg pollution in the environment that thereby prolongs the impacts of past Hg emissions. Availability of FRN chronometry to reconstruct soil Hg accumulation rates poses a powerful new tool to quantify Hg deposition and trends across much larger spatial scales than previously possible, and should advance the understanding of Hg deposition, accumulation, and fate in the context of changing global environment.

### Abstract Graphics



271

## Mercury legacy from historical silver refining in Hispanic America: a tale from Guanajuato, Mexico

Wang F<sup>1</sup>, Loria A<sup>1</sup>, Schindler M<sup>1</sup>, Ramos-Arroyo Y<sup>2</sup>

<sup>1</sup>University of Manitoba, <sup>2</sup>Universidad de Guanajuato

Silver production in Hispanic America between the 16th and 19th centuries is thought to be one of the largest sources of anthropogenic mercury emissions in history. Recent reviews of the chemistry involved in the mercury-aided silver refining process reveal that a large amount of the mercury may not have been immediately released to the atmosphere as previously thought; instead it may have persisted locally in the form of calomel (in which mercury is present as the monovalent Hg(I)) and may have a lasting impact on the local environment and communities. Here we show that mercury used in the silver refining process centuries ago in the Guanajuato Mining District of Mexico continues to elevate present-day concentrations of gaseous elemental mercury (GEM) throughout the region. GEM in the ground-level air at various locations across the region was found to be more than two orders of magnitude higher than the expected ambient background values. Exceedingly higher concentrations, up to 44,700 ng/m<sup>3</sup>, were found in the interstitial air of reprocessed mineral waste, sediment, and soil. Mineralogical analysis of sediment samples shows the presence of mercury-bearing nano-mineral assemblages containing both mercury-silver amalgam phases and mercury-sulfide nanoparticles. Monovalent Hg(I) was detected analytically in extracted solutions, but was not identified mineralogically in the solid, suggesting most of the calomel had already disproportionated to elemental and divalent mercury. Our results imply that the contribution of historical silver refining in Hispanic America to atmospheric mercury emissions must be re-evaluated to account for cumulative releases of GEM to the present-day. Long-term mercury monitoring and human health studies are also advised to assess the chronic impact of the legacy mercury in the region.

## Remediation of Mercury-Contaminated Former Industrial Facilities in Urbanized Areas

Carrillo-Sheridan M<sup>1</sup>

<sup>1</sup>Anchor QEA, LLC

Throughout the USA, urban centers are undergoing revitalization and redevelopment. The federal Brownfields Utilization, Investment and Local Development Act (2018) and state-level grants/tax credit programs incentivize developers to redevelop former industrial facilities, often for residential use. Federal and state historic tax credit programs provide additional incentives for building owners to redevelop former industrial facilities while maintaining original building character and features. In the past 30 years, several former industrial facilities in urban centers have had their redevelopment plans interrupted due to the discovery of elemental mercury within the building structure (including walls and floors). This presentation will examine the types of industrial processes of the 19th and early 20th century that utilized elemental mercury as either a raw material or within certain types of manufacturing equipment; hypotheses regarding migration of mercury from manufacturing areas into building fabric; and potential for mercury exposure to current or future building occupants. A case study will also be presented detailing a recently completed (2023) remediation of multiple mercury-contaminated former industrial buildings located in a residential area in one of the most urbanized areas in the USA. The case study will include:

- An overview of the means and methods employed to locate and map elemental mercury contamination in the different buildings, including between layers of concrete floors and within masonry and wood structures.
- Strategies employed to stabilize mercury-contaminated materials and limit mercury vapor generation for worker protection during building decontamination.
- Building deconstruction methods.
- Community air monitoring performed to document site remediation work was protective of surrounding residential community.
- Post-demolition assessment and remediation of mercury-contaminated subsurface piping, foundations, and soils.
- Treatment methods developed to stabilize in-situ elemental mercury in subsurface areas that could not be removed or remediated due to the presence of critical urban infrastructure.

## Mercury Speciation and HAP Emissions in Commercial Sludge Combustion Plant

Jang H<sup>1</sup>, Choi M<sup>1</sup>, Chu J<sup>1</sup>

<sup>1</sup>Yonsei University

Waste sludge is characterized by high moisture, volatile compounds, toxic compounds, and ashes. The economical operation of commercial fluidized bed combustion (FBC) plants is important for reducing operational costs. We selected a commercial FBC plant for industrial waste sludge combustion to investigate the mass balance of the FBC process and the performance of the air pollution control device. Based on fuel analysis, the flow rate of incineration air was calculated as 4,567 Nm<sup>3</sup>/h. After FBC combustion, the flow rate of the incineration gas increased to 8493.8 Nm<sup>3</sup>/h. Analysis of the heat balance showed that some heat potential was lost through leakage during the combustion process. The temperature of the incineration gas decreased to 200°C at the inlet of the air pollution control device. Concentrations of hazardous gaseous pollutants (HAPs) such as fine particulate matter, heavy metals, and dioxin from sludge combustion before and after air pollution control devices were measured and analyzed at commercial operating conditions of one typical incinerator. Most of the emission data at stack showed under the environmental regulatory limits. Mercury and some heavy metals emissions have been reduced significantly as co-beneficial effects since the air pollution control configuration was well arranged and installed to control the regulatory gases such as NO<sub>x</sub>, SO<sub>2</sub>, particulates, and dioxin. Sludge, especially generated from industrial plants, contained measurable amounts of acidic materials and heavy metals including Hg. According to hazardous air pollutant emission testing of sampling points, the operation factors of lime slurry injection for SO<sub>x</sub> and HCl at the semi-dry reactor were 64.20 and 4.81 kg/h, respectively. In the wet scrubber, the operation factors of NaOH for SO<sub>x</sub> and HCl were 23.88 and 3.14 kg/h, respectively. At these operation factors, the available waste generation at the semi-dry reactor and WA were optimized to 76.6 and 42.57 kg/h, respectively.

## Melting Himalayas and Mercury Export: Results and Perspectives from Everest Proglacial Rongbuk River and Trans-Himalayan Koshi River

Zhang Q<sup>1</sup>, Sun X<sup>1</sup>

<sup>1</sup>State Key Laboratory of Tibetan Plateau Earth System, Resources and Environment, Institute of Tibetan Plateau Research, Chinese Academy of Sciences

Rapid recession of glaciers in the Himalayan region has raised concerns regarding the release of legacy pollutants, including mercury (Hg), and its potential impact on downstream ecosystems. We conducted continuous and seasonal sampling in the Everest Rongbuk Glacier-fed river and the trans-Himalayan Koshi River, respectively. In the Rongbuk River, the concentrations of total Hg (THg) and methyl Hg (MeHg) were found to be  $1.56 \pm 0.85$  ng/L and  $0.057 \pm 0.025$  ng/L, respectively. These levels were comparable to global background levels and were primarily influenced by the presence of total suspended particulate matter (TSP). Based on the annual runoff and average Hg concentration, the estimated annual export fluxes of THg and MeHg were 441 g and 16 g, respectively, with yield rates of THg and MeHg measured at  $1.6 \mu\text{g}/\text{m}^2/\text{year}$  and  $0.06 \mu\text{g}/\text{m}^2/\text{year}$ , respectively. The overall annual Hg export through meltwater runoff in the Himalayan region was estimated to be approximately 337 kg/year. In the Koshi River, the THg concentration in surface water ranged from 0.64 to 32.96 ng/L, with an average level of  $5.83 \pm 6.19$  ng/L. The THg concentration followed the order of post-monsoon > monsoon > pre-monsoon. Particulate Hg (PHg) accounted for an average of 63% of THg and demonstrated a positive correlation with THg across all three seasonal samplings, indicating that the variation in PHg concentration played a significant role in the seasonal and spatial distribution of THg in the Koshi River water. The annual Hg exports and fluxes in the Koshi River were estimated to be 339.04 kg and  $3.88 \mu\text{g}/\text{m}^2/\text{year}$ , respectively, and are expected to further increase under continuous warming conditions. Our analysis shed light on the environmental impact of glacier retreat in the Himalayas and emphasizes the need of integrated monitoring and research on Hg in glacier runoff and trans-Himalayan rivers.

275

## The climate-mercury-fish nexus: A synthetic assessment from sub-Arctic and Arctic marine ecosystems

Bank M

<sup>1</sup>Norwegian Institute Of Marine Research, <sup>2</sup>University of Massachusetts Amherst

Food production systems and human diet choices have critical implications for climate change and environmental sustainability. Increasingly, ocean food resources are recognized as a source to meet global nutritional needs of a growing population and to address deepening problems from human hunger. The Northeast Atlantic Ocean (NEAO) is a large and important fishery and marine fish are sources of both nutrients and contaminants, including methylmercury which is highly toxic. However, despite its environmental and public health importance, critical questions and processes of mercury pollution cycling in the ocean remain unresolved, and poorly understood. Here, using complex systems analyses, mercury speciation measurements, stable isotope tracer models, and Bayesian information theory I present and synthesize new scientific findings and propose novel ideas about the relationships between climate, mercury pollution, marine fish, and ocean and human health. I will present a wide array of simple and complex modeling approaches including 'big data' analyses of (1) mercury and speciation in coastal and offshore marine fish communities in the NEAO, (2) mercury in atmospheric deposition and seawater from the NEAO, (3) information theory predictors and metrics, and (4) human health risk assessment using decision sciences. Mercury data models in different environmental matrices, from a wide array of ecosystem types throughout the NEAO, will be discussed to understand process drivers in the context of global environmental change. Future modeling scenarios will also be considered in the context of mercury pollution recovery at local, national, and global scales. I also describe and discuss these findings and models in the context of the UN Sustainable Development Goals, the UN Minamata Convention on Mercury, and the new UN Science-Policy Panel on Chemicals, Waste, and Pollution Prevention.

## Climate change effects on mercury cycling in high-altitude environments: insights and perspectives from research in the

### Nam Co basin on the Tibetan Plateau

Li M<sup>1,2,3</sup>, Zhang Q<sup>1,2</sup>, Wang J<sup>1,2</sup>, Lu Z<sup>1,2</sup>

<sup>1</sup> State Key Laboratory of Tibetan Plateau Earth System, Environment and Resources (TPESER), Institute of Tibetan Plateau Research, Chinese Academy of Sciences, <sup>2</sup>University of Chinese Academy of Sciences, <sup>3</sup>Department of Environmental Science, Stockholm University

The retreat of the cryosphere due to climate change, particularly glacier melt and permafrost thaw, has emerged as a key factor amplifying mercury (Hg) export. High mountain regions, especially those in the Tibetan Plateau, are undergoing rapid cryospheric changes, necessitating an in-depth investigation into the Hg cycling dynamics under the intertwined impact of various evolving environmental factors. After conducting an extensive literature review and thorough investigation, we identified the Nam Co Basin as a research hotspot for mercury cycling in the high mountain ranges of the Tibetan Plateau, involving various environmental media - atmosphere, sediment, water, and biosphere. The main findings indicate that mercury in these environments is mostly within the background values of the Northern Hemisphere, with atmospheric total gaseous mercury (TGM) at  $1.33 \pm 0.24$  ng/m<sup>3</sup>, lake sediment concentration at  $30.47 \pm 8.23$  ng/g, and aquatic at  $2.67 \pm 1.58$  ng/L. However, there is significant enrichment in mercury within lake food chains and fish bodies. The mercury released from glacier melting in this basin is  $2.74$   $\mu$ g/m<sup>2</sup>/year, which is higher than in the Arctic and Antarctic. Glacier meltwater input significantly affects Hg concentration in off-shore lake water, displaying higher concentration and spatial variation than the central lake water. Nam Co basin, renowned for its diverse and expansive cryospheric elements including glaciers, permafrost, snow, and lake ice, provides a solid research foundation and can serve as a “Paradigmatic Basin” for in-depth studies on mercury cycling changes and responses to climate change in high mountain areas. We call upon integrated analysis focused on mercury dynamics among different cryospheric elements in this watershed, identifying primary factors driving mercury transport and transformations, and exploring potential ecological implications as the cryosphere undergoes intensive changes. This can contribute to a scientific theoretical basis for understanding and managing mercury pollution in high-altitude environments in the future.

## Methylmercury formation in Cambodian rice paddy soil

Chuong M<sup>1</sup>, Skyllberg U<sup>2</sup>, Phan K<sup>3</sup>, Irgum K<sup>1</sup>, Björn E<sup>1</sup>

<sup>1</sup>Department of chemistry, Umea University, <sup>2</sup>Department of Forest Ecology and Management, Swedish University of Agricultural Science, <sup>3</sup>Faculty of Science and Technology, International University

Rice paddy is considered as one hotspot type of environment for methylmercury (MeHg) production. The formation of MeHg is predominantly driven by different anaerobe microorganisms and the activity of these microbes is controlled by the availability of metabolic electron donors and acceptors. The process of MeHg formation is also controlled by the availability of inorganic mercury (HgII) to such microbes. The solubility and availability of HgII depends on its chemical speciation, which is mainly controlled by the interaction of HgII with reduced sulfur (S) compounds. However, major knowledge gaps exist regarding how Hg-S interactions control MeHg formation in wetlands, in particular at varying redox condition. Moreover, the topic of MeHg formation has not been studied in Cambodia and there is thus a general lack of information regarding the process. The main objective of the study presented here is to understand how chemical speciation of S control formation of MeHg in selected Cambodia rice paddy soil. Soil samples from low-land and high-land regions were collected during late wet and dry seasons. In low-land regions, three soil types were sampled: Krokor, Prateah Lang, and Prey Khmer. The amount of MeHg, total Hg (THg), key soil geochemical and nutrient parameters were analyzed using spectrometry-based techniques. Results showed that the concentration of MeHg and THg in soil samples ranged from 0.13 to 1.0 ng/g and from 2.5 to 110 ng/g respectively. There is no significant difference in the amount of MeHg and THg between wet and dry season but the concentrations are significantly higher in Krokor soil than in Prateah Lang and Prey Khmer soil. It is also found that THg is a main driven for MeHg production which is partly contradictory compared to previous reports from boreal wetlands and Chinese rice paddies with higher amount of soil THg.

## Regional 3D atmosphere and ocean models to quantify the impact of oceanic sources on the regional Hg budget.

Walsh J<sup>1</sup>, Bieser J<sup>1</sup>, Matthias V<sup>1</sup>, Travnikov O<sup>2</sup>

<sup>1</sup>Helmholtz-zentrum Hereon, <sup>2</sup>J. Stefan Institute

Mercury (Hg) is subject to significant biological and chemical transformations, of which is largely facilitated in the marine environment. These processes are also responsible for the re-emission of dissolved gaseous mercury (DGM) and the production of toxic Hg species such as monomethylmercury (MMeHg). Previous studies (e.g., Bratkič et al., 2016; Zivkovic et al., 2022) from the South Atlantic Ocean observed a linear correlation between DGM and dissolved inorganic carbon (DIC), and DGM and Nitrate+Nit, and presented strong evidence for DGM production by organic matter remineralisation. However, there is a discernible lack of marine studies assessing the electron reduction potential in seawater, specifically regarding Nitrate+Nit and the reducing potential of the water to produce DGM. In the South Atlantic Ocean, dimethylmercury (DMeHg) shows a negative correlation with oxygen which likely has an influence on reducing potential in the seawater, as low oxygen levels would induce more reductive conditions. In this study, we aim to calculate the electron reduction potential (E<sub>o</sub>) in the South Atlantic Ocean within the context of the UK-GEOTRACES cruise GA10 data. Furthermore, we will present results of a model study about the extent of the South Atlantic Ocean as a source of Hg to the atmosphere via Hg degassing, where the reduction potential of the seawater supports the production of DGM. Considering the importance of the South Atlantic, a regional 3D ocean biogeochemistry model (ICON: Icosahedral Nonhydrostatic Weather and Climate Model, and ECOSMO II: ECOSystem MOdel) will offer a spatial, temporal, and biological understanding of the distribution of Hg in the Southern Hemisphere. Combining observations with advanced ecosystem modelling will help to gain a clearer understanding for the effect of organic matter remineralisation in the South Atlantic Ocean on the reduction of inorganic Hg (II) and the formation of elemental mercury and DGM in surface waters.

## Potential use of genus *Cistus* in phytotechnologies in Almadén mine area (Spain)

Millán R<sup>1</sup>, Pérez-Sanz A<sup>2</sup>, Sierra M<sup>1</sup>, Carrasco-Gil S<sup>1</sup>, Schmid T<sup>1</sup>

<sup>1</sup>CIEMAT - Departamento de Medio Ambiente, <sup>2</sup>Autonomous University of Madrid

The Almadén mining district (Ciudad Real, Spain) is one of the richest mercury areas in the world. In this area, a wide range of mercury-tolerant plants are present and they can be used as ecosystem services. This work has been carried out with plant samples collected under field conditions in the same Almadén experimental plot. The experimental plot was divided into three previously characterised subplots to ensure that all the sampled plants had grown in similar soil conditions. The objective of this study was to evaluate if there were differences between the absorption and distribution of Hg of five species of the genus *Cistus* in spontaneous growth and to evaluate their potential application in phytotechnologies. Several physicochemical parameters have been evaluated to characterise the soil (pH, organic matter content, EC, CEC, total Hg and available Hg). At the same time, the potential of the five plant species of the genus *Cistus* (*C. albidus*, *C. crispus*, *C. ladanifer*, *C. monspeliensis* and *C. salviifolius*) present in the study area for their use in phytoextraction or phytostabilisation phytotechnologies has been studied and compared. This work delves into phytoextraction, which involves the use of plants to extract contaminants from the soil and translocate them to the aerial parts, thus eliminating them from the soil, and phytostabilisation, a technique in which plants are used to avoid the bioavailability of toxic metals in the soil, reducing their mobility. The optimisation of these techniques involves the correct selection of the plant species with the greatest phytoremediation potential. Based on the uptake of mercury by the plants sampled in this study, its potential use in phytotechnologies was established, classifying them as phytoextractors (*Cistus albidus*, *C. ladanifer* and *C. monspeliensis*) and phytostabilisers (*C. crispus* and *C. salviifolius*).

## Lessons Learnt from 20-years of mercury analysis in tuna from the South West Pacific: Establishing a regional reference laboratory for long-term mercury monitoring in the Pacific Island Region

Lal V<sup>1</sup>

<sup>1</sup>The University Of The South Pacific

Mercury (Hg) and its compounds in seafood pose a significant threat to human health, particularly for Pacific Island Communities where consumption of seafood is the main source of protein. Data on Hg levels in fish and other seafoods from the Pacific Islands are scarce. The aim of the present study was to report long-term concentrations of total Hg content in several types of tuna which are commonly consumed in the Fiji and other Pacific Islands as well as exported globally. The results of the study were used to determine health risk arising from consumption of tuna and trends in total Hg in the edible tissues of 2000 tuna samples of different species (Albacore, Yellowfin, Skipjack and Bigeye). Moreover, 27 species of fish and 3 species of shellfish have also been analysed for total mercury. Total Hg was determined by strong acid (HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>/HCl) digestion, addition of bromine chloride, reduction with sodium borohydride and analysis via hydride generation atomic absorption spectroscopy. The total mercury in tuna samples ranged from 0.05 to 0.9 mg/Kg. Although a limited number of analyses were conducted on some shellfish and fish species, it is clear that there is detectable to low level Hg in such edible seafood. More data on Hg levels in the larger species of fish and human body mercury levels are needed to better assess the health risk. In addition, it is important to undertake long term monitoring of environmental samples such as air, sediments and rainwater to better understand the issue of Hg bioaccumulation and release in the Pacific. Limited data on environmental samples are available through collaboration with the Asia Pacific Mercury Monitoring Network (APMMN), United States Environment Protection Agency (US EPA) and Taiwan EPA. These data are the first to indicate the levels of Hg in the environment and possible trends.

## Mercury contamination in the former Hg-mining area of Abbadia San Salvatore (central Italy) and remediation: the status of the art

Vaselli O<sup>1</sup>, Nisi B<sup>2</sup>, Bianchi F<sup>3</sup>, Cabassi J<sup>2</sup>, Rappuoli D<sup>4</sup>, Meloni F<sup>1</sup>, Esposito A<sup>4</sup>, Piccinelli F<sup>4</sup>

<sup>1</sup>Department Of Earth Sciences, <sup>2</sup>CNR-Institute of Geosciences and Earth Resources, <sup>3</sup>S.B.C., Geologi Associati, <sup>4</sup>Unione dei Comuni Amiata Val d'Orcia

The mining activity of the Hg(HgS)-rich ore deposits in the Mt. Amiata district stopped in 1982 since the demand of mercury dramatically collapsed, mostly because of its elevated toxicity. Among the many Mt. Amiata mining areas, that of Abbadia San Salvatore was the most important center of exploitation of cinnabar and production of liquid mercury. Previous investigations evidenced that the mining and industrial activity has caused a significant impact on the environmental matrices.

To facilitate the remediation activities in the mining concession, since 2013 numerous surveys have been carried to measure gaseous elemental Hg (GEM), whose concentrations achieved >50,000 ng/m<sup>3</sup> in the edifices hosting the Gould and Nesa furnaces, and dissolved and suspended Hg in the shallow aquifer inside the mining area, whose contents were up to 400 microg/L. Mercury was also determined in the soils adjacent to the production areas of liquid mercury with concentrations up to 2%, likely deriving from the tailings buried in this area and deriving from the old furnaces, e.g. Cermak-Spirek. The monitoring activity allowed to plan specific solutions to reduce the presence of high concentrations of GEM in the mining headquarter as well as in the workers changing rooms and so forth. In most cases, GEM values were >2000 ng/m<sup>3</sup>, i.e. above the threshold limits required by the regional authority to consider reclaimed a specific site (300 and 500 ng/m<sup>3</sup> outdoor and indoor respectively). In this study, we reviewed the geochemical activity carried out in the environmental matrices inside the former mining area of Abbadia San Salvatore and adjacent areas as part of the remediation program aimed at restoring the area and destined to an archeometallurgical museum and public park after that in 2008 an agreement between the previous owner of the mining concession (ENI-Agip Division) and the Municipality of Abbadia San Salvatore was signed.

## Evaluation of long-term mercury accumulation fluxes in Antarctic ice-free regions using a paleolimnological approach. Preliminary assessment from the GEOCHEM Project

Corella J<sup>1</sup>, Saiz-Lopez A<sup>2</sup>, Sierra M<sup>3</sup>, Millán R<sup>3</sup>, Garralón A<sup>3</sup>, López-Martínez J<sup>4</sup>, Spolaor A<sup>5</sup>, Schmid T<sup>3</sup>  
<sup>1</sup>National Museum of Natural Sciences - CSIC, <sup>2</sup>Institute of Physical Chemistry - CSIC, <sup>3</sup>Department of Environment - CIEMAT, <sup>4</sup>Faculty of Sciences - Autonomous University of Madrid (UAM), <sup>5</sup>Institute of Polar Sciences - National Research Council (ISP-CNR)

Mercury is a global pollutant subject to long-range transport, posing a threat to even pristine regions such as Antarctica. Mercury can be released to the atmosphere by natural and anthropogenic processes. Unfortunately, there is still a reduced comprehension of the controlling mechanisms driving mercury influx and cycling in remote regions from the Southern Hemisphere. The objective of this work is to develop an updated database of Hg fluxes in coastal Antarctica that will enhance our comprehension of the causes of Hg concentration variability over time at a sub-continental scale. Within the framework of the GEOCHEM project (PID2021-125778OB-I00), funded by the Spanish Ministry of Science, we are using lake sediments from different sites within the South Shetland Islands, an archipelago about 100 km north of the Antarctic Peninsula, to evaluate the drivers of mercury accumulation in Antarctic terrestrial ecosystems at different time scales and in different geological domains. Results show that there is a need to develop a critical assessment of how each sedimentary record accumulates and retains Hg in order to adequately use natural archives to reconstruct spatiotemporal gradients in atmospheric Hg deposition. The reconstructed Hg fluxes evolution within different climatic periods during the Holocene, punctuated by different volcanic eruptive events, reveals a more comprehensive picture of how the Hg loading and cycling vary under various global environmental changes and human impact scenarios. In this case, climatic conditions are directly affecting the presence of Hg in lake sediments.

## Distribution of Potentially Toxic Elements (PTE) and ecological risks in the “Le Lame” Hg-rich solid mine waste mining dump (Abbadia San Salvatore, central Italy)

Nisi B<sup>1</sup>, Meloni F<sup>2</sup>, Vaselli O<sup>2</sup>, Cabassi J<sup>1</sup>, Montegrossi G<sup>1</sup>, Bianchi F<sup>3</sup>, Rappuoli D<sup>4</sup>

<sup>1</sup>CNR-IGG, <sup>2</sup>Department of Earth Sciences, <sup>3</sup>Department of Earth Sciences, <sup>4</sup>CNR-Institute of Geosciences and Earth Resources, <sup>5</sup>CNR-Institute of Geosciences and Earth Resources, <sup>6</sup>S.B.C., Geologi Associati, <sup>7</sup>Unione dei Comuni Amiata Val d'Orcia

The Mt. Amiata district (central Italy) was classified as the 4th largest producing Hg-district. Since 1925, more than 50% of mercury worldwide was provided by the Mt. Amiata mining area and, about 70% of it was from the Abbadia San Salvatore (ASS) mine. Tailings accumulated during ore processing were stored in the “Le Lame” mining dump covers an area of roughly 120,000 m<sup>2</sup>, thus becoming a potential pollution source for the surrounding environment. Solid mine wastes consist of multiple elements including sulfides, Fe-Mn oxides, carbonates, silicates, and Potentially Toxic Elements (PTE). In contaminated soils, PTE can be mobilized and transferred to surface and groundwater systems and up-taken by soil biota. The mobility of PE in the environment can be affected by several factors, e.g. redox potential, pH and bacterial activity. In this study, we present the geochemical results obtained from the top and sub-soils developed on the waste material from Le Lame solid mine waste mining dump. The aim of this work was to obtain detailed information on the distribution of PTE (e.g. Hg, Sb, As, Be, Cr, Co, Cd, V, Zn, Cu, Fe, Mn, Ni, Pb, Tl) and the respective enrichment factor (EF) and ecological risk (ER) indexes. In 2022 a soil sampling was carried out in 22 sites at two depths (0.8-1.2 m and 1.2-2.5 m). Only Hg, Sb and As, after aqua regia extraction were found to have concentrations higher than the Italian Legislation, which regulate the threshold concentrations of contamination, being characterized by the following ranges 6.6-890 mg/kg, 1-1980 mg/kg and 5-88 mg/kg, respectively.

## If You Don't See It Doesn't Mean It Is Not Working: Sample Size And The Effectiveness Evaluation Of The Minamata Convention

Qureshi A<sup>1</sup>, Sunderland E

<sup>1</sup>IIT Hyderabad

Reducing human exposure to mercury is a primary objective of the Minamata Convention. Using simple statistical calculations and the USEPA one-box toxicokinetic model, we simulate the number of samples required to statistically detect a reduction in dietary mercury exposure reflected in concentrations human hair, the most analyzed human biomarker. We consider future scenarios when dietary mercury exposures have been reduced by 1%, 5%, 10%, 20% and 30% through actions motivated by the Minamata Convention. Considering monitoring sample sizes of 50, 100, 500 and 1000, we find that when exposure reductions were 1% and 5%, the sampled distributions of mercury concentrations in hair under baseline and exposure reduction scenarios were not significantly different (at  $\alpha < 0.05$ ) more than 95% and 46% of the times, respectively. That is, there was a failure to detect a difference (reduction in exposure) even though it existed, a type-II error. This means that while the convention was being effective, it was difficult to detect it when the mitigation measures were mild. Number of samples required to detect 1%, 5%, 10%, 20% and 30% reductions in human hair mercury levels, with  $\alpha < 0.05$  and statistical power = 0.8, were order of 40000, 1300, 300, 70 and 30, respectively. Results were largely consistent across population sizes (10000 to 1 million) and initial baseline exposures (0.01, 0.05 and 0.1  $\mu\text{g}/\text{kg}/\text{d}$ ). Thus, a smaller sample size (order of 100) would probably suffice for analyzing communities that experience high baseline mercury exposures, which are then drastically reduced by intervention. On the contrary, minor global reductions in emissions may not likely be reflected in human hair of general populations, even though they are being effective. TOfuscation is compounded when general populations change their fish consumption habits. That is, the convention was effective, only it was not being observed clearly.

## Mercury isotope fractionation characteristics in raw mill system and air pollution control devices of cement clinker production

Wen M<sup>1,2,3</sup>, Wu Q<sup>1,2,3</sup>, Wang S<sup>1,2,3</sup>, Li Z<sup>1,2,3</sup>, Ouyang D<sup>1,2,3</sup>, Wang Y<sup>1,2,3</sup>

<sup>1</sup>School of Environment, Tsinghua University, <sup>2</sup>State Key Joint Laboratory of Environmental Simulation and Pollution Control, <sup>3</sup>State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex

Mercury stable isotopes have become powerful tracers for identifying mercury emission from cement clinker production sources. However, mercury isotope signals shift between raw materials and atmospheric emissions due to the transformation of mercury in raw mill system and air pollution control devices, increasing the uncertainty of isotopic fingerprints of mercury sources. This research measured gaseous oxidized mercury (Hg<sup>2+</sup>), gaseous elemental mercury (Hg<sup>0</sup>) and particle bound mercury (Hg<sub>p</sub>) in flue gas from inlet and outlet of the raw mill system and the air pollution control devices of a pre-calcliner cement plant. Compared with the average  $\delta^{202}\text{Hg}$  of raw materials ( $-0.28 \pm 0.10\text{‰}$ ), the lighter isotopes accumulated in stack emission of kiln tail. Besides,  $\delta^{202}\text{Hg}$  of Hg<sup>2+</sup> of the stack emission decreased from  $-0.62\text{‰}$  to  $-0.94\text{‰}$  during the off-stream of raw mill system, while that of Hg<sup>0</sup> increased from  $-1.01\text{‰}$  to  $-0.40\text{‰}$  and that of Hg<sub>p</sub> did not change apparently. During the raw mill operating stage, the  $\delta^{202}\text{Hg}$  of Hg<sup>2+</sup> at the inlet and the outlet of the raw mill system were  $-0.42\text{‰}$  and  $-1.38\text{‰}$  respectively, and that of Hg<sup>0</sup> were  $-1.02\text{‰}$  and  $-0.37\text{‰}$ , which displayed contrary variation characteristics. These phenomena could be attributed to complex adsorption/desorption reaction between gaseous mercury and raw meal in raw mill system which had different isotope fractionation coefficient. The results suggested the effect of raw mill system and air pollution control devices on mercury isotope fractionation in cement clinker production should be fully considered during tracing mercury pollution via mercury isotopic signatures. In addition, mercury fractionation values of atmospheric emission may be calculated by fractionation coefficients of corresponding mercury transformation reactions.

## Mercury and selenium blood levels in Kyrgyz pregnant women from Hg contaminated and control area (Aidarken vs Kara-Suu)

Tursunova V<sup>1</sup>, Falnoga I<sup>2</sup>, Snoj Tratnik J<sup>3</sup>, Šlejkovec Z<sup>4</sup>, Mazej D<sup>5</sup>, Stajniko A<sup>6</sup>, Kocman D<sup>7</sup>, Muratov Z<sup>8</sup>, Tuhvatshin R<sup>9</sup>, Sharshenova A<sup>10</sup>, Bugubaeva M<sup>11</sup>, Horvat M<sup>12</sup>, Stegnar P<sup>13</sup>

<sup>1</sup>International Medical Faculty, Osh State University, <sup>2</sup>Jožef Stefan Institute, <sup>3</sup>Jožef Stefan Institute, <sup>4</sup>Jožef Stefan Institute, <sup>5</sup>Jožef Stefan Institute, <sup>6</sup>Jožef Stefan Institute, <sup>7</sup>Jožef Stefan Institute, <sup>8</sup>International Medical Faculty, Osh State University, <sup>9</sup>Kyrgyz State Medical Academy, <sup>10</sup> International Higher School of Medicine, <sup>11</sup>International Medical Faculty, Osh State University, <sup>12</sup>Jožef Stefan Institute, <sup>13</sup>Jožef Stefan Institute

Aidarken (Khaidarkan = 'The Great Mine') is a region with mercury production from cinnabar ore and to a lesser extent from mercury-antimony-fluorite ore and waste recycling. The mine-smelter was established in 1941, almost stopped operating in 2009 (flooding), and restarted in 2018 with reduced capacity (from hundreds t/year to tens). Recent smelting emissions of elemental mercury vapor are low however, with past pollution legacies, the health effects for the general population are still possible. We have followed mercury (Hg) and selenium (Se) as a protective essential element in pregnant women residing in Aidarken and the control area.

Pregnant women aged 19 – 38 y (n = 91, 3rd trimester) were recruited between 2020 and 2021 in the Aidarken (n = 56) area and the Hg uncontaminated Kara-Suu area (n=35). The fasting blood samples were analyzed for hematological parameters and trace elements (ICP-MS). Whole blood Hg and Se were related to maternal data (age, gestation week, BMI, hemoglobin, fetal sex, goiter, residency) and newborns' length to residency and maternal characteristics by multivariable linear regression analysis.

Blood Hg and Se in the Aidarken group were slightly higher than in the control group (GMs, ng/mL: Hg 0.42 vs 0.12; Se 118 vs 105); differences persisted after adjustment for selected variables. Only for boys, newborns' length was slightly higher in the Aidarken group compared to the control group (GMs: 55 vs 52 cm) and persisted even after adjustment, although negatively affected by maternal Se levels. Goiter was associated with higher Hg and Se, but it did not affect newborns' length.

Slightly elevated blood Hg in the Aidarken group indicates a low risk of prenatal Hg exposure.

Simultaneous elevation of Se could point to elevated antioxidant levels (e.g. glutathione peroxidases, selenoprotein P) representing adaptive stress response on living in an area with multi-elemental environment pollution.

## An improved remote sampling technique for atmospheric pollutants

Horvat M<sup>1,2</sup>, Horvat M<sup>1,2</sup>, Neary B<sup>3</sup>, Rogers T<sup>3</sup>, Dexter M<sup>3</sup>, Corns W<sup>3</sup>

<sup>1</sup>Jožef Stefan Institute, <sup>2</sup>Department of Environmental Sciences, Jožef Stefan Institute, <sup>3</sup>PS Analytical

Mercury stands out as a significant global pollutant, prompting 137 nations to endorse the Minamata Convention—an international agreement aimed at safeguarding human health and the environment from human-induced mercury emissions. Articles 19 and 22 within the treaty mandate continuous monitoring and efficacy assessment. However, certain regions face challenges in implementing these measures due to insufficient infrastructure for deploying monitoring equipment to track atmospheric pollutant concentrations continuously. Passive samplers emerge as a practical solution in such cases, boasting advantages like cost-effectiveness, user-friendliness, low maintenance, and independence from electricity or gases. Despite their benefits, there exists considerable uncertainty in passive sampler sampling uptake rates, potentially leading to inaccurate assessments of pollution levels. Corrections for uptake rate variations necessitate consideration of changing meteorological conditions during the sampling period. Addressing these challenges, we propose an innovative sampling technique involving gold on silica traps. This method reduces sampling rate uncertainties by employing a flow-calibrated, battery-operated micropump. The device exhibits superior mass loadings, thereby enhancing detection limits. The rechargeable battery pack, powered by solar energy, offers a six-day operational span without sunlight and requires less than four hours for a full charge in dim sunlight. To ensure accuracy, a data logger continuously monitors the voltage which is being used to calculate the sampling flow throughout the entire sampling period based on voltage-calibrated measurements. In contrast to conventional samplers calibrated in laboratory conditions, our sampler is calibrated in real environmental settings. Extensive testing against an online continuous mercury analyzer, as well as comparison with samplers operating on AC power and mass flow controllers, validates the efficacy of this new sampling approach which operates on AC power and mass flow controllers.

## Multi-model atmospheric simulations under the Multi-Compartment Mercury Modeling and Analysis Project (MCHgMAP)

Travnikov O<sup>1</sup>, Angot H<sup>2</sup>, Dastoor A<sup>3</sup>, Feinberg A<sup>4</sup>, Roy E<sup>5</sup>, Ryjkov A<sup>3</sup>

<sup>1</sup>Jozef Stefan Institute, <sup>2</sup>Institut des Géosciences de l'Environnement, <sup>3</sup>Environment and Climate Change Canada, <sup>4</sup>Blas Cabrera Institute of Physical Chemistry, <sup>5</sup>Massachusetts Institute of Technology

The evaluation and attribution of long-term changes in mercury (Hg) pollution levels in the environment, employing monitoring and modeling methods, are crucial tasks for assessing the effectiveness of current and future mitigation policies. Changes in observed Hg levels reflect a combined effect of anthropogenic and natural factors, necessitating suitable tools to isolate the impacts attributable to emission regulations. A recently launched research initiative, the Multi-Compartment Hg Modeling and Analysis Project (MCHgMAP), aims to inform the effectiveness evaluations of the Minamata Convention on Mercury (MC) and the Convention on Long-Range Transboundary Air Pollution (CLRTAP) through multi-model simulations and the analysis of spatial and temporal trends in Hg environmental pollution. The MCHgMAP assessment consist of a series of model experiments using off-line coupled atmospheric, marine, and multi-media mass balance models to account for changes in primary anthropogenic and secondary Hg sources as well as environmental conditions in the Hg cycling between land, atmosphere, and ocean.

The atmospheric component of the study employs four global chemical transport models – GEM-MACH-Hg, GEOS-Chem, GLEMOS, and WACCM – to simulate atmospheric transport and air-surface exchange of Hg from 2010 to 2020. Enhanced consistency between the models is achieved by utilizing unified primary and secondary emissions datasets. The first phase of the study focuses on assessing the spatial patterns and temporal trends of Hg levels in remote and affected regions according to the Baseline scenario, and evaluating simulated trends against a compilation of long-term measurements. Additionally, a perturbation scenario aims to isolate the effect of temporal changes in anthropogenic emissions on Hg levels from the influence of changing environmental factors. Multiple trend analysis methods are applied to both observed and modeled Hg concentrations and deposition to maximize the information obtained from observed and modeled time series.

## The Sources and Transport of Mercury in Glacial Meltwater on the Tibetan Plateau

Wang J<sup>1,2</sup>, Zhang Q<sup>1,2</sup>, Li M<sup>1,2</sup>, Sun X<sup>3</sup>

<sup>1</sup>Institute Of Tibetan Plateau Research Chinese Academy Of Sciences, <sup>2</sup>University of Chinese Academy of Sciences, Beijing 100049, China, <sup>3</sup>School of Environmental and Resource Sciences, Shanxi University, Taiyuan 030006, China

Mercury, a global pollutant, accumulates in glaciers through atmospheric deposition and is subsequently transported downstream via glacial meltwater. Glaciers are experiencing significant changes under global warming, characterized by the expansion of ablation zones and the continual development of glacial drainage systems. Consequently, the contribution of subglacial environments to overall glacial mercury output becomes increasingly significant. However, current research on the sources and migration of mercury in meltwater runoff under glacier retreats remains insufficient, particularly in the mercury output from subglacial environments. To comprehensively investigate the release and transport of mercury under the glacier retreats, we conducted long-term sampling and monitoring of different glacial rivers in the Tibetan Plateau. Our study yielded three primary findings. Firstly, subglacial environments exhibit a significant capacity for mercury output, with higher mercury concentrations observed in subglacial rivers compared to supraglacial rivers. Secondly, we elucidated the mechanisms of mercury input into meltwater runoff: during the rising limb of the hydrograph, mercury input in meltwater runoff is primarily determined by the availability of mercury, whereas during the recession limb, hydraulic action plays a predominant role. Finally, mercury in meltwater runoff demonstrates significant seasonal variations, with its concentration and form primarily influenced by suspended particulate matter (SPM) and discharge. The correlation between mercury and SPM characteristics varies across different seasons. In summary, we elucidate the important role of glacier drainage system retreats on the temporal and spatial variations of glacier mercury output, emphasizing the significance of mercury output from subglacial environments, and delineating the variations, input mechanisms, and influencing factors of mercury in meltwater runoff. These findings provide a scientific theoretical basis for understanding and managing mercury pollution in glacier environments in the future.

## Mercury and other trace elements in the sediments and representative biota of an anthropogenically impacted Estuary

Mirjankar P, Duddi M, Hashmi A, Priyanka, Adyel T, Schultz A, Subramaniam K, Qureshi A<sup>1</sup>

<sup>1</sup>IIT Hyderabad

Estuaries are dynamic ecosystems that function as reservoirs for mercury (THg) and methylmercury (MeHg), with these contaminants stored in both the bottom sediment and the water column. In this work, we will present the concentrations of THg and MeHg and their co-occurrences with other toxic trace elements such as lead, cadmium, chromium and others, in sediments and biota (mussels, shrimps and crabs) of an estuary heavily impacted by discharges of fly ash from coal-fired power plants, municipal discharges, and petrochemical industries further upstream. Mercury analysis was conducted using a direct mercury analyzer while other elements were detected using ICP-MS. Further, we are analyzing the samples using SEM-XRD and XRF to better assess the contamination of sediments with fly ash. Results clearly show a spike in concentrations of THg (mean 42  $\mu\text{g}/\text{kg}$ ), and other heavy metals in zones receiving fly ash discharges. Mercury concentrations being 40 times higher than sediments in near a beach town less impacted by anthropogenic activities. Mean concentrations in sediments of the rest of the studies estuarine locations were 7 to 14  $\mu\text{g}/\text{kg}$ . Geoaccumulation index calculation revealed the entire studied estuary to be contaminated, with the heaviest contamination close to fly ash contaminated locations. Mean THg concentrations in shrimps were 10  $\mu\text{g}/\text{kg}$  and in mussels 41  $\mu\text{g}/\text{kg}$ , while mean MeHg concentrations were 8  $\mu\text{g}/\text{kg}$  and 25  $\mu\text{g}/\text{kg}$ , respectively. The lower MeHg:Thg ratio in mussels is likely a reflection of ingestion of contaminated sediments in addition to microbiota and lower MeHg assimilation. Further results on spatial distribution of mercury, in association with other elements, sediment organic matter and possible fly ash contamination will be presented.

## Metrological Study of a Continuous Flow Calibration Technique for Atmospheric Mercury

Horvat M<sup>1</sup>, Corns W<sup>3</sup>, Živković I<sup>1,2</sup>, Waqar Ali S<sup>1,2</sup>, Vijayakumaran Nair S<sup>1,2</sup>, Horvat M<sup>1,2</sup>

<sup>1</sup>Jožef Stefan International Postgraduate School, <sup>2</sup>Department of Environmental Sciences, Jožef Stefan Institute, <sup>3</sup>PS Analytical

Monitoring low concentrations of gaseous elemental mercury (GEM) in the atmosphere continuously and at high resolution requires robust measurement techniques and corresponding calibration capabilities. Ongoing challenges exist in achieving continuous calibration for GEM, especially at ambient concentrations (1–2 ng m<sup>-3</sup>). This study introduces a continuous flow calibration method for GEM, traceable to the NIST 3133 Standard Reference Material (SRM). The calibration method was assessed using a Zeeman atomic absorption spectrometry (Zeeman AAS) system with background correction. GEM standard continuously flowed by reducing Hg<sup>2+</sup> from liquid SRM NIST 3133, allowing for traceable calibration of Zeeman AAS. Atmospheric GEM measurements obtained with the calibrated Zeeman AAS were compared with two methods: manual gold amalgamation atomic fluorescence spectrometry (AFS) calibrated through the chemical reduction of NIST 3133 and automated gold amalgamation AFS calibrated using the mercury bell-jar syringe technique. The comparisons revealed that the factory-calibrated Zeeman AAS underestimated concentrations below 10 ng m<sup>-3</sup> by up to 35% relative to the other two determination methods. However, applying a calibration based on SRM NIST 3133 for traceable calibration of Zeeman AAS resulted in better comparability with other methods for the low-concentration samples under 5 ng m<sup>-3</sup>.

## Use of corrected reactive mercury measurements for model evaluation: Analysis and implications for global model estimates

Travnikov O<sup>1</sup>, Gačnik J<sup>1</sup>, Vijayakumaran Nair S<sup>1</sup>, Živković I<sup>1</sup>, Horvat M<sup>1</sup>, Sprovieri F<sup>2</sup>, Tassone A<sup>2</sup>, Pirrone N<sup>2</sup>

<sup>1</sup>Jozef Stefan Institute, <sup>2</sup>Institute of Atmospheric pollution Research

Measurements of reactive mercury (RM) are highly valuable for both understanding mercury redox processes in the atmosphere and evaluating chemical transport models. The latter is particularly important for providing reliable information on mercury concentration and deposition, as well as their source attribution, for evaluating the effectiveness of the Minamata Convention. Model evaluation against observations largely relies on comparing simulated and observed concentrations of gaseous elemental mercury and wet deposition. However, a significant part of simulated processes remains unevaluated, including near-ground formation/decomposition of RM and its dry deposition to terrestrial ecosystems. This gap can be filled by evaluating model performance against RM measurements.

The majority of presently accessible historical RM measurements have been conducted using the KCl-coated denuder technology, which is well-recognized for inaccurately quantifying gaseous oxidized mercury, resulting in biased low measured values. To rectify existing RM observations, an extensive literature review has been performed, revealing the dependence of the underestimation of denuder-based RM measurements on a number of ambient factors. These empirically-derived dependencies were applied for posterior adjustment of a global dataset of RM observations from national and international monitoring networks and utilized for evaluating chemical transport models.

Comparison of simulated RM concentrations with corrected observations has allowed revealing additional model uncertainties, which can be caused by a number of factors, including uncertainties of anthropogenic emissions speciation in accessible emissions inventories, missing RM redox mechanisms in the near-ground air, and uncertainties of RM dry deposition. In all cases, currently available model estimates of mercury deposition to ecosystems can be significantly biased high or low depending on prevailing factors. Additional model sensitivity simulations have been performed to analyze the effect of these uncertainties on the estimated mercury global deposition patterns, suggesting that current model estimates possibly underpredict transport of mercury from industrial regions to remote regions.

## Mercury exposure, fish consumption and neurodevelopment: findings from the Northern Adriatic birth cohort study

Snoj Tratnik J<sup>1</sup>, Falnoga I<sup>1</sup>, Mazej D<sup>1</sup>, Neubauer D<sup>2</sup>, Kodrič J<sup>2</sup>, Stropnik S<sup>2</sup>, Prpić I<sup>3</sup>, Barbone F<sup>4</sup>, Rosolen V<sup>4</sup>, Horvat M<sup>1</sup>

<sup>1</sup>Jozef Stefan Institute, <sup>2</sup>University Medical Centre, <sup>3</sup>The Clinical Hospital Center of Rijeka, <sup>4</sup>University of Udine, <sup>5</sup>Central Directorate for Health, Social Policies and Disability

At low dose of exposure, methyl mercury may not pose a problem for the majority of healthy adult population, but could trigger adverse biological response during early life, leading to cognitive problems, learning, memory and motor dysfunctions later in childhood.

The Northern Adriatic study explored prenatal and childhood exposure to methyl mercury from fish consumption and its association with cognitive, language and motor development of children.

Nutritional as well as genetic aspects were considered in association analysis as important players that could diminish or worsen an adverse response to early life exposure(s). The overall results

showed no negative effect of prenatal mercury exposure on cognitive abilities of children at 18 months of age, but rather a positive effect on account of fish consumption during pregnancy.

Selenium, which is an important constituent of seafood showed positive association with language abilities of children. Children who were carriers of apolipoprotein ε4 allele showed significantly lower cognitive scores with higher mercury exposure than non-carriers. The observed effect was not large, but important in the global societal context as 17% of the study population were carriers of the susceptible gene variant.

The follow-up of the study population at 7-8 years of age confirmed positive effect of seafood consumption, and also some other nutrition-related life-style attributes, on cognitive performance for majority of the children. Some additional gene polymorphisms were also revealed as important factors of susceptibility or resilience. Although certain relationships that were observed remain to be explained, the overall observation of small effect of mercury seems to be masked or compensated by various factors – this is particularly important in light of the advanced assessment of risk from cumulative exposure to mercury which will enable setting a more realistic threshold levels of toxicity in vulnerable human populations.

## Mercury in plankton: analysis of the influence of environmental conditions on Hg bioaccumulation in the context of diverse Baltic lagoons

Wojdasiewicz A<sup>1</sup>, Wilman B<sup>1</sup>, Zarzeczńska A<sup>1</sup>, Popławska A<sup>1</sup>, Kuztal A<sup>1</sup>, Woźniczka A<sup>2</sup>, Kornijów R<sup>2</sup>  
<sup>1</sup>University Of Gdańsk, <sup>2</sup>Marine Fisheries Institute - National Research Institute

Plankton, as the primary biological link in the trophic chain, plays a major role in incorporating and transporting chemicals in the food web. Mercury, due to its toxicity and ability to bioaccumulate and biomagnify, is one of the more dangerous pollutants found in natural waters. Therefore, estimating potential exposure to Hg of higher trophic levels, including humans, requires a better understanding of its distribution especially in shallow, partially enclosed lagoons in urban areas.

Three lagoons in the southern Baltic Sea region were selected for the study: the smallest, most saline, semi-open Puck Lagoon (PL); the largest, with a poorly developed shoreline, separated by the Vistula Spit from the Gulf of Gdansk, with which it is connected by two narrow channels - the Vistula Lagoon (VL); and the least saline, containing the estuary of the Oder, where a port of fundamental importance to the national economy is located - the Szczecin Lagoon (SL).

Samples were collected using plankton nets in August and September 2023. Plankton samples were divided by size: 3 groups in the VL, SL and 5 groups in the PL. Total mercury concentration was analyzed using an automatic mercury analyzer (DMA - 80).

The size of plankton cells determines the penetration of pollutants, including mercury into the trophic web. Smaller phytoplankton cells have a larger adsorption surface area and can also be food for small zooplankton with a small oral apparatus. Thus, we can expect smaller zooplankton to be more heavily loaded with Hg compared to zooplankton feeding on larger phytoplankton cells. On the other hand, the largest zooplankton that also feed on smaller zooplankton are more heavily loaded with the toxic metal. This is especially important for small and juvenile fish with small oral apparatus feeding on plankton.

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## Bioaccumulation and transfer of mercury in the body of cosmopolitan moon jellyfish (*Aurelia aurita*)

Wojdasiewicz A<sup>1</sup>, Beldowska M<sup>1</sup>, Weydmann-Zwolicka A<sup>1</sup>

<sup>1</sup>University Of Gdańsk

Global climate warming is increasing the length of vegetation season in the temperate climate zone. This results in an increase in the annual biomass of phytoplankton and zooplankton, which promotes the growth of gelatinous plankton, of which moon jellyfish (*Aurelia aurita*) is a representative. As a result, this species strengthens its role in the trophic web and in chemical elements cycles in the marine environment.

Mercury (Hg) bioaccumulates, and is prone to biomagnification, therefore it is a potential danger to marine ecosystems. The purpose of this study was to estimate the bioaccumulation of Hg, the percentage of its fraction in different parts of *A. aurita*, to identify the site of Hg accumulation and its transfer inside the body of jellyfish.

Moon jellyfish were collected from 27 stations in the southern Baltic Sea (n = 1156) and divided into mesoglea, oral arms, and gonads. Total mercury (THg) and Hg fractions were determined by thermodesorption using an automatic mercury analyzer (DMA-80).

THg results showed that the growth of jellyfish occurred faster than mercury bioaccumulation - bio-dilution. The highest THg concentrations in the gonads may indicate reproduction as a way to detoxify. The study showed varying percentages of the mercury fractions studied between *A. aurita* tissues. Gonads had the highest proportion of labile fractions, the most bioavailable, absorbed by the body mainly from food. This indicates the transfer of these fractions from the oral arms to the gonads. The oral arms and mesoglea showed a much higher proportion of the stable form of HgS than the gonads, indicating the accumulation of this fraction on the surface of the jellyfish from water and suspended particulate matter (probably fluffy layer). Differences in the percentage of Hg fraction between tissues are mainly due to their function in the body and contact with the environment.

## A Multi-Year Record of Atmospheric Gaseous Elemental Mercury Concentrations at a Regional Site in the South African Interior

Bredenkamp L<sup>1</sup>, Van Zyl P<sup>1</sup>, Jaars K<sup>1</sup>, Martin L<sup>1,2</sup>, Josipovic M<sup>1</sup>

<sup>1</sup>Atmospheric Chemistry Research Group, Chemical Resource Beneficiation, North-West University,

<sup>2</sup>South African Weather Service

South Africa is one of the most prominent emitters of mercury (Hg) globally and the introduction of legislative measures to control the atmospheric concentrations thereof is imminent. Atmospheric Hg monitoring has been ongoing in this region since 1995, but publicly available data has been limited to long-term monitoring at a marine background site (Cape Point), and several short-term measurement campaigns at inland locations. Extended continuous in situ measurements in the anthropogenically impacted South African interior will provide greater insight into atmospheric Hg concentrations for the entire South Africa. This study examines atmospheric Hg concentrations at Welgegund, a regional site located in the northern interior of South Africa, which is impacted by air masses passing over the most significant Hg source areas in southern Africa and a clean background region. Gaseous elemental mercury (GEM) concentrations were continuously measured from April 2021 to December 2023 with in situ Hg vapour analysis, aimed at identifying temporal trends and interannual variability.

## Mercury and methylmercury profiles in the high productivity area of the Southern Atlantic Ocean

Biester H<sup>1</sup>, Pérez Rodríguez M<sup>1</sup>, Cañan A<sup>1</sup>, Bracher A<sup>2</sup>, Wiegmann S<sup>3</sup>, Torres-Rodriguez N<sup>4</sup>, Dufour A<sup>4</sup>, Heimbürger-Boavida L<sup>4</sup>

<sup>1</sup>Technische Universität Braunschweig, <sup>2</sup>Alfred Wegener Institute Helmholtz Center for Polar and Marine Research, <sup>3</sup>Institute of Environmental Physics, University of Bremen, <sup>4</sup>Aix Marseille Université, CNRS/INSU, Université de Toulon, IRD, Mediterranean Institute of Oceanography (MIO)

Methylmercury (MeHg) bioaccumulates in the marine food chain and phytoplankton is the main entry point. Data on Hg and MeHg in productive areas such as the highly productive Southern Ocean is limited to few studies only. We present data of 6 vertical profiles (7000 m max) of unfiltered dissolved total Hg (THg) and MeHg taken in the South Atlantic Ocean (52°15.6'S, 7°10.8'W - 55°10'S, 34°30'W). Medians of THg in samples of individual depth profiles range between 0.33 and 0.61 pmol L<sup>-1</sup> (min 0.14 max 0.93, mean 0.47 pmol L<sup>-1</sup>) and between 0.18 and 0.45 pmol L<sup>-1</sup> (min 0.03 max 0.64, mean 0.30 pmol L<sup>-1</sup>) for MeHg, which is at the high end of previous reported values. Proportions of MeHg show high median values between 43 and 71 % (max. 90 %). The two high productivity sites show high chlorophyll a concentrations between 135 and > 170 µg L<sup>-3</sup> in the surface layer (upper 200 m), whereas the other profiles were below 10 µg L<sup>-3</sup>. Highest concentrations of THg and MeHg were found at the high productivity sites, although these sites show also the highest variability (factor ~3). Lowest values of THg and MeHg concentrations were observed in the surface layer at the two productive sites likely due to scavenging of THg and MeHg by organic particles. Most profiles show increasing MeHg concentrations with depth and decreasing oxygen concentrations and highest values and proportions in the oxygen minimum zone. However, high MeHg concentrations were observed even at depths below 5000 m under oxic condition at the two productive sites. Our results show that highly productive areas in the ocean are hotspots of MeHg production in the water phase even at great depth and that deep sea sediments including hadal sediments are not a source of water column MeHg.

## Mercury and Methylmercury in deep-sea sediments of the high productivity area of the Southern Atlantic Ocean

Biester H<sup>1</sup>, Pérez-Rodríguez M<sup>1</sup>, Oskamp L<sup>1</sup>, Benkhattab Sindlev M<sup>2</sup>, Glud R<sup>2</sup>

<sup>1</sup>Technische Universitaet Braunschweig, <sup>2</sup>HADAL – Danish Center for Hadal Research, Nordcee, Department of Biology, University of Southern Denmark

Methylmercury (MeHg) bioaccumulates in the marine food chain and sediments are considered major sinks of MeHg. The distribution of MeHg in deep-sea sediments and its relationship to primary production is poorly understood. We investigated total Hg (THg) and MeHg as well as chl-a, organic carbon (Corg) concentrations and oxygen penetration in sediments at 5 sites in the productive Southern Atlantic (52°15.6'S, 7°10.8'W - 55°10'S, 34°30'W). Short cores (45 cm max) were extracted from a highly productive site (St9, -3794 m, chl-a 156 ng cm<sup>-3</sup>), a station near the Sandwich Trench (St16, -5002 m, chl-a 6 ng cm<sup>-3</sup>), two sites within the trench (St15, -8066 m, chl-a 55 ng cm<sup>-3</sup> and St17, -7596 m, chl-a 1269 ng cm<sup>-3</sup>) and a less productive site (St3, -3420 m; chl-a < 0.5 ng cm<sup>-3</sup>). Corg concentrations were low across all stations, with median values from 0.18 % to 0.87 % and highest concentrations at the productive sites. Median THg concentrations in all cores vary between 10 and ~40 ng g<sup>-1</sup> and MeHg concentration range between 0.06 and 0.1 ng g<sup>-1</sup>. Both were highest at the productive stations and correlate with Corg. MeHg proportions range between 0.25 – 0.52 %, with the highest relative content of MeHg in the cores with low Corg concentrations (St3 and St15) and the lowest MeHg proportions at the productive sites. MeHg occurs in the uppermost sediments where oxygen penetration indicates that MeHg is at least partly derived from sinking particles. THg in the cores from the low productivity stations shows a slightly negative correlation ( $R^2=0.3$ ) with C/N ratios and a positive correlation with the proportion of MeHg ( $R^2=0.3$ ), suggesting different Hg contents in sinking particles (zooplankton versus algae remains) or Hg losses during organic matter degradation. These relations were not observed in the cores from the productive sites.

## Enhanced Mercury Immobilization in Contaminated Soil with Biochar:

### A Comparative Study of Coconut Shell, Rice Husk, and Corn-Cob Biochar

Kusnarta I<sup>1</sup>, Suwardji S<sup>1</sup>, Fahrudin F<sup>1</sup>, Wangiyana W<sup>2</sup>, Sukartono S<sup>3</sup>, Fokke B<sup>4</sup>, Bensaiah C<sup>4</sup>, Ismawati Y<sup>5</sup>, Huda B<sup>5</sup>, Ismaranti Y<sup>5</sup>, Maharani A<sup>5</sup>, Buftheim S<sup>5</sup>, Proboretno N<sup>5</sup>

<sup>1</sup>Department of Soil Science, Faculty of Agriculture, Universitas Mataram, <sup>2</sup>Centre for Sustainable Farms System (CESFARMS), Universitas Mataram, <sup>3</sup>Department of Agronomy, Faculty of Agriculture, Universitas Mataram, <sup>4</sup>TAUW Foundation, <sup>5</sup>Nexus3 Foundation

Mercury (Hg) contamination in soil is dangerous because it can have significant harmful effects on the environment, food chain, and human health. Therefore, affordable, effective and long-lasting cleanup techniques are needed. Hg-contaminated soil in a former of artisanal and small-scale gold mining (ASGM) in Taliwang, West Sumbawa District, West Nusa Tenggara Province was used to compare the effectiveness of three distinct biochars made from corn cob (CC), rice husk (RH), and coconut shell (CS) as mercury immobilizer.

Characterization of the biochars using scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) reveals different morphology and functional groups. CC has a more porous structure and high hydroxyl group occurrence and has a striking performance among other biochars. At the bench scale, three different biochars were applied in three layers of depth of the soil (0-10, 10-25, 25-50 cm). The results show that CC is more successful in immobilizing Hg in soil compared to RH and CS. CC's distinct physicochemical characteristics are responsible for the holding capability of CC biochar toward Hg in soil.

The study highlights the significance of locally sourced-biochars in maximizing remediation efficiency. The study offers insightful information on the possible use of biochars for mercury remediation in soil.

300

## Global warming-induced vegetation changes affect atmospheric mercury cycling

Chen L<sup>1</sup>, Chen Q, Xu Z, Zhou Q, Zhang Y

<sup>1</sup>East China Normal University

Mercury (Hg) is a ubiquitous, persistent, and neurotoxic pollutant on the planet, which can readily volatilize in the atmosphere. Vegetation uptake of atmospheric Hg is one of the most important routes of atmospheric Hg removal, which serves as a critical driver of the global biogeochemical cycling of Hg. Climate change has induced the changes in vegetation activities, consequently contributing to the changes in vegetation Hg uptake and atmospheric Hg cycling. This study integrated a stomatal conductance model into an atmospheric chemical transport model and investigated the impacts of changes in vegetation activities on atmospheric Hg distribution globally. Results show that the increase of vegetation activities during the last 40 years has induced a net increase of approximately 300 Mg for the atmospheric Hg deposition globally, which is larger than previous estimates. However, strong heterogeneities have been observed for the changes, mainly depending on vegetation greening or browning over specific regions. Hotspots of increasing atmospheric Hg deposition mainly concentrate in Central Africa, South Amazon, and East Asia, while hotspots of decreasing deposition mainly concentrate in North Amazon and parts of African regions. The net increase of atmospheric Hg deposition has driven a decrease of atmospheric Hg concentrations particularly the Northern Hemispheric background concentrations.

## Mercury and legacy contaminants in glacier cryoconite over the Peruvian Andes

Moreno-Brush M<sup>2</sup>, Keyssner L<sup>1</sup>, Cruz R<sup>3</sup>, Clason C<sup>4</sup>, Blake W<sup>5</sup>, Beard D<sup>5</sup>, Millard G<sup>5</sup>, Quincey D<sup>6</sup>, Horna D<sup>2</sup>, Biester H<sup>1</sup>

<sup>1</sup>Environmental Geochemistry Group, Institute of Geoecology, Technische Universität Braunschweig, <sup>2</sup>Centro de Investigación y Tecnología del Agua (CITA), Universidad de Ingeniería y Tecnología (UTEC), <sup>3</sup>Autoridad Nacional del Agua, <sup>4</sup>Department of Geography, Durham University, Lower Mountjoy, South Road, <sup>5</sup>School of Geography, Earth and Environmental Sciences, University of Plymouth, <sup>6</sup>School of Geography, University of Leeds

The cryosphere, holding 70% of the world's freshwater, is undergoing significant change due to global warming, impacting communities and ecosystems in glacier-fed catchments. Additionally, glaciers, serving as important natural archives of atmospheric constituents, act as secondary sources for both natural and anthropogenic contaminants during melting, releasing stored pollutants from ice, snow and glacier sediments. Cryoconite, a globally prevalent mixture of mineral and organic material on glacier surfaces, efficiently accumulates and concentrates contaminants.

Cryoconite composition has been extensively investigated worldwide; however, its geochemistry remains poorly understood, especially in the Andes region. We investigate the geochemical composition of cryoconite collected from six different glaciers (Artesonraju, Chaupijanca, Chuecon, Yanaucsha, Chumpe and Cavalca) in the Peruvian Andes, home to 71% of the world's tropical glaciers. The goal is to assess variations among and within glaciers and evaluate potential downstream risk of released contaminants. Chemical analyses include total mercury (Hg), fallout radionuclides (Cs137, Pb210, Pb214, and Am241), major and trace elements and organic matter content and composition. Preliminary findings reveal large variations in Hg concentrations (8 to 1,497 µg/kg; median 97 µg/kg) between glaciers and within the same glacier. While Chuecón glacier (central Peru) exhibited the highest median concentration, no significant atmospheric Hg deposition was found in samples from Chumpe glacier (southeastern Peru), near the country's largest small-scale gold mining area. Additionally, fallout radionuclide data from Artesonraju glacier (northern Peru) suggest possible inter-hemispheric transport of radionuclide contaminants. The source of Hg in the samples, as well as the relationship with and controls of organic matter and major/trace elements on cryoconite geochemistry, is still being explored. Nevertheless, certain Peruvian Andes glaciers seem to act as sources of Hg and fallout radionuclides to downstream ecosystems, potentially compromising water resource quality and underscoring the need to understand the cycling, bioavailability, and fate of these pollutants.

## The role of mercury exposure on the stress landscape of a wintering Arctic seabird species, the Brunnich's Guillemot *Uria lomvia*.

Grissot A<sup>1</sup>, Kitaysky A<sup>2</sup>, Strøm H<sup>3</sup>, Albert C<sup>1</sup>, Lambert C<sup>1</sup>, Bråthen V<sup>4</sup>, Descamps S<sup>3</sup>, Elliott K<sup>5</sup>, Ezhov A<sup>6</sup>, Frederiksen M<sup>7</sup>, Kolbeinsson Y<sup>8</sup>, Labansen A<sup>9</sup>, Lorentzen E<sup>3</sup>, Merkel F<sup>7</sup>, Mosbech A<sup>7</sup>, Thórarinnsson T<sup>8</sup>, Fort J<sup>1</sup>

<sup>1</sup>Littoral, Environnement Et Sociétés (lienss), Umr 7266 Cnrs – La Rochelle Université, <sup>2</sup>University of Alaska Fairbanks, Institute of Arctic Biology, Department of Biology & Wildlife, <sup>3</sup>Norwegian Polar Institute (NPI), Fram Centre, <sup>4</sup>Norwegian Institute for Nature Research (NINA), <sup>5</sup>Department of Natural Resource Sciences, McGill University, <sup>6</sup>Murmansk Marine Biological Institute, <sup>7</sup>Aarhus University, Department of Bioscience, Arctic Research Centre (ARC), <sup>8</sup>Northeast Iceland Nature Research Centre, <sup>9</sup>Greenland Institute of Natural Resources

Winter represents a critical period for Arctic seabirds, during which they can be exposed to harsh environmental conditions (low temperatures, storms...) and to high levels of chemical contaminants, especially mercury (Hg). However, exposure to these stressors may largely vary spatially in the marine environment, leading to contrasting spatial exposition to acute stressors and bear various subsequent effects on bird fitness and population dynamics. Given that seabirds are the most threatened group of birds in the world, and Hg pollution is a major threat to the marine environment, understanding the link between Hg exposure and stress levels is thus essential in a conservation perspective, both at the scale of species and marine ecosystems.

Here, we focus on the Brunnich's Guillemot, a seabird species with breeding colonies widespread all over the Arctic, and a known wintering distribution covering most of the Northern Atlantic Ocean. By combining measurements of mercury concentrations in bird feathers with individual winter distribution (extracted from bird-borne tracking devices), we first mapped the large scale distribution of bird contamination during winter. We then apply a similar approach to map the stress landscape (i.e. distribution of bird stress level) of birds during the same period. Comparison of Hg spatial variations with the stress landscape, as well as with other environmental parameters (e.g. SST, Chla...) allows a better understanding of the drivers of seabird stress at very large spatial scale and the role played by Hg.

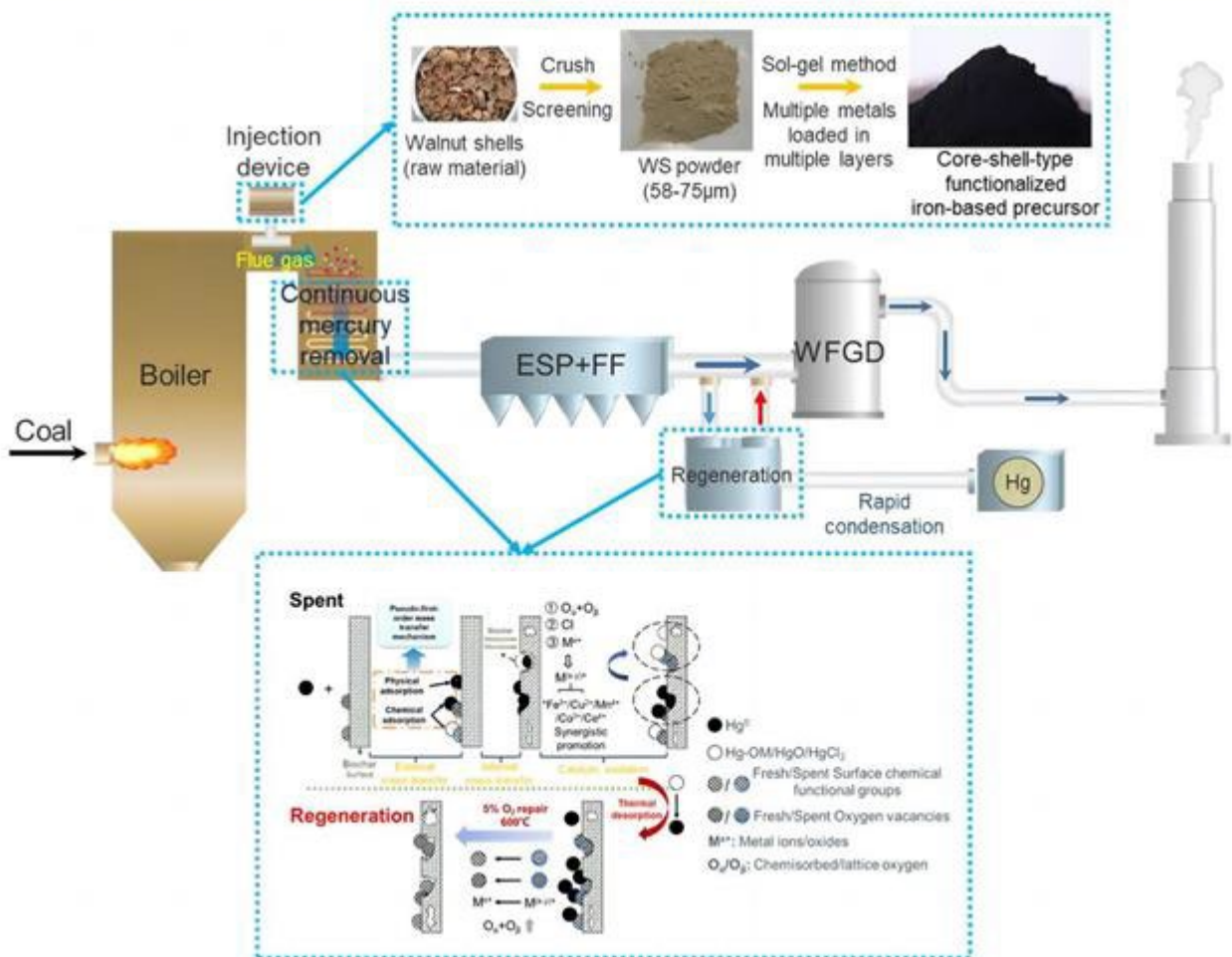
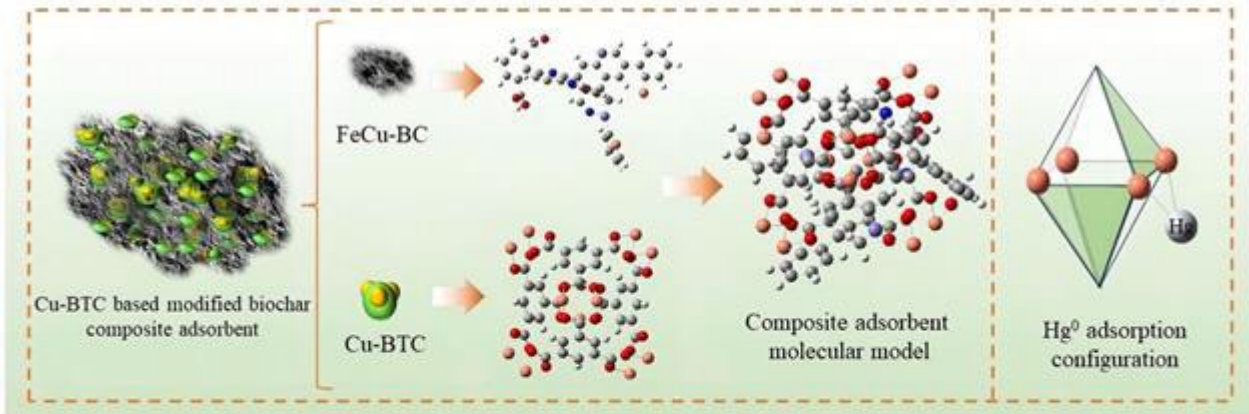
## Study on Mercury Removal Performance and Mechanism of Cu-BTC/FeCu-BC Composite Adsorbent

Jia L<sup>1</sup>, Jin Y<sup>1</sup>, Fan B<sup>1</sup>, Cheng P<sup>1</sup>, He L<sup>1</sup>, Nie H<sup>1</sup>, Yu Y<sup>1</sup>

<sup>1</sup>Taiyuan University of Technology

Composite adsorbents were prepared using a modified biochar based on MOFs by employing an in-situ growth method. The structural design involved doping modified biochar with Fe/Cu polymetallic and Cu-BTC as MOFs material. Both materials contained unsaturated metal centers and oxygen-containing functional groups. The Hg<sup>0</sup> removal characteristics of the samples were analyzed to identify the adsorption and oxidation reaction sites. The study also investigated the coupling and synergistic mechanisms between Cu-BTC and modified biochar, along with the various types of active centers present. Additionally, a molecular structure model of the composite adsorbent was constructed based on a comprehensive study of microscopic properties. The adsorption process of Hg<sup>0</sup> on the surface of the composite adsorbent was theoretically calculated using density functional theory, adsorption kinetics, and the fractional-wave state density function. This analysis aimed to further understand the underlying mechanism of mercury removal and the key mechanisms involved. The Cu-BTC material showed better mercury removal performance compared to the modified biochar. Furthermore, the Cu-BTC-based modified biochar samples, obtained by combining the two materials, exhibited significantly improved mercury removal performance. The optimal loading ratio was found to be 50%, resulting in a high mercury removal performance of 239.18 µg/g. The composite adsorbent primarily consisted of an aromatic structure, including two pyridinium azobenzenes, one anthracene benzene, and one anthracene benzene, with the molecular formula C<sub>75</sub>H<sub>34</sub>O<sub>28</sub>N<sub>3</sub>Fe<sub>2</sub>Cu<sub>13</sub> and the molecular weight Mr=2361.5. The synergistic effect of polymetallic clusters, oxygen vacancies, and carbon skeleton contributes to the exposure of active centers. Additionally, modified biochar, acting as the substrate carrier, provides more metal centers and carbon skeletons within the loaded crosslinked MOFs. This enhances the electron acceptor capacity and transferability of the reaction system. Moreover, the prevention of self-aggregation of metal oxide particles during heat treatment promotes the removal of Hg<sup>0</sup> by synergistically promoting the dispersion of metal centers.

### Abstract Graphics



## Monitoring Mercury Impact on Children Living in Artisanal and Small Scale Gold Mining (ASGM) Hotspots

Anissa A<sup>1</sup>, Dewi P<sup>1</sup>, Ismaranti Y<sup>1</sup>, Huda B<sup>1</sup>, Damayanti R<sup>1</sup>, Fitriani E<sup>1</sup>, Ismawati Y<sup>1</sup>

<sup>1</sup>Nexus3 Foundation

Mercury is a hazard for children who live in artisanal and small-scale gold mining (ASGM) hotspots. They are highly exposed to mercury from the gold extraction process in their neighborhood which affects their growth and development. This study investigates the level of mercury in children's hair (Hg-hair), their intelligence quotient, and DNA damage in children 6 to 12 years of age living in two ASGM sites in West Nusa Tenggara Province, Indonesia. The result shows that all children (n=29) living in both ASGM areas have high Hg-hair levels of >1 ppm with the highest Hg-hair at 49.1 ppm. Unexpectedly, 5 out of 6 children who live far from the gold processing area have Hg-hair >1 ppm of mercury level in their hair, indicating the potential mercury contamination from other sources such as food intake through dietary from local fields as well as fish consumption. The study also assessed children's intelligence quotient (IQ) using Wechsler Intelligence Scale for Children (WISC) III. The results showed that 14.3% of children had low average IQ values, 20% were within the borderline, and 8.6% were extremely low. Comet assay analysis shows that in 8 out of 10 children, their DNA damage ranges from mild to extreme severity.

These findings provide devastating evidence of mercury poisoning in children who live in ASGM areas. Prohibition of the use of mercury to extract gold, early screening for pregnant mothers, and mitigation of mercury pollution supported by strong policies and regulations are needed to secure a better future for children.

## Health Hazard of Mercury-contaminated Fish from the Indonesian Marine Fish Ecosystem

Huda B<sup>1</sup>, Nugroho A<sup>2</sup>, Ismawati Y<sup>1</sup>, Proboretno N<sup>1</sup>, Sabilillah A<sup>2</sup>, Nadar Y<sup>2</sup>, Ganggananda R<sup>2</sup>, Ismaranti Y<sup>1</sup>, Maharani A<sup>1</sup>, Sonia S<sup>1</sup>, Anissa A<sup>1</sup>, Astuti P<sup>1</sup>, Zaki K<sup>1</sup>, Burton M<sup>3</sup>, Evers D<sup>3</sup>

<sup>1</sup>Nexus3 Foundation, <sup>2</sup>Faculty of Biology, Universitas Gadjah Mada, <sup>3</sup>Biodiversity Research Institute  
Mercury (Hg) has been recognised as a global pollutant from anthropogenic activities and regulated under the Minamata Convention. This study shows Hg levels in marine fish collected from eight Indonesian provinces. Fish which were commonly consumed by the local communities were collected from fish auction sites and fish markets. Five species of fish sampled, namely *Lethrinus* sp., or snapper (from West Sumatra), *Sphyrna putnamae* or barracuda (from Lampung), *Megalaspis cordyla* or tengkek fish (from Jakarta), *Caranx sexfasciatus* or pompano fish (from North Sulawesi), and *Gymnocranius grandoculis* (from West Nusa Tenggara)—have Hg contents that either reach or exceed the allowable limit of 0.5 mg/kg established by the World Health Organization.

Due to the bioaccumulation and biomagnification of mercury in the fish food chain, the results show a natural inclination of higher mercury concentration as fish weight increased ( $R^2=0.62$ ,  $p<0.05$ ). To assess the degree of hazards from consuming Hg-contaminated fish and prevent the potential health concerns associated with Hg poisoning, we conducted an analysis on the Estimated Weekly Intakes (EWI) and Total Hazard Quotient (THQ). The results show that 30 of 87 fish samples (34.50%) have THQ value of more than 1, and 15 of 87 fish samples (17.24%) from 8 provinces have EWI values > PTWI (Provisional Tolerable Weekly Intake) values (PTWI = 4 µg/kg for Hg).

It is necessary to continue mercury monitoring especially in fish commonly consumed by the local communities. Sustainable mercury monitoring will provide a better understanding about the status and potential impact of mercury in fish and biodiversity to protect vulnerable populations, especially children and women of child-bearing age. Integrated and multidisciplinary research and monitoring of mercury is needed to secure safe food chains and mercury-free ecosystems.

306

## "Mercury in the Ocean": IAEA's Global Network of Analytical Laboratories for Mercury Data Collection.

Azemard S<sup>1</sup>, ALONSO HERNANDEZ C<sup>1</sup>

<sup>1</sup>IAEA Marine Environment Laboratories

With over 70 per cent of the Earth's surface covered by oceans, they are vital to maintaining livelihoods by providing food, regulating global climate, and preserving biodiversity. With threats such as pollution from radioactive and non-radioactive contaminants, climate change, ocean acidification and deoxygenation affecting marine life, food security and human health, the attainment of SDGs relating to ocean health remain in question.

For more than 60 years, the IAEA has helped Member States build capacity to assess coastal and marine pollution and improve seafood safety by developing and validating analytical methods for measuring contaminants, producing certified reference materials, and applying stable isotope techniques to study pollution processes and determine the sources of contaminants. By collecting this data, Member States can better understand the status of ocean pollution and make evidence-based decisions when regarding ocean sustainability.

Under the "Ocean Health" initiative, the IAEA will support the establishment a Global Network of Analytical Laboratories to collect data on mercury in marine ecosystems, using isotopic and derived nuclear techniques.

The objective of this communication is to present the composition of the network, as well as the main activities and results to be archived in the 2024-2027 cycle.

## Ecological factors differentially affect mercury levels in two species of sympatric pinnipeds from the southern Indian Ocean

Bustamante P<sup>1</sup>, Thebault J<sup>Littoral Environnement et Sociétés</sup>, Brault-Favrou<sup>1</sup> M<sup>Littoral Environnement et Sociétés</sup>, Churlaud C<sup>Littoral Environnement et Sociétés</sup>, Guinet C<sup>Centre d'Etudes Biologiques de Chizé</sup>, Cherel Y<sup>Centre d'Etudes Biologiques de Chizé</sup>

<sup>1</sup>La Rochelle University

Because they return to land to breed, pinnipeds can be used as bioindicators of spatial and temporal variations of Hg contamination of the marine ecosystems. In the southern Indian Ocean, two species of fur seals, the Antarctic fur seal *Arctocephalus gazella* and the Subantarctic fur seal *A. tropicalis* breed in sympatry on the Crozet Archipelago. In such predators, Hg is found in high concentrations due to its biomagnification, with diet and foraging habitat playing a major role in exposure. However, little is known about the factors influencing Hg exposure in closely-related top predators. The two fur seals show foraging segregation between males and females within each species and among species. Here, we examined the significance of various factors (species, sex, feeding habitats [ $\delta^{13}\text{C}$ ] and trophic position [ $\delta^{15}\text{N}$ ]) on total and organic Hg concentrations in whole blood of the two fur seal species. First, over 80% of the THg was under organic form in both species. Second, no significant gender differences were found on average, but Hg concentrations varied widely between males of *A. gazella* (0.039-1.767  $\mu\text{g}\cdot\text{g}^{-1}$  dw), thus contrasting to the females (0.410-0.935  $\mu\text{g}\cdot\text{g}^{-1}$  dw), and to the males and females of *A. tropicalis* (0.523-0.936 and 0.528-1.109, respectively). In males of *A. gazella*, Hg concentrations decreased with increasing latitude (using  $\delta^{13}\text{C}$  as a proxy), and in both species increased with trophic position (using  $\delta^{15}\text{N}$  as a proxy), as a consequence of Hg biomagnification along the food webs. This study shows that ecological segregation is essential to consider in biomonitoring investigations, with individuals feeding in Antarctic waters being less exposed to Hg (lower  $\delta^{13}\text{C}$  values), while individuals feeding on mesopelagic fish (myctophids) are more exposed (higher  $\delta^{15}\text{N}$  values) than those eating pelagic crustaceans (Antarctic krill).

## Evaluating the Minamata Convention Implementation in Slovenia

Usenik V<sup>1,2</sup>, Kontić D<sup>1</sup>, Kocman D<sup>1</sup>, Horvat M<sup>1,2</sup>

<sup>1</sup>Jožef Stefan Institute, <sup>2</sup>International Postgraduate School Jožef Stefan

This study presents the development of a comprehensive framework for evaluating implementation of Minamata Convention in Slovenia, focusing on its effectiveness and key determinants. The central hypothesis asserts that systematic organization of responsibilities and enhanced cooperation among sectors play a crucial role in ensuring consistent adherence. Our approach integrates administrative and environmental metrics to inform decision-making, evaluation of actions taken by involved parties, scrutinizing changes in mercury supply and emissions, and investigating impacts on the environment and vulnerable populations. The study also provides an insight on how well existing (or planned) measures align with the Convention's objectives of protecting human health and the environment.

To achieve these goals, we employ an integrated and participatory approach, involving stakeholders and incorporating scientific, environmental, technical, financial, and economic information. This inclusive method is deemed essential for addressing identified issues and meeting regulatory requirements. The study aims to offer valuable insights into the Minamata Convention's effectiveness in Slovenia over the short, medium, and long term.

In addition to addressing critical gaps in the Convention's implementation, such as risk mitigation measures and monitoring of mercury levels, the research puts forward strategic recommendations for ongoing and future efforts. The findings are expected to contribute to the establishment of a comprehensive evaluation framework, that would help in guiding the systematic implementation of international conventions related to hazardous substances at the national level. This framework promotes cooperation, consistent implementation, and a participatory approach to environmental policy and management.

309

## Scaling up Mercury-Free Processing Technology: Installation of MFPS and Promoting Mercury-Free Processing Technologies in Burkina Faso

Kabre S<sup>1</sup>

<sup>1</sup>Artisanal Gold Council

### Introduction

Gold extraction through the use of mercury remains the predominant method employed by thousands of artisanal miners in Burkina Faso for processing ore into gold. This process, while providing direct and indirect employment to over one million individuals, significantly impacts the local economy. Each stage of the amalgamation presents opportunities for mercury release into the environment, underscoring the urgency for prioritizing the adoption of mercury-free alternatives in countries such as Burkina Faso, where artisanal mining communities are prevalent.

Addressing these challenges necessitates a comprehensive approach to encourage the transition away from mercury use.

Since 2019, planetGOLD Burkina Faso has been implementing a project aimed at addressing these issues. The project comprises four key components including an assessment of the regulatory of the ASGM sector, the provision of training to miners on mercury-free ore processing technology.

PlanetGold Burkina Faso has installed mercury-free processing systems and developed training programs to reduce mercury usage in the project area.

### The approach :

The presentation will delineate the experiences gleaned from project implementation, with a focus on the executing agency's perspective. It will elucidate lessons learned regarding equipment selection and installation, methodological approaches, and the integration of the community into decision-making processes. Insights from the MFPS installation will inform strategies for organizing future facilities more effectively.

Furthermore, the presentation will underscore the significance of the education component, aimed at elevating basic knowledge of ore processing into a nationally recognized technical qualification. Activities supporting the promotion of mercury-free processing technology, including artisanal miner training programs, awareness-raising campaigns, and inter-site exchange visits, will also be outlined

### Content :

- Lessons learned from planetGOLD MFPS installation
- Activities promoting mercury-free processing technology
- Artisanal miners' preferences
- Optimization of technology for artisanal miners in the Burkina Faso context
- Conclusion

### Abstract Graphics



310

## Methylation, demethylation and reduction in coastal waters of the Mediterranean Sea and Atlantic Ocean

Kleindienst A<sup>1</sup>, Tessier E<sup>1</sup>, Torres-Rodriguez N<sup>2</sup>, Asensio O<sup>1</sup>, Gassie C<sup>1</sup>, Heimbürger-Boavida L<sup>2</sup>, Guyoneaud R<sup>1</sup>, Amouroux D<sup>1</sup>

<sup>1</sup>Université de Pau et des Pays de l'Adour, E2S-UPPA, CNRS, IPREM, Institut des Sciences Analytiques et de Physico-chimie pour l'Environnement et les Matériaux, , <sup>2</sup>Aix Marseille Université, CNRS, IRD, Univ. Toulon, Mediterranean Institute of Oceanography (MIO)

In addition to atmospheric deposition, the coastal ocean receives mercury (Hg) and nutrients from continental runoff. The Hg inputs may influence microbial methylmercury (MeHg) production and bioaccumulation in fish. Thus far, only few studies have quantified in-situ MeHg production in the ocean. Here we combine Hg speciation measurements, incubation experiments with species-specific enriched Hg isotopic tracers, and microbial diversity analysis (16S rDNA sequencing) to investigate potential Hg transformations (methylation, demethylation, reduction) along vertical profiles of coastal stations in the Gulf of Lion in the Mediterranean Sea and the Bay of Biscay in the Atlantic Ocean.

We observed an increase of MeHg, dimethylmercury (DMHg), and dissolved gaseous mercury concentrations with depth in both systems. DMHg always dominated the subsurface MeHg pool (up to 100 %). MeHg species concentrations were generally higher in the Gulf of Lion (max 0.47 pM) than in the Bay of Biscay (max 0.19 pM).

Mercury methylation was detected in both systems exclusively in unfiltered deep waters. The production of DMHg was ubiquitous in deep waters. Highest potential methylation rates coincided with the highest abundance of potential Hg methylators, based on 16S rDNA diversity analysis. Photochemical Hg transformations (demethylation, reduction) were always considerably faster than dark transformations (demethylation, reduction), and dark processes were always higher in the presence of particles, thus potentially biotically driven. While dark MeHg demethylation in unfiltered deep waters was not observed in the Gulf of Lion, substantial dark MeHg demethylation was observed in the Bay of Biscay.

Our results suggest that the higher subsurface ambient MeHg concentrations in the Gulf of Lion are likely controlled by a combination of higher MeHg production (to DMHg) and negligible demethylation. Overall, MeHg concentrations and methylation potentials were low in surface waters including the Bay of Biscay despite continental Hg input, suggesting in-situ methylation controlled MeHg subsurface maxima.

311

## Investigating the distribution and abundance of bacterial species influenced by particle size of suspended particulate matter and mercury levels in freshwater system

Kotnik J<sup>1</sup>, Rijavec T<sup>2</sup>, Živković I<sup>2</sup>, Kotnik J<sup>2</sup>, Lapanje A<sup>2</sup>, Horvat M<sup>2</sup>

<sup>1</sup>International Postgraduate School Jožef Stefan, <sup>2</sup>Institut Jožef Stefan

This research delves into the interplay between bacterial communities' development and the size of suspended particles present in freshwater. The aim is to unravel bacteria's natural distribution and abundance along size fractions ranging from 0.2 to 180.0 micrometres ( $\mu\text{m}$ ), gaining insight into the relationship dependent on particle size.

Particle size influences the surface area for bacterial colonisation as increased surface area can promote bacterial growth and activity. Particle size also influences the dispersion in aquatic environments – the size of particles to which bacteria attach can dictate the dispersal patterns in the water column. Furthermore, particle surfaces serve as attachment sites for bacterial biofilm formation and their size dictates the complexity and stability of biofilms.

The subject of the study is a freshwater ecosystem, specifically a river, which is characterised by a strongly present pollutant, mercury. Thus, the research extends beyond bacterial characterisation, seeking to understand how a potent pollutant affects bacterial communities, focusing on size-dependent dynamics. Water samples will be subjected to size fractionation via filtration, and DNA will be isolated. Subsequent polymerase chain reaction (PCR) amplification and sequencing facilitate the targeted assessment of the genetic information in the microbial communities within size fractions. Furthermore, by gaining information on the concentration and distribution of mercury along size fractions, we expect to reveal size-specific adaptations and preferences of bacteria in response to varying pollutant levels as well as identify possible bioaccumulation patterns.

This unique focus on size-dependent dynamics provides novel insights into microbial communities in polluted environments, where implications of the research could extend to the realm of bioremediation. Especially in the context of pollutant stress, certain size fractions may carry communities with enhanced ability to accumulate or metabolise mercury, providing potential bioindicators for pollution levels and unveiling potential candidates for bioremediation strategies.

## Fate, transport, and bioavailability of mercury downstream cyanidation plants in a major ASGM-impacted river

Plunkett S<sup>1</sup>, Bernhardt E<sup>2</sup>, Ruiz M<sup>3</sup>, Mena C<sup>4</sup>, Pan W<sup>5</sup>, O'Neal S<sup>6</sup>, Hsu-Kim H<sup>1</sup>

<sup>1</sup>Civil and Environmental Engineering, <sup>2</sup>Biology, <sup>3</sup>Civil and Environmental Engineering, <sup>4</sup>Geography Institute, <sup>5</sup>Global Health Institute, <sup>6</sup>School of Public Health

Adding elemental mercury and cyanide to gold-rich ores is a common extraction technology in artisanal and small-scale gold mining. In Portovelo, Ecuador's gold mining capital, nearly 100 cyanidation plants process hard rock ore after mercury amalgamation. Many plants subsequently discharge mercury and cyanide-laden effluent into the Puyango-Tumbes river. The Puyango-Tumbes flows into northern Peru where it is the only irrigation source for Tumbes, a prominent rice-growing region in this arid landscape.

We analyzed mercury and cyanide concentrations in surface waters and sediments along the entire 160 km length of the Puyango-Tumbes until it discharges into the Pacific Ocean. Downstream of Portovelo, mercury concentrations in unfiltered surface waters peaked at 4000 ng L<sup>-1</sup> and declined but remained elevated at concentrations over 250 ng L<sup>-1</sup> throughout the surveyed length. In irrigation water collected 160 km downstream of the processing plants, mercury concentrations averaged 610 ng L<sup>-1</sup> (maximum concentration 1659 ng L<sup>-1</sup>). This water is used to flood rice paddies-wetland environments that are particularly prone to methylmercury production as well as accumulation in the rice grain. We present on the fate of mercury deposited into these paddies and rice uptake of (methyl)mercury and other metalloids.

Visual Minteq modeling suggests that mercury speciation is dominated by mercuric cyanides complexes in the first 50 km downstream of ore processing. We hypothesized that the presence of cyanide would decrease methylmercury concentrations in surface water by suppressing microbial activity but instead found the contaminants to be positively correlated. While mercuric cyanide complexes can be directly assimilated by fish, their bioavailability to methylating microorganisms is not known. Understanding the fate and bioavailability of mercury along this complex pollution gradient is important for assessing health risk for the people of Tumbes (population of 110,000) that rely on this water supply, and similar communities downstream of ASGM activity worldwide.

313

## Long-term Monitoring of Mercury in Swedish Freshwater Systems

Jonsson S<sup>1</sup>, Sundbom M<sup>1</sup>

<sup>1</sup>Department of Environmental Science, Stockholm University

Sweden has for decades conducted environmental monitoring of lakes and watercourses, including levels of mercury in biota, with the aim of understanding and monitoring their ecological status. Previous studies have demonstrated declining Hg concentrations in pike as well as correlations between, for example, pH, sulfate, and TOC (Total Organic Carbon) with mercury in fish. Here, we have conducted an evaluation of more recent trends in fish mercury levels, and how they have responded to changes in the environment and water quality.

## Critical assessment of incubation experiments using isotopically enriched mercury compounds in seawater

Kleindienst A<sup>1</sup>, Tessier E<sup>1</sup>, Duval B<sup>1</sup>, Koenig A<sup>2</sup>, Guyoneaud R<sup>1</sup>, Amouroux D<sup>1</sup>

<sup>1</sup>Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, Institut des Sciences Analytiques et de Physico-chimie pour l'Environnement et les Matériaux, <sup>2</sup>Université Grenoble Alpes, CNRS, INRAE, IRD, Grenoble INP, IGE

Understanding primary drivers and rates of mercury (Hg) species transformations is crucial for the accurate modeling and projection of methylated Hg in marine and aquatic systems. Incubation experiments in field or laboratory studies employing stable isotopic tracers have advanced our understanding of potential Hg transformation pathways, however, their comparability and accuracy have remained a question due to the use of different experimental and analytical protocols.

In this study, we evaluate a protocol for incubation experiments at near ambient tracer concentrations (around 10 pM <sup>199</sup>Hg(II) and 1 pM MM<sup>201</sup>Hg) including volatile Hg species by conducting incubation experiments on three distinct coastal seawaters. We perform a comprehensive quality assessment (e.g. mass balance over incubation period, relative standard measurement uncertainty) notably incorporating volatile Hg species for the first time. We discuss potential factors hampering inter-comparability among studies when different experimental and analytical protocols were employed (e.g. higher spiking levels).

We achieved good experimental reproducibility for both introduced incubation tracer <sup>199</sup>Hg(II) and MM<sup>201</sup>Hg, with a mean relative standard deviation (RSD) between experimental replicates of ~1.7 % and ~1.5 %, respectively. While experimental reproducibility was slightly lower for newly formed <sup>199</sup>Hg(0), <sup>201</sup>Hg(II) and <sup>201</sup>Hg(0) with a mean RSD of ~10 %, ~13 % and ~22 %, respectively. Mass balance assessments were good for both introduced incubation tracer for unpurged samples (mean of 99.2 % for <sup>199</sup>Hg and 100.5% for <sup>201</sup>Hg) and purged samples (mean of 100.5 % for <sup>199</sup>Hg and 102.2 % for <sup>201</sup>Hg). The relative standard measurement uncertainty computed for <sup>199</sup>Hg(II), MM<sup>199</sup>Hg, <sup>201</sup>Hg(II) and MM<sup>201</sup>Hg aligned well with the experimental reproducibility.

This work presents a detailed, critically evaluated experimental and analytical protocol that allows the accurate determination of methylation, reduction, demethylation and reductive demethylation rates in seawater. We provide comprehensive recommendations for conducting incubation experiments in seawater, aiming to enhance inter-comparability among different studies.

315

## Taking into account the phycosphere: what does it mean for regional Hg and MeHg bioaccumulation?

Garcia Arevalo I<sup>1</sup>, Amptmeijer D<sup>2</sup>, Bieser J<sup>2</sup>, Knoery J<sup>1</sup>

<sup>1</sup>Contamination Chimique des Ecosystèmes Marins CCEM - Ifremer, <sup>2</sup>Institute of Coastal Systems – Analysis and Modeling, Helmholtz-Zentrum Hereon

The accumulation of dissolved mercury by phytoplankton presents the largest concentration step along aquatic food chains. However, individual cell uptake mechanisms and the mechanisms governing Hg transformation within plankton are still poorly understood. Particularly, the phycosphere, the unstirred boundary layer in the immediate vicinity of an algal cell, has not been considered in Hg-phytoplankton dynamics, even if its interactions may influence the bioaccumulation of Hg by phytoplankton.

To explore the phycosphere's role at the regional scale, we performed several experiments to obtain internally consistent kinetic parameters of cellular accumulation and transformation of Hg species. We used conventional (i.e., concentration) and advanced (i.e., isotopic composition) methods to track mercury uptake, as well as intra and extracellular transformation in phytoplankton. We then devised and used a three-compartment model to examine the transfers of mercury. The lab-grown phytoplankton compartments that were considered included the complexation of Hg with dissolved ligands in the exposure medium, the adsorption of dissolved Hg species into the phycosphere, and its subsequent cellular internalization.

The aim of the present study is to explore the regional impact of micro-scale mercury species transfers to and into phytoplankton on larger scale in a bioaccumulation model combining the ECOSMO II ecosystem model and the MERCY mercury speciation model in a 1D water column. To do so, we ran the models using the conditions and rates from our in-vitro experiments.

The results show the phycosphere as an essential compartment for Hg species accumulation and its role in the internalization of Hg. Furthermore, we observed the phycosphere proved to be a microenvironment fit mercury methylation, especially when associated to microorganisms from coastal seawater.

Ultimately, these results help to better understand the distribution of Hg between its dissolved and particle phases.

## Vegetation Influences Mercury Accumulation in Permafrost Peatlands

Haugk C<sup>1</sup>, Brach A<sup>1</sup>, Hugelius G<sup>2</sup>, Kuhry P<sup>2,3</sup>, Sannel B<sup>2,3</sup>, Tarbier B<sup>2</sup>, Jonsson S<sup>1</sup>

<sup>1</sup>Department of Environmental Science and Analytical Chemistry, Stockholm University, <sup>2</sup>Department of Physical Geography, Stockholm University, <sup>3</sup>Bolin Centre for Climate Research, Stockholm University

Northern peatlands have historically acted as a globally important sink for atmospheric mercury (Hg). To what extent vegetation regimes are affecting Hg accumulation in these systems is, however, not well understood. Here, we investigated Hg profiles in nine peat cores, originating from sites in west-central Canada (n=4) and northern Fennoscandia (n=5). Their peat accumulation history has been characterized in previous studies using plant macrofossil analysis. Additionally, for available sections we calculated the long-term carbon accumulation rate (LARCA) and introduce the long-term mercury accumulation rate (LARMA). Highest Hg concentrations were found close to the peat surface in all cores with 218  $\mu\text{g Hg kg}^{-1}$  soil as a maximum value (Selwyn Lake peat core). Increased Hg concentrations were identified in rootlet layers, indicating dry conditions and slower peat accumulation rates at the time of Hg deposition. This means drier vegetation regimes compared to wetter regimes record higher Hg concentration. Our study confirms peat as a valuable record of past Hg deposition, and suggests that vegetation patterns may drive Hg concentration in Arctic soils and its long-term accumulation rates.

317

## Fate of Land Derived Mercury in Coastal Ecosystems

Barale I<sup>1</sup>, Jonsson S<sup>1</sup>

<sup>1</sup>Department of Environmental Science, Stockholm University

Mercury is a toxic element that bioaccumulates in aquatic food webs to levels of concern for human and wildlife health. To address this concern, the Minamata Convention, established in 2013 (<https://mercuryconvention.org/>), aims to safeguard human health and wildlife well-being from the adverse effects of Hg exposure. Key actions outlined in this treaty involve reducing human-caused Hg emissions and managing areas already contaminated to mitigate Hg pollution. However, linking Hg emissions to their environmental impact is challenging, especially in dynamic environments like coastal oceans. Here, I will present my PhD project, which aims to generate knowledge that can help us understand the environmental consequences of Hg in coastal ecosystems.

## Mercury Mobility in Permafrost Peatlands of northern Scandinavia

Haugk C<sup>1</sup>, Azaroff A<sup>1</sup>, Johansson M<sup>2</sup>, Li M<sup>3</sup>, Thompson L<sup>4,5</sup>, Urrea M<sup>6</sup>, Jonsson S<sup>1</sup>

<sup>1</sup>Department of Environmental Science and Analytical Chemistry, Stockholm University, <sup>2</sup>Department of Physical Geography and Ecosystem Science, Lund University, <sup>3</sup>Institute of Tibetan Plateau Research, University of Chinese Academy of Sciences, <sup>4</sup>Department of Renewable Resources, University of Alberta, <sup>5</sup>Hatfield Consultants, <sup>6</sup>Department of Ecology, Environment and Earth Science, Umeå University

Permafrost experiences rapid transformations through ongoing thaw, thereby releasing mercury (Hg) and potentially forming hotspots for Hg methylation as organic matter is degrading. If Hg is remobilized and bioaccumulated as Methylmercury (MeHg) in food webs, it can be of health concern to northern communities and wildlife. We have investigated the Hg cycling in permafrost peatlands, including both natural thaw gradients and a long-term snow fence field experiment. The natural thaw gradients sampled were located in four peatland sites in northern Norway and Sweden. In total, 47 peat plateau cores, representing intact permafrost conditions, and 47 fens soil cores, representing thawed permafrost conditions, were collected and characterized based on their distribution of total Hg, MeHg and organic matter. Where permafrost peat had degraded into wet fens, we found higher levels of MeHg while the total Hg levels were lower upon thaw. These results suggest both increased methylation and remobilization of Hg due to eroding peatlands. The field experiment site we investigated is located in a peatland in Abisko in northern Sweden. Here, we will present analysis of the same parameters as above in six manipulated plots with snow fences that simulate ongoing permafrost thaw and compared them to six control plots. The focus lies not only on the effect of winter warming on Hg mobilization but will also include data of seasonal variations. Looking at the distribution and transformation of Hg on a regional scale combined with the data from a local field experiment helped us to better understand Hg mobility from thawing permafrost systems of northern Scandinavia.

319

## Modelling mercury bioaccumulation in reared clams from a temperate polluted lagoon

Rosati G<sup>1</sup>, Solidoro C<sup>1</sup>, Canu D<sup>1</sup>

<sup>1</sup>National Institute Of Oceanography And Applied Geophysics - Ogs

The bioaccumulation of mercury (Hg) and methylmercury (MeHg) in commercially available fish and shellfish species leads to global human exposure to Hg and poses a health concern. Hg concentrations in marine invertebrates are generally lower than in fish of higher trophic levels. However, in lagoons and coastal ecosystems located near historical or active pollution sources, Hg accumulation in lower trophic level organisms can be substantial. The Venice Lagoon is a valuable ecosystem that has been contaminated by the dumping of industrial waste from a former chlor-alkali plant, resulting total Hg concentrations in surface sediments currently from ranging 0.3 to 1.6 ug/g, depending on proximity to the historical Hg source.

We have developed a model for the bioaccumulation of Hg and MeHg in the bivalve *R. philippinarum* by integrating uptake and excretion dynamics into an existing bioenergetic model. The model is applied to the Venice lagoon to assess the influence of environmental variability on bioaccumulation as well as potential Hg content in specimens of different sizes at sites intended for clam farming and harvesting, which are characterized by different degrees of sediment contamination. Realistic meteorological influences and dynamic concentrations of Hg species in organic detritus for each site are obtained through an offline coupling with a biogeochemical model for the Hg cycle. The integrated model helps to estimate the relative importance of different factors for Hg bioaccumulation in clams. It also provides a management tool to assess both the suitability of different areas for clam farming and the optimal size range of clams for human consumption.

320

## Mercury (Hg) in bottled water from different countries: determination at nanogram/sub-ng per liter levels and human health risk assessment

Vardè M<sup>1</sup>

<sup>1</sup>CNR-Institute of Polar Sciences

Mercury (Hg) is a naturally occurring toxic element found worldwide, released from both natural and anthropogenic sources. Its long lifetime allows for complex transformations, deposition, and potential impact on uncontaminated areas. Methylmercury, known for its heightened toxicity, is predominantly acquired by humans through the consumption of fish and seafood, whereas the intake of inorganic mercury from drinking water and non-alcoholic beverages is comparatively minimal.

The global consumption of bottled waters (BW) is rising annually, with a significant portion of the population relying on them. Despite numerous publications on heavy metals in BW, mercury determination often lacks the sensitivity required for ultratrace levels <sup>1</sup>. Few surveys at regional and national scales <sup>2,3</sup> have studied Hg at nanogram/sub-nanogram per liter levels and conducted human health risk assessments for long-term exposure.

To address these gaps, we analyzed thirty-four bottled water samples from twelve countries (Croatia, France, Germany, Italy, Morocco, Norway, Poland, Serbia, Slovenia, Switzerland, Turkey, United Kingdom). Samples were processed in a dedicated clean room facility, and total mercury analyses were conducted using a modified US-EPA 1631 method with Cold Vapor Atomic Fluorescence Spectrometry-CVAFS (MercurPlus, Analytik Jena). Validation included certified reference materials, different Hg standard solutions, and recovery checks through matrix spikes and duplicates.

Hg concentrations within the ng/sub-ng per liter range form the basis for a comprehensive health risk assessment. Adherence to national/international standards for bottled waters, typically with total mercury concentration threshold below 1 or 2 µg/L ensures public health safety and, through the provision of preliminary data, enhances our understanding of mercury levels, facilitating an accurate assessment of potential health risks associated with consumption.

## Formation of refractory methylmercury pools by particle adsorption

Gindorf S<sup>1</sup>, Tirunaghari A<sup>1</sup>, Jonsson S<sup>1</sup>

<sup>1</sup>Stockholm University Department of Environmental Science

Monomethylmercury (MMHg) is a bioaccumulating neurotoxin that poses a risk to wildlife and humans. We are still lacking key information to fully understand the bioavailability of MMHg for uptake at the base of aquatic food webs. One important puzzle piece missing, is lacking knowledge of the extent of refractory MMHg pools, here referred to as the MMHg bound to particles and unavailable for desorption. In this study, we quantified the formation of refractory MMHg pools in slurries prepared from different types of soils (organic rich peat soil, mineral soil, and a mineral-rich stream sediment) and waters (stream, pond, fjord) using an isotopically labelled MMHg tracer. After tracer addition, the adsorption of MMHg onto the particulate matter was studied for up to 48 hours. In a secondstep, the water was exchanged to study the desorption of the particle-bound MMHg tracer for up to 8 weeks. Refractory MMHg pools in different slurries were calculated based on the partitioning of the added tracer during the adsorption and desorption steps. We found refractory pools to be formed in all soil-water combinations tested. The data reveals a general trend where a higher organic fraction in the solid matrix corresponds to a greater fraction of MMHg entering the refractory pool. Moreover, higher dissolved organic matter concentrations in the water relate to lower refractory MMHg. This information will help us to relate water and particle properties to the potential for transport and bioavailability of MMHg bound to terrestrial particles.

## Innovative analytical methodologies to facilitate Hg detection in remote areas

Diez S<sup>1</sup>, Fontàs C, Marrugo-Madrid S, Turull M, Marrugo-Negrete J

<sup>1</sup>IDAEA - CSIC

Efficient and straightforward techniques are essential for facilitating mercury monitoring, aiming to acquire reliable and significant data regarding contamination in aquatic environments. In this context, chemically functionalized membranes emerge as pivotal, representing one of the most promising developments in membrane technology today. This study investigates the potential of Polymer Inclusion Membranes (PIMs), a type of functionalized membrane, to address various analytical challenges in mercury (Hg) analysis and monitoring. PIMs consist of a polymer providing mechanical strength and a carrier responsible for the extraction process. Our research demonstrates the efficacy of a PIM as a sorbent for extracting Hg from diverse natural waters, including seawater, without being influenced by water matrix effects. Furthermore, considering the problems associated with both preservation and storage of aqueous samples for ambient-level Hg analysis, we explore the application of PIMs as a suitable material for preserving the metal until the appropriate analysis is conducted. Notably, the concentration of Hg extracted in PIMs remains stable over time, with measurements recorded over a period of 5 years. These robust results suggest PIMs as a suitable tool for Hg monitoring in remote areas.

To assess Hg contamination in Colombian freshwater ecosystems near artisanal and small-scale gold mining (ASGM) areas, field sampling was conducted. PIMs were deployed at sites along the Atrato River and abandoned mining ponds (AMPs), which were deserted at various times between 1997 and 2019 (6–15 years). The outcomes of these measurements will be presented and discussed.

323

## Environmental exposures and maternal-infantile health in Rondonia, Brazilian Amazon: who can we blame besides mercury?

Diez S<sup>1</sup>, Cunha M, Marques R, Guimaraes J, Gago P

<sup>1</sup>IDAEA - CSIC

Low exposure levels to environmental risks can be a risk to the fetus, through transplacental circulation and after birth, breast-feeding. Our objective was to evaluate, in pregnant women from a reference maternity of the state of Rondonia, Brazilian Amazon, the exposure to mercury and the adverse birth outcomes. We made a transversal study with pregnant women that resided in Rondonia state, with a single pregnancy and no use of tobacco, alcohol or drugs during pregnancy. Data on the pregnancy, negative outcomes (malformations, low weight at birth, prematurity), socio-demographic characteristics and birth data were obtained through questionnaires and clinical records. Mother hair samples were taken for analysis of mercury and organic pollutants, to evaluate the risks for mother and newborns. Preliminary data are given as absolute and relative frequencies. We evaluated 330 mother/baby pairs so far. Prematurity affected 57% of newborns, low weight at birth, 53% and congenital malformations (CMs), 37%. The most frequent CMs were related to cardiovascular, digestive, muscular-skeletal and neurological problems. About 68% of newborns required intensive neonatal care. Most mothers were under 35 years old, were married or in stable relationships (70%), had completed medium education or higher (58%), had a family revenue of less than two minimum wages, (~ 530 USD) and relied on well water.

The observed birth outcomes can be related to individual and clinical factors, as well as to environmental exposures to mercury, other metals and pesticides and maternal hair data on these risk factors may help to relate environmental quality and maternal-infantile health, allowing faster decision making and better health services to the local population.

## The role of catchment properties on mercury dynamics

Gindorf S<sup>1</sup>, Baptista-Salazar C<sup>1</sup>, Liem-Nguyen V<sup>1</sup>, Giesler R<sup>2</sup>, Mörtz C<sup>3</sup>, Jonsson S<sup>1</sup>

<sup>1</sup>Department of Environmental Science, Stockholm University, <sup>2</sup> Department of Ecology and Environmental Science, Climate Impacts Research Centre, Umeå University, <sup>3</sup>Department of Geological Sciences, Stockholm University

Large amounts of mercury (Hg) have been stored in permafrost soils over millennia. As a result of climate change and Arctic amplification some of this Hg may be released into the Arctic environment where it can undergo microbial methylation producing the neurotoxin methylmercury (MeHg). MeHg bioaccumulates in food webs and poses a threat to humans and wildlife. In this study, we investigate how catchment properties affect the transport and bioaccumulation of total mercury (THg) and MeHg in Swedish high-latitude catchments comprising tundra, birch, and boreal forest ecosystems. We analyzed THg, MeHg, and over 60 ancillary parameters in 26 different streams and lakes along a climate and vegetation gradient (67.5 to 68.5 °N and 18 to 21.5 °E) in August 2020. We use a parafac model to study the importance of dissolved organic matter (DOM) characteristics for the fate of Hg in our dataset. Using multivariate analysis, differences in water type and catchment system are evident in ancillary parameters. THg and MeHg levels rank as Boreal > Birch > Tundra in lakes and streams while lakes exhibit higher MeHg and MeHg%. A strong positive correlation of THg and dissolved organic carbon in combination with a strong anticorrelation of THg and relative fluorescence efficiency (RFE, an indicator for algal vs. non-algal DOM) suggests terrestrial matter as the source of aquatic THg. We observe highest MeHg % in the Tundra lakes compared to the two catchments which can indicate higher in-situ methylation in Tundra lakes. We observe a positive correlation of MeHg% with protein-like DOM, which can further indicate higher bacterial activity related to a higher MeHg fraction of THg. Overall, our study suggests that catchment properties may be important determinants for the fate of remobilized terrestrial Hg.

325

## GASEOUS MERCURY IN AN ARTISANAL SMALL-SCALE GOLD MINING IN COLOMBIA

Diez S<sup>1</sup>, Laza-Durante , Urango-Cárdenas I, Durante-Yáñez E, Marrugo-Negrete, J

<sup>1</sup>IDAEA - CSIC

Mercury (Hg) is a hazardous element easily dispersed through the air, posing a significant threat to ecosystems and human well-being. Artisanal small-scale gold mining (ASGM) stands out as a primary source of mercury contamination. ASGM, characterized by low-tech and machinery use, is typically undertaken by individuals, groups, or communities, leading to numerous unclosed and unrehabilitated mines and resulting in substantial environmental liabilities. Hence, according to Minamata Convention, evaluating contamination levels in abandoned mining sites is imperative. This study focuses on characterizing mercury concentration in the air within an environmental liability located in the southern region of the Ayapel swamp, in the department of Córdoba, Colombia. The study area encompasses 2.4 hectares of mining soil with mercury concentrations around 1680.62  $\mu\text{g kg}^{-1}$ . Two surveys were conducted using a mercury analyzer RA-915M (Lumex Instruments, Canada) – one during the dry season and another during the rainy season. Results revealed higher concentrations during the first sampling, contrasting with relatively lower concentrations during the second sampling. This variance was attributed to factors such as rainfall, strong winds, increased vegetation cover, and decreased temperature. The interaction of these elements influences Hg evaporation dynamics and mobility.

While the highest recorded concentration was 137.62 ng Hg m<sup>-3</sup>, staying below the Colombian standard limit of 1000 ng Hg m<sup>-3</sup>, it is crucial to acknowledge this as an environmental concern due to mercury's persistent nature in the air, posing potential harm over extended periods.

## Investigating Mercury (Hg) and Water Stable Isotopes Composition ( $\delta^{18}\text{O}$ and $\delta^2\text{H}$ ) in Bottled Waters: A survey Study in Italy

Vardè M<sup>1,2</sup>, Dreossi G<sup>2</sup>, Radaelli M<sup>2</sup>, Peschiutta M<sup>2</sup>, Masiol M<sup>2</sup>, Stenni B<sup>2</sup>

<sup>1</sup>CNR-Institute of Polar Sciences, <sup>2</sup>Department of Environmental Sciences, Informatics and Statistics

In the last years, several studies have been conducted on bottled waters (BW) at national, regional, and worldwide scale considering major and trace elements, organic compounds and/or emerging contaminants. Hitherto, a few studies focused on mercury, and water stable isotopes determination of bottled waters are available in the literature. Therefore, this kind of research on BW can periodically be useful for understanding the potential variation of these parameters over time. Italy is one of the main producers of BW and Italians are the greatest consumers of natural mineral waters per capita in the European Union. The natural mineral water sources (natural spring and groundwater) across Italy, are generally placed on flood plains or mountain slopes. European and national regulations established that BW must be microbiologically pure without any purification process because they originate from aquifers or underground reservoirs. Total mercury (Hg), stable isotopic composition ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) and additional physico-chemical parameters have been evaluated on selected bottled waters purchased in the Italian stores. Bottle samples from different Italian water catchments all over Italy are here characterized to be representative of different hydrogeological conditions. Numerous brands of BW representing different water typologies (still, sparkling, naturally sparkling, and slightly sparkling), bottled in different packaging, have been considered. Instrumental analyses (e.g.: CVAFS, Cavity Ring-Down Spectroscopy) were carried out in the laboratories of CNR and Ca' Foscari University. The main objective of this work is to investigate the occurrence of Hg in Italian bottled waters considering  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and deuterium excess, as well as the differences on physico-chemical parameters, (approx. ten years later, after the last national surveys) taking into account their wide representativeness of the geographical area and geological provenance.

327

## Statistically evaluating the performance of mercury passive air sampler at a regional background site in South Africa

Jaars K, Job X, van Zyl P, Bredenkamp L, MacSween K, Josipovic M, Martin L, Vakkari V, Kulmala M, Laakso L

<sup>1</sup>Atmospheric Chemistry Research Group, Chemical Resource Beneficiation, North-West University,

<sup>2</sup>Atmospheric Chemistry Research Group, Chemical Resource Beneficiation, North-West University,

<sup>3</sup>Atmospheric Chemistry Research Group, Chemical Resource Beneficiation, North-West University,

<sup>4</sup>Atmospheric Chemistry Research Group, Chemical Resource Beneficiation, North-West University,

<sup>5</sup>Environment and Climate Change Canada, <sup>6</sup>Atmospheric Chemistry Research Group, Chemical Resource Beneficiation, North-West University, <sup>7</sup>South African Weather Service c/o CSIR, <sup>8</sup>Finnish Meteorological Institute, <sup>9</sup>Institute for Atmospheric and Earth System Research, University of Helsinki, <sup>10</sup>Finnish Meteorological Institute

South Africa has been ranked among the top ten mercury emitters globally, with emissions from coal-fired power plants being the most significant contributor. The Minamata Convention on Mercury seeks to reduce global mercury emissions, but monitoring networks in Africa face limitations due to cost and logistics. Passive air samplers, like the Mercury Passive Air Sampler (MerPAS<sup>®</sup>), offer a cost-effective solution to expand atmospheric mercury measurements. This study evaluates MerPAS<sup>®</sup> accuracy, precision, and reliability in the South African environment.

Using the Tekran<sup>®</sup>-developed MerPAS<sup>®</sup>, the study compares it with active in situ atmospheric mercury sampling at a well-equipped South African monitoring station, Welgegund Atmospheric Measurement Station. The statistical evaluation shows that MerPAS<sup>®</sup> accurately measures atmospheric mercury concentrations and complements active sampling, making it valuable for improving spatial resolution.

The successful evaluation of MerPAS<sup>®</sup> in South Africa has significant implications for mercury monitoring efforts in Africa. By overcoming logistical constraints and providing a cost-effective passive air sampler, atmospheric mercury monitoring networks can be significantly expanded in the region. This is crucial for understanding mercury distribution and its environmental impact, supporting South Africa's commitment to the Minamata Convention.

In conclusion, the MerPAS<sup>®</sup> performs well in South African atmospheric conditions, offering a reliable and cost-effective method for atmospheric mercury monitoring. Its integration into the South African Mercury Network could significantly improve spatial resolution and contribute to a comprehensive global understanding of atmospheric mercury distribution and its implications for environmental health.

## Genetic determinisms involved in mercury resistance mechanism in a sulfate reducing bacterium: impact on mercury accumulation and methylation

Barrouilhet S<sup>1</sup>, Monperrus M<sup>2</sup>, Gassie C<sup>1</sup>, Le Bars M<sup>1</sup>, Dolla A<sup>3</sup>, Khalfaoui Hassani B<sup>1</sup>, Guyoneaud R<sup>1</sup>, Isaure M<sup>1</sup>, Goni Urriza M<sup>1</sup>

<sup>1</sup>Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, <sup>2</sup>Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, <sup>3</sup>CNRS, MIO, LCB-UMR7283, Aix-Marseille Université

Mercury resistance mechanisms are well characterized in aerobic microorganisms, although they remain unidentified in anaerobes. Since some anaerobic bacteria are able to transform Hg(II) into methylmercury (MeHg), deciphering Hg resistance mechanisms is necessary to understand how anaerobes deal with Hg toxicity and if there is a relationship between Hg(II) resistance and methylation. Differential transcriptomic analysis on the sulfate reducing bacterium *Pseudodesulfovibrio hydrargyri* BerOc1 identified a cluster of genes overexpressed at 0.5  $\mu$ M of Hg(II). These genes display homologies with both metal sensor and efflux systems. In this study, the role of this cluster of genes in Hg resistance and methylation was determined. For this, single and double BerOc1 mutant strains, deleted for either the metal sensor ( $\Delta$ sms) or the efflux system ( $\Delta$ sfx), or both, were generated and their phenotypes were compared to the wild-type strain (wt). Mutants were sensitive to Hg(II) at the concentrations above 0.5  $\mu$ M, pinpointing this concentration as the threshold concentration inducing Hg resistance mechanisms in the wt strain. Moreover,  $\Delta$ sfx cells accumulated up to 10 times more Hg(II) than wt, whereas  $\Delta$ sms and double mutant cells accumulated up to 200 times less Hg(II). Surprisingly, MeHg production was decreased for all the mutant strains, even in the  $\Delta$ sfx that showed higher intracellular Hg(II) contents. These results suggest that Hg(II) accumulated intracellularly are not fully available for methylation. Altogether, our results support a combined two-level resistance mechanism: a first resistance (low level) induced by a periplasmic Hg-scavenging sensor and a second resistance (higher level) induced by the efflux system. This study highlights, for the first time, a mechanism of Hg resistance in anaerobic bacteria. This finding is a key step toward understanding the MeHg and Hg(II) dissemination in ecosystems.

## Photochemical reduction of oxidised mercury in atmospheric aerosol water

Han D<sup>1,2</sup>, Wu Q<sup>2,3</sup>, Wang S<sup>2,3</sup>, Shi J<sup>1,4</sup>

<sup>1</sup>Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, <sup>2</sup>School of Environment, Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, <sup>3</sup>State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, <sup>4</sup>State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences

Atmospheric oxidised mercury (Hg(II)) deposition on the Earth's surface endangers biota and humans. The photoreduction of Hg(II) competes with deposition and thereby modifies global mercury cycling, yet the pathways and mechanisms of PBM photoreduction remains poorly understood. Herein, we reveal this process by comprehensively using field observations, mercury stable isotope analyses and controlled experiments. We found that water-soluble organic carbon (WSOC) decides photoreduction of particle bound mercury (PBM) in aqueous aerosols within light, resulting large positive  $\Delta^{199}\text{Hg}$  mass independent fractionation (MIF). The  $\Delta^{199}\text{Hg}$  values in wet haze episodes were significantly higher than that in clean period, induced by aerosol phase state shifts from semisolid to liquid state results from aerosol water content (AWC) increasing. The photoreduction of PBM induced by carboxylic (-COOH) functional groups within WSOC coordinated with Hg(II) dominant PBM photoreduction in wet aerosols, takes place via both direct and indirect pathways, demonstrated with positive correlation between WSOC and  $\Delta^{199}\text{Hg}$ , and large positive  $\Delta^{199}\text{Hg}$  MIF in aerosols. This crucial role played by WSOC in the photoreduction of PBM in wet aerosols is likely widespread in the atmosphere, and can be expected to significantly influence global mercury transformations and regional depositions. The Hg(II) photoreduction rate constant of aerosol water is 3–6 times higher than those observed in other tropospheric aqueous phases (e.g. rainwater, fog). We therefore highlight that the Hg(II) photoreduction mediated by carboxyl ligands is a crucial driving factor for global mercury cycling, and play a remarkable role in reshaping isotopic compositions of mercury in the tropospheric aqueous phase.

## Microbial interactions between sulfate reducing bacteria and anoxygenic phototrophs affect Hg methylation

Scuvée D<sup>1</sup>, Vigneron A<sup>1</sup>, Guyoneaud R<sup>1</sup>, Tessier E<sup>1</sup>, Gassie C<sup>1</sup>, Xue J<sup>1</sup>, Amouroux D<sup>1</sup>, Khalfaoui-Hassani B<sup>1</sup>, Goñi Urriza M<sup>1</sup>

<sup>1</sup>Iprem University Of Pau

Methylmercury is mainly produced by anaerobic microorganisms, including sulfate reducing bacteria (SRB). In natural environments, SRB cohabit with other microorganisms that could modify the methylmercury production. However, pure culture studies do not consider the interactions between microorganisms that co-exist in the same environment. Controlled cocultures, mixing strains with different ecological role, can be an alternative strategy to better understand the effect of microbial interactions on mercury methylation. Among microbial interactions, the coupling of sulfate-reducers (heterotrophs, able to methylate mercury) and anoxygenic phototrophs (autotrophs, sulfo-oxidizers, some able to reduce Hg<sup>2+</sup>) serves as a model for studying microbial interactions linking carbon and sulfur biogeochemical cycles, and probably, mercury cycle. In this work, we investigated the mercury transformation capacities of microbial consortia composed of the SRB and the mercury methylating bacterium, *Desulfobulbus propionicus* 1pr3, and either a purple-sulfur phototrophic bacterium, *Allochromatium vinosum* DSM180 or a purple-no-sulfur phototrophic bacterium, *Rhodobacter capsulatus* SB1003. The methylmercury production of *D. propionicus* grown with *A. vinosum* increased 10 times compared to its production when *A. vinosum* was absent, revealing the synergic effect of microbial interactions. The use of the sulfide by *A. vinosum*, that is produced by *D. propionicus*, may modify the mercury speciation, and the released mercury may become available for methylation by *D. propionicus*. By contrast, methylmercury production remained unchanged in cocultures with *R. capsulatus*.

The transcriptomic response of cocultures in the presence or absence of Hg<sup>2+</sup> was monitored in parallel. Neither the addition of Hg in cocultures nor the bacterial partner significantly changed transcriptomic profile of *D. propionicus*. However, expression profiles of *A. vinosum* and *R. capsulatus* changed in the Hg presence, albeit in different ways.

The results presented in this work demonstrate that microbial interactions impact the level of methylmercury produced in controlled co-cultures, suggesting that similar phenomena occur at the environmental level.

## Addressing Measurement Uncertainties of the Isolation Methods for Methylmercury Speciation in Low-Level Urine Samples

Alilović A<sup>1</sup>, Živković I<sup>1,2</sup>, Horvat M<sup>1,2</sup>

<sup>1</sup>International Postgraduate School Jožef Stefan, <sup>2</sup>Institute Jožef Stefan

Mercury speciation in urine samples is particularly analytically challenging, due to very low methylmercury (MeHg) concentrations, possible matrix interferences, and potential production of MeHg from inorganic Hg (Hg(II)), when latter is present in much higher concentrations. Typically, limited urine volume (few milliliters per individual) is available for speciation, necessitating a method capable of speciation in volumes as low as 1 mL. The conventional nitric acid digestion method often proves insufficient, as it enables processing of only small amounts of urine digest. This study explored direct distillation as alternative isolation method for MeHg determination in urine. Thirty-two urine samples underwent analysis using both distillation and acid digestion, with results compared. For both methods, measurement uncertainty was determined according to the ISO Guide to the expression of uncertainty in measurement (ISO/GUM), which is key for result comparison. The distillation method demonstrated a significant advantage by facilitating MeHg separation from the matrix and reducing Hg(II) concentrations in the distillate. This led to diminished interferences during the ethylation step, improved peak shapes, and enhanced quantification reliability. Notably, the distillation method exhibited lower uncertainty, especially at the lowest MeHg concentrations (<7 pg/g urine), compared to the acid digestion method. The main contributor to high measurement uncertainty of the acid digestion method is poor sample repeatability, probably attributable to matrix interferences that cause distorted peaks difficult to properly integrate. In the lowest concentration range, the main contributor to uncertainty of the distillation method is also sample repeatability, although appreciably lower than in the acid digestion (ur,sample repeatability = 7.0% versus 14.9%, respectively). As MeHg concentrations increased, the contribution of sample repeatability decreased, with an observed increase in standard repeatability and recovery effects on total uncertainty. Overall, this study underscores the advantages of the distillation method in improving the reliability of MeHg speciation in urine samples.

## Mercury Exposure Assessment and Model Validation through Controlled Tuna Consumption Study

Alilović A<sup>1</sup>, Klemenčič P<sup>2</sup>, Jagodic Hudobivnik M<sup>2</sup>, Živković I<sup>1,2</sup>, Snoj Tratnik J<sup>1,2</sup>, Falnoga I<sup>2</sup>, Palir N<sup>1,2</sup>, Mazej D<sup>2</sup>, Horvat M<sup>1,2</sup>

<sup>1</sup>Jožef Stefan International Postgraduate School, <sup>2</sup>Institute Jožef Stefan

Despite being an essential component of a balanced diet, fish consumption is also the primary route of human exposure to methylmercury (MeHg). Prevailing assumptions in human health risk assessment are that all mercury in fish is MeHg, and that 95-100% of ingested MeHg is bioavailable. Recent studies challenge these assumptions, suggesting potential errors that lead to an overestimation of risks associated with seafood consumption. The foundational studies supporting these assumptions are often outdated and possess significant limitations. To address uncertainties in current exposure and health risk assessments, this study aims to validate pharmacokinetic models by creating a realistic scenario for MeHg exposure through controlled consumption of tuna steaks. Sixteen volunteers, including six controls, were recruited at the Jožef Stefan Institute in Ljubljana. In the experimental group, each of the 10 participants received 5 yellowfin tuna steaks (approximately 300 grams each) to consume over 5 consecutive days. Total mercury and methylmercury concentrations were measured in each raw steak. Participants recorded daily preparation methods, drinks, and side dishes for the tuna steaks. Blood and urine samples were collected from volunteers before the tuna consumption week, every 2 days during that week, and once a week for 13 post-consumption weeks. Hair samples were taken twice: before the tuna consumption, and at the end of the experiment for retrospective analysis. Multi-elemental analysis and mercury speciation analysis were performed for samples of whole blood, plasma, erythrocytes, urine, and hair. The kinetics of mercury deposition and clearance were investigated, and the levels measured were compared to levels predicted by an in-house physiologically-based pharmacokinetic (PBPK) model, aiming to identify potential limitations in the current model.

333

## Insights into Hg<sup>0</sup> air-sea exchange using long-term atmospheric observations from coastal monitoring sites

Molepo K<sup>1</sup>

<sup>1</sup>Helmholtz-zentrum Hereon

Long-term atmospheric gaseous elemental mercury (Hg<sup>0</sup>) observations from coastal monitoring stations in the Northern (NH) and Southern Hemisphere (SH) were analysed to study Hg<sup>0</sup> air-sea exchange. The observations were combined with air mass back trajectories to trace the sources and recent history of air masses sampled at the sites. The back trajectories showed that the stations sample mostly air masses from the marine boundary layer (MBL), suggesting that the weak seasonal and diurnal variability observed at the sites is inherent of Hg<sup>0</sup> MBL conditions and not an artefact of mixing of air masses from different environments. We investigated the relationship between observed Hg<sup>0</sup> concentrations and recent air mass residence time in the MBL. At all sites, we found a gradual increase in Hg<sup>0</sup> concentrations with recent air mass residence time in the MBL, followed by a steady state. The observed pattern is consistent with the thin film gas exchange model, which predicts net ocean Hg<sup>0</sup> emissions into the atmosphere until the ocean surface dissolved gaseous Hg (DGM) concentration matches the atmospheric Hg<sup>0</sup> concentration divided by Henry's law constant. This provides evidence that ocean Hg<sup>0</sup> emissions directly influence observed concentrations at these sites. Using the relationship between Hg<sup>0</sup> concentrations and recent air mass MBL duration, we estimated ocean Hg<sup>0</sup> emission fluxes and surface ocean DGM concentrations. We obtained fluxes in the range of 0 – 3.8 and 0 – 4.51 ng m<sup>-2</sup> h<sup>-1</sup> for the NH and SH, respectively, and mean DGM concentrations in the range of 4.16 – 6.73 and 4.50 – 4.87 ng m<sup>-3</sup> in the NH and SH, respectively. Our flux and DGM estimates compared well to in-situ measurements reported in the literature. This study highlights the applicability atmospheric Hg<sup>0</sup> observations from coastal monitoring sites in determining ocean Hg<sup>0</sup> emission fluxes as well as surface ocean DGM concentrations.

## Historical trends of mercury accumulation in sediment cores from the Wider Caribbean Region

Bolaños Alvarez Y<sup>1</sup>, Ruiz Fernández A<sup>2</sup>, Sanchez Cabeza J<sup>2</sup>, Alonso Hernández C<sup>3</sup>

<sup>1</sup>Centro de Estudios Ambientales de Cienfuegos, <sup>2</sup>Unidad Académica Mazatlán, Instituto de Ciencias del Mar y Limnología, Universidad Nacional Autónoma de México, <sup>3</sup>International Atomic Energy Agency, Marine Environment Laboratories-Radioecology laboratory

A comprehensive assessment of the temporal trends of mercury (Hg) concentrations and fluxes was investigated in 13 coastal environments of the Wider Caribbean through the analyses of lead-210 (<sup>210</sup>Pb) dated sediment cores. Hg concentrations (19 - 18761 ng/g) ranged widely observed, even at background levels (38 - 100 ng/g). Most Hg concentration profiles displayed an upward trend, with maxima occurring within the last two decades. The sediment cores from Havana Bay and Sagua River Estuary in Cuba, Port-au-Prince Bay in Haiti, and Cartagena Bay in Colombia were identified as heavily contaminated, for which these sites can be considered regional Hg hotspots. Such Hg enrichment in Havana Bay and Port-au-Prince Bay might be the result of the wastewater discharge from highly populated cities, over 2 million inhabitants each, as well as the runoff from watersheds affected by significant erosion rates. The records from Sagua River Estuary and Cartagena Bay indicated legacy Hg contamination associated with the operation of chloralkali plants, making these sites highly ecologically vulnerable. These findings represent a significant contribution to the limited regional data on contaminants in the Wide Caribbean Region, establishing a baseline for future studies on Hg contamination, and providing reference information that could be useful for the evaluation of the effectiveness of the Minamata Convention.

## Mercury species, stable isotopes and distribution of total mercury in coastal sediments of Honda Bay, Palawan, Philippines

Samaniego J<sup>1</sup>, Gibaga C<sup>1</sup>, Tanciongco A<sup>1</sup>, Quierrez R<sup>1</sup>, Reyes R<sup>1</sup>, Gervasio J<sup>1</sup>, Rasay A<sup>1</sup>

<sup>1</sup>Department of Science and Technology - Philippine Nuclear Research Institute

Honda Bay, which is located in the east-coast of Palawan Island in the Philippines, is considered as one of mercury hotspots in the world due its proximity with abandoned Palawan Quicksilver Mine. Previous studies in this area stated that there is an increasing mercury contamination in the marine sediment. A total of 166 marine sediment samples were collected and analyzed for total mercury using direct mercury analyzer and part of the samples were subjected to mercury speciation and isotopic characterization to determine the dominant species and source of the contamination. Results showed that the Honda Bay wharf and the mouth of Tagbueros River are identified spots with high mercury concentrations in Honda Bay with Hg concentrations of around 5 and 11 mg/kg, respectively. These spots have become the point sources of Hg contamination in the coast as sediment spreads to a large coastal area brought by tidal currents and the wave energy action. Results of the speciation showed that the predominant species of mercury in the sediment was reduced mercury, but the presence of oxidized mercury was still prevalent. Mercury isotopes in ore, marine and river sediment samples had the lowest  $\delta^{202}\text{Hg}$  ( $-0.59\%$  to  $-1.61\%$ ) and  $\Delta^{199}\text{Hg}$  ( $+0.00$  to  $+0.24\%$ ) and small variance measured values but there was significant positive  $\Delta^{199}\text{Hg}$  and negative  $\delta^{202}\text{Hg}$  values in the biota that were correlated with light penetration depth in the sea. This suggest that photochemical degradation of methylmercury prior to incorporation of remaining MeHg into the food web. Mercury stable isotopic composition demonstrated that the Hg in marine and river sediments and biota can be traced from the ores of the abandoned mercury mine area. This study shows the increase of mercury in the marine sediments through time and its implications on the ecological and health risks among the residents in the area.

## Transformation of methylmercury at the beginning of the Arctic spring bloom

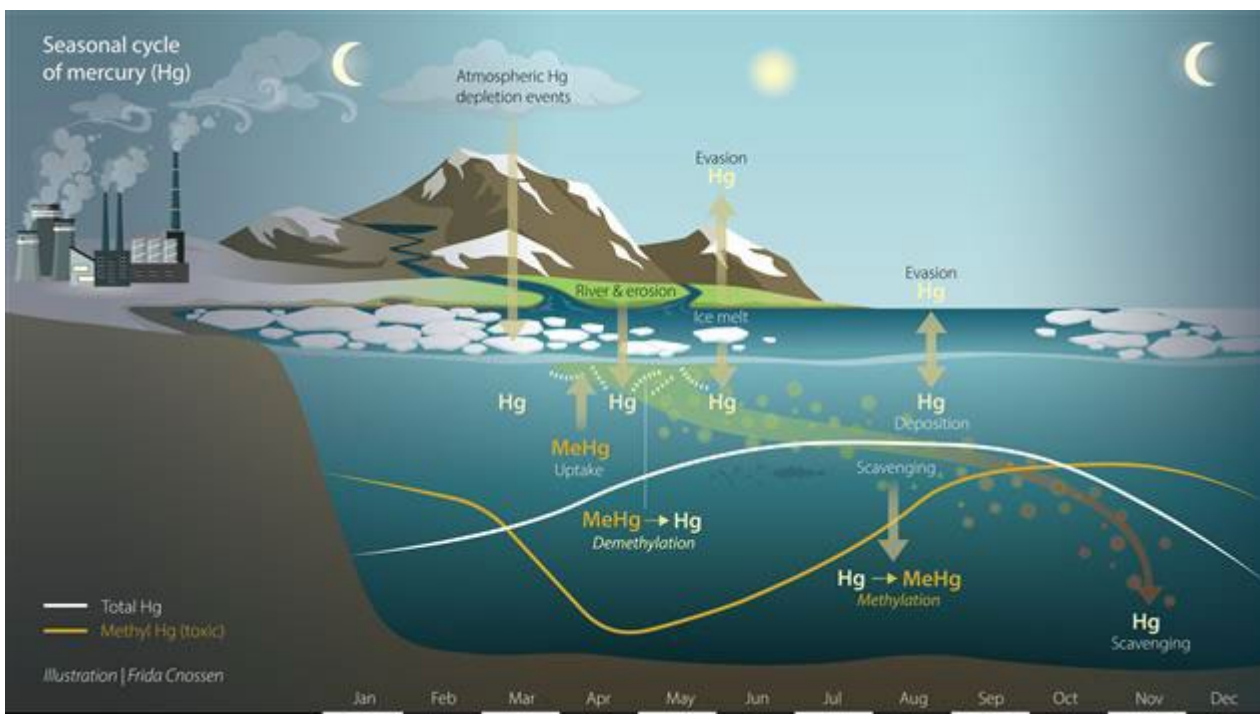
Kohler S<sup>1</sup>, Heimbürger-Boavida L<sup>2</sup>, Assmy P<sup>3</sup>, Müller O<sup>4</sup>, Thiele S<sup>4,5</sup>, Digernes M<sup>1</sup>, Ndungu K<sup>6</sup>, Ardelan M<sup>1</sup>

<sup>1</sup>Department of Chemistry, Norwegian University Of Science And Technology (ntnu), <sup>2</sup>Aix-Marseille Université, CNRS/INSU, University de Toulon, IRD, Mediterranean Institute of Oceanography (MIO),

<sup>3</sup>Norwegian Polar Institute, <sup>4</sup>Department of Biological Sciences, University of Bergen, <sup>5</sup>Bjerknes Centre for Climate Research, <sup>6</sup>Norwegian Institute for Water Research (NIVA)

The uptake of methylated mercury (MeHg) still remains a concern in Arctic food webs. Bioconcentration of seawater monomethylmercury (MMHg) into phytoplankton leads to bioaccumulation in the Arctic food web. Although there are known seasonal changes in biological activity in the region, little is known about the seasonal cycling during the late winter of total mercury (THg) and MeHg in the Arctic Ocean. Here, we investigated THg and MeHg in seawater sampled from the northwestern Barents Sea during late winter and spring. In the upper 500 m, the THg concentrations are significantly higher in spring ( $0.64 \pm 0.09$  pmol L<sup>-1</sup>) compared to late winter ( $0.53 \pm 0.07$  pmol L<sup>-1</sup>), driven by seasonal sources to surface waters such as atmospheric deposition and the dynamics of changing sea ice conditions. MeHg concentrations in spring however, were significantly lower ( $41 \pm 39$  fmol L<sup>-1</sup>) compared to late winter ( $85 \pm 42$  fmol L<sup>-1</sup>). We hypothesize that most MeHg is biotically demethylated by both phytoplankton and bacteria, supplemented by losses from photodemethylation and evasion. Our results highlight potential demethylation of methylmercury coinciding with the Arctic spring bloom. Finally, we use our new data in conjunction with previously published seasonal data in the region to visualize a simplified seasonal mercury cycle in the Arctic marginal ice zone.

### Abstract Graphics



337

## Measuring and modeling mercury transformation and flux processes downstream of the historical Black Butte Mercury Mine (Oregon, USA).

Eckley C<sup>1</sup>, Luxton T, Knightes C, Millard G, Goetz J, Wade A, Eagles-Smith C, Dent S, Silvertooth J, Crawford J

<sup>1</sup>Us Epa

Biotic and abiotic geochemical processes impact the extent to which inorganic mercury (Hg) is transformed to methylmercury (MeHg) and accumulates in biota. These processes vary in response to natural and anthropogenic characteristics across the landscape. The objective of this study was to identify how key processes controlling total-Hg (THg) and MeHg concentrations vary within a watershed that contains both lotic and lentic (reservoir) conditions, which are impacted by Hg releases from a historical Hg mine and smelter (Black Butte Mine Superfund Site Oregon USA). The processes investigated in this study were: fluxes of THg and MeHg between the sediment and water and MeHg production and degradation rates within the sediment, water, and periphyton. The processes were measured using stable isotope additions of inorganic Hg and MeHg as part of short-term incubation experiments. The relative importance of these processes was contextualized through comparisons with outputs from the Water Quality Analysis Simulation Program (WASP8) model that simulates Hg dynamics in this watershed. The initial study results have shown that sediment MeHg production rates were generally higher in the reservoir compared to within the riverine system. However, the impact of sediment MeHg production rates on overlying water concentrations varied depending on the flux rate from the sediment to the overlying water—which varied spatially throughout the watershed. Within the water-column of the river, MeHg concentrations appear to be influenced by methylation within periphyton communities. There were large differences in photo-degradation rates of MeHg between the river and reservoir. The river system was more shaded (lower incoming solar radiation) due to riparian vegetation and as a result had low MeHg photo-degradation rates compared to the open water of the reservoir. Overall, these results highlight the watershed-scale variables that influence the production, degradation, and flux of MeHg downstream of a contaminated site.

338

## Understanding dark abiotic mercury reduction by natural organic matter - experimental work based on model compounds

Szubska M<sup>1,2</sup>, Björn E<sup>3</sup>, Zhu W<sup>1</sup>, Skjellberg U<sup>1</sup>

<sup>1</sup>Swedish University of Agricultural Sciences, <sup>2</sup>Institute of Oceanology of the Polish Academy of Sciences, <sup>3</sup>Umeå University

The dark abiotic reduction of Hg(II) to elemental Hg(0) driven by the cation of natural organic matter (NOM) is an important mercury transformation process. It can occur in anoxic environments, largely affecting the reemission of mercury from soils and sediments to the atmosphere. Abiotic mercury reduction and consequent Hg(0) evasion could be significant for mercury transformation cycle in wetlands and peatlands, especially rich in organic matter.

Two major factors controlling Hg(II) reduction are: availability of electron donors and chemical speciation of mercury. In the environment both factors are controlled by natural organic matter constituents. To mimic these reactions, we set-up controlled experiments using well-defined model compounds. We varied the chemical speciation of Hg(II) covering strong complexes with thiols, weaker complexes with acetate, and intermediate stability complexes with chloride ions. Electron donation was modelled by the quinone AQDS (Anthraquinone), considered a relevant representative of similar types of groups in NOM. Experiments were performed in the pH range 3.0-6.5, what refers to various terrestrial environments.

The results so far indicate that pH, electron donation and the chemical speciation of Hg(II), factors largely in control by NOM chemical composition dictate rates of Hg(II) reduction and thus Hg(0) formation and evasion. Experimental results could be linked with geophysical and chemical characteristics of different environments and have an impact on mercury reemission or availability for in situ methylation.

## Exploring Selenium-Mercury Interactions in Human Systems: Insights from Controlled Fish Consumption and Biomarker Analysis

Alilović A<sup>1</sup>, Klemenčič P<sup>2</sup>, Jagodic Hudobivnik M<sup>2</sup>, Živković I<sup>1,2</sup>, Snoj Tratnik J<sup>1,2</sup>, Falnoga I<sup>2</sup>, Palir N<sup>1,2</sup>, Mazej D<sup>2</sup>, Horvat M<sup>1,2</sup>

<sup>1</sup>International Postgraduate School Jožef Stefan, <sup>2</sup>Institute Jožef Stefan

Selenium (Se)-dependent protection against mercury toxicity has been recognized for over 60 years. In this study, a group of 10 volunteers were exposed to Hg and Se through controlled fish consumption. Additionally, 6 individuals were recruited as controls, who consumed no fish or seafood. Each experimental group volunteer consumed 5 tuna steaks (250-300 g/portion) over 5 consecutive days. THg, MeHg, and Se were measured in steaks, human blood, plasma, erythrocytes, hair, and urine before and after consumption, with measurements taken once a week for 13 consecutive weeks. Initial Hg and Se concentrations in biological samples varied between participants. However, all showed similar whole blood THg and MeHg concentration-time trends: linear increase during consumption, peaking the day after the last steak, and then biphasic first-order elimination. Maximum THg (and MeHg) concentrations reached showed a strong positive correlation with THg (MeHg) dose per kilogram body weight. Se concentrations in whole blood exhibited a slight variable increase after consumption, with no correlation with Se dose per kilogram body weight. Plasma Se mirrored plasma Hg trends, peaking simultaneously, and decreasing towards the end of the study. Erythrocyte THg and MeHg mirrored whole blood, while Se increased post-consumption and remained elevated. Urinary Se profiles resembled erythrocytes Hg but not THg urine trends. Despite continuing research, Se-Hg interactions in biological systems are still far from being thoroughly understood and further efforts are needed to unravel the intricate dynamics at play. To enhance the interpretation of these trends and relationships, additional analysis will investigate Se speciation and explore the potential role of other factors governing the uptake, distribution, and excretion of Hg and Se compounds following fish consumption. This aims to unveil their respective roles in terms of health benefits and adverse effects.

## Methylmercury in water from newly inundated forest landscapes

Eklöf K<sup>1</sup>, Wallin M<sup>1</sup>, Zannella A<sup>1</sup>, Ecke F<sup>2</sup>, de Jong J<sup>1</sup>, Laudon H<sup>1</sup>

<sup>1</sup>Swedish University of Agricultural Sciences, <sup>2</sup>University of Helsinki

Sweden, such as many other countries, has extensively drained forest wetlands to improve forest productivity. Restoring these formerly drained peatlands is encouraged to mitigate the effects of droughts and floods, improve biodiversity, and sequester carbon. An increasing number of inundations in the forest landscape are also created by an increasing beaver population. Beavers, that were at the verge of extinction in large parts of Europe and North America in the early 20th century, have repopulated large parts of their former distribution range.

Inundation of terrestrial soils, can, however, mobilize legacy mercury (Hg) and promote the microbial transformation of inorganic Hg to its bioaccumulative form methyl-Hg (MeHg). Earlier studies have shown soil inundations to cause elevated MeHg concentrations in water and aquatic biota, but it is less known where and how wetlands can be restored or created to reduce the risk of elevated MeHg in water.

We sampled 33 restored wetlands and close-by references, i.e. non-restored drained wetlands, from north to south of Sweden. The sites encompass variation in landscape factors and different landscape type. Samples were collected in the outlet of the wetlands during two seasons. During one campaign we also samples water in the outlet of 15 beaver ponds and reference sites without beavers.

THg concentrations, but not MeHg concentrations, were elevated in restored wetlands compared to references. Instead, MeHg concentrations were elevated in the beaver ponds. A critical difference between restored wetlands and those created by beavers, is that the latter will be found on all sorts of land, while the former represent previously drained wetlands. These results indicate that restoring drained wetlands do not promote the formation of MeHg to the same extent as inundation of other terrestrial soils, including upland soils, by beavers.

341

## Using the Global Biotic Mercury Synthesis to better understand adverse impacts of methylmercury availability on biodiversity.

Evers D<sup>1</sup>

<sup>1</sup>Biodiversity Research Institute

An important provision of the Minamata Convention on Mercury is to monitor and evaluate the effectiveness of the adopted measures and eventually relate to impacts on the environment and biological diversity. Here, we describe peer-reviewed biotic mercury (Hg) concentrations (>550,000) at relevant geographic and temporal scales for continents and oceanic basins. We use established adverse effect levels for fish, birds and mammals to assess risk. Ecologically sensitive sites - where biota have above average methylmercury tissue concentrations - are known throughout the world. Efforts to model spatial patterns of biotic Hg exposure and risk that can be subsequently related to ecosystem sensitivity at local, regional and global spatial levels could help establish effective programs to evaluate negative impacts to biological diversity.

## Canada's Global mercury passive sampling network study

MacSween K<sup>1</sup>, Stupple G<sup>1</sup>, Steffen A<sup>1</sup>

<sup>1</sup>Environment And Climate Change Canada

The atmosphere forms the key pathway for the global distribution of mercury (Hg). Monitoring its spatial and temporal variation within the atmosphere is key to evaluating regulatory measures, such as the Minamata Convention on Mercury, that look to reduce the environmental and health impacts of Hg exposure, and to understand its behavior in response to climate perturbations. In response to the need for greater monitoring capabilities, we have introduced a global mercury passive sampler network comprised of pre-existing and expanded monitoring networks. The use of Tekran MerPAS<sup>®</sup> enables coverage across a much broader spatial range, including areas that currently lack sufficient Hg measurements due to difficult to reach environments and/or, the highly specialised nature of traditional measurement techniques. This study, which has been ongoing since 2019, has 102 sites operating across 42 countries. Concentrations are determined based on total Hg accumulated on the carbon sorbent by the MerPAS<sup>®</sup>, normalized by time exposed and the sampling rate. Global Hg concentrations show significant spatial and temporal variability with a global average mercury concentration of 1.57ng m<sup>-3</sup> (SD 0.91ng m<sup>-3</sup>). Concentrations peak in April to June (Q2, 1.69 ng m<sup>-3</sup>) and minimum during January to March (Q1, 1.43 ng m<sup>-3</sup>). Tropics show highest concentrations with little seasonal variation (annual Avg 1.68 ng m<sup>-3</sup>). While Southern Hemisphere has the lowest concentrations (1.29 ng m<sup>-3</sup>) which a clearer seasonality, maxima October to December (Q4) and minima Q1. The strong global picture of atmospheric mercury concentrations developed by this global program provides valuable information on atmospheric Hg patterns and helps to inform the progress of regulatory actions.

343

## Denuders, filters and diffusive barriers: A ‘breakthrough’ study of reactive mercury species.

Stupple G<sup>1</sup>, MacSween K<sup>1</sup>, Steffen A<sup>1</sup>

<sup>1</sup>Environment And Climate Change Canada

The complex cycling of mercury in the atmosphere has rendered sampling of all Hg species a challenge. Current methods in use define the type of Hg species by operational set-up. Understanding what is measured is important for accurately quantifying Hg’s species and behavior. To better quantify the influence of different filter media on Hg measurements a series of experiments were undertaken at Alert NU, Canada. Inlet filter media of PTFE filter, cation exchange membrane (CEM), and Radiello<sup>®</sup>, were field tested for breakthrough of reactive gaseous mercury (RGM) using parallel Tekran 1130/1135 and Tekran<sup>®</sup> 2537x analyzer systems during the spring of 2018 and 2019. Paired speciated measurements had a high level of agreement (R<sup>2</sup> of 0.94 and 0.90 in 2018 and 2019 respectively identical setups). One system was operated according to the SOP, while the second operated with 3 different inlets. The inlet was replaced with 47mm 0.2 µm PTFE filter, a 47mm 0.45µm CEM, and a Radiello<sup>®</sup> (diffusive barrier used in passive samplers, pore size: 0.25µm). The resulting breakthrough of RGM and PHg were compared between the two systems. PTFE filter inlet measured 49% (2018) and 59% (2019) of the mercury that was measured on the unaltered reference system indicating a significant of RGM breakthrough. The Radiello<sup>®</sup> and CEM filters had minimal breakthrough, 3.9% and 1.7% respectively when compared to the reference system. Paired Tekran 2537x analyzers were run with PTFE and CEM inlet filters without the speciation glassware to determine if breakthrough of RGM on the PTFE inlet would be measured by the analyzer. A slight high bias was observed on the PTFE filtered TGM system indicates that RGM can be measured by a TGM setup with PTFE filtered inlet. This clearly demonstrated that filter media type will determine the Hg species measured.

344

## Developing a Global Mercury Threat Assessment based on mapping ecosystem sensitivity to methylation and risk of mercury contamination.

Tear T<sup>1</sup>, Burton M<sup>1</sup>, Evers D<sup>1</sup>

<sup>1</sup>Biodiversity Research Institute

The combination of impacts from pollution, climate change and correspondingly biodiversity loss is amplified by habitat losses or overexploitation leading to a “triple planetary crisis” that presents an existential threat. While global conventions individually address these crises, there is growing recognition they need to be addressed collectively. An essential first step is to map these threats at spatial scales relevant to policy development and strategy implementation. We present the first global mercury threat assessment (GMTA) that combines two key factors, sensitivity of ecosystems to mercury contamination and the risk of anthropogenic mercury pollution. We present evidence that separating naturally occurring environmental factors with human-influenced processes can be helpful in developing strategies addressing the reduction of mercury as a pollutant, and for assessing their effectiveness. We document that biodiversity priorities at global, continental, and regional scales are highly threatened by mercury, particularly areas governed by Indigenous Peoples and Local Communities. We present evidence that it is necessary to create higher resolution threat maps using the same data structure but replacing global data with more relevant, detailed local information via a Regional Mercury Threat Assessment (RMTA) to support national level strategy development and effectiveness evaluation. We show that high levels of mercury threat correlate with mercury contamination to fish and people, and that areas with limited mercury inputs can still suffer from significant impacts driven primarily by the sensitivity of ecosystems to mercury methylation. We acknowledge that much more work needs to be done to strengthen these mapping tools to become better predictive models of impacts to nature and people that would be helpful in shaping strategy development and implementation. We propose an adaptive management framework to build from and suggest that the GMTA provides a critical and essential first step if global efforts to address the triple crises are ultimately successful.

345

## The intersection of mercury threat and global biodiversity conservation prioritization areas

Burton M<sup>1</sup>, Tear T<sup>1</sup>, Evers D<sup>1</sup>

<sup>1</sup>Biodiversity Research Institute

Pollution and climate change are increasingly recognized as interconnected with biodiversity loss in what has come to be known as the “Triple Planetary Crisis.” The impacts of these issues are not homogeneously distributed across the globe, so understanding spatial patterns in their overlap can help target policy and conservation focused interventions. Mercury is a pollutant of global concern and is a neurotoxin that impairs physiological and neurological function with elevated concentrations documented to reduce reproductive success and can cause behavioral changes that reduce fitness. In order to assess the impacts of mercury on biodiversity, we first prioritized global biodiversity conservation areas by combining biodiversity significance, unique ecological features, habitat condition, conservation management, and ecosystem services using transparent weighting functions. Crucially, the prioritization exercise was integrated across three realms (terrestrial, freshwater, and coastal marine) to identify globally significant biodiversity conservation priority areas. In order to understand the potential impacts of mercury on biodiversity, we overlaid a global map of mercury threat, defined as a combination of ecosystem sensitivity to mercury contamination and risk of anthropogenic mercury pollution over the priority areas. The intersection of these two spatially explicit datasets highlight areas where the potential impact of mercury on biodiversity is highest. The areas identified should be targeted for future biomonitoring efforts to better inform our understanding of the mechanisms underlying the fate and movement of mercury through ecosystems resulting in impacts to biota. The resulting patterns can also illuminate industries and sectors where regulatory and other forms of intervention can have the largest impact on reducing the threat of mercury to biodiversity.

## Trends in mercury, lead and cadmium concentrations in European streams and rivers between 2000 and 2020

Eklöf K<sup>1</sup>, von Brömssen C<sup>1</sup>, Huser B<sup>1</sup>, Åkerblom S<sup>1</sup>, Augustaitis A<sup>2</sup>, Veiteberg Braaten H<sup>3</sup>, de Wit H<sup>3</sup>, Dirnböck T<sup>4</sup>, Elustondo D<sup>5</sup>, Grandin U<sup>1</sup>, Holubová A<sup>4</sup>, Kleemola S<sup>6</sup>, Krám P<sup>7</sup>, Lundin L<sup>1</sup>, Löfgren S<sup>1</sup>, Markensten H<sup>1</sup>, Moldan F<sup>8</sup>, Pihl Karlsson G<sup>8</sup>, Rönneback P<sup>1</sup>, Valinia S<sup>9</sup>

<sup>1</sup>Swedish University of Agricultural Sciences, <sup>2</sup>Agriculture Academy, Vytautas Magnus University,

<sup>3</sup>Norwegian Institute for Water Research (NIVA), <sup>4</sup>Ecosystem Research and Environmental Information Management; Environment Agency Austria, <sup>5</sup>University of Navarra, Institute for Biodiversity and Environment BIOMA, <sup>6</sup>Finnish Environment Institute, <sup>7</sup>Czech Geological Survey, <sup>8</sup>IVL Swedish Environmental Research Institute, <sup>9</sup>Ensucon AB

Within the International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP IM) and the Swedish monitoring program, mercury (Hg), lead (Pb), and cadmium (Cd) have been monitored in natural or semi-natural catchments in Europe. Here we evaluated the temporal trends of Hg, Pb and Cd concentrations from year 2000 to 2020 in 23 (Hg), 25 (Pb) and 14 (Cd) streams and rivers across Europe, using nonparametric Seasonal Mann-Kendall tests to detect trends for the full period of evaluation and generalized additive mixed models to detect if and when trends are changing.

Decreasing trends were observed in 30% (Hg), 40% (Pb) and 57% (Cd) of the watercourses for the full period of evaluation. However, these decreasing trends were mainly observed during years 2000-2005 for Hg and during years 2000-2015 for Pb and Cd. Towards the end of the evaluation period (2015-2020) more watercourses showed significant increasing, rather than decreasing trends of Hg, Pb and Cd.

The overall downward trends were likely driven by declining deposition of metals over Europe, especially for Pb and Cd. The fact that metal trends are increasing towards the end of the study period is interpreted as a legacy effect of metals retained in the soil. The legacy effect may be especially strong for Hg, as mass-balance data from three of the Swedish catchments showed that runoff contained only some few percent of the total annual Hg deposition. Aqueous recovery from acidification and ongoing browning of surface waters at northern latitudes, may also contribute. Here we found trends in organic carbon to covary with the seasonal variation in Hg and Pb, but not the interannual trends. This study highlights the need for long-term monitoring and the suitability of robust statistical methods that can detect multidirectional trend changes in long-term data.

## Mercury stocks in discontinuous permafrost and their mobilization by river erosion and sedimentation in the Yukon River Basin

Smith I<sup>1</sup>, Ke Y<sup>2</sup>, Geyman E<sup>2</sup>, Reahl J<sup>2</sup>, Douglas M<sup>2,4</sup>, Seelen E<sup>1</sup>, Magyar J<sup>2</sup>, Mutter E<sup>3</sup>, Dunne K<sup>2,5</sup>, Fischer W<sup>2</sup>, Lamb M<sup>2</sup>, West J<sup>1</sup>

<sup>1</sup>University Of Southern California, <sup>2</sup>California Institute of Technology, <sup>3</sup>Yukon River Inter-Tribal Watershed Council, <sup>4</sup>Massachusetts Institute of Technology, <sup>5</sup>Delft University of Technology

The Arctic is warming four times faster than the global average. This warming threatens to destabilize permafrost region soils — potentially liberating the large amounts of mercury (Hg) that have accumulated in permafrost landscapes over thousands of years. While the potential release of Hg has received considerable attention due to its threat to ecosystem and human health, Arctic Hg stocks remain poorly constrained as Arctic soils are currently under-sampled for Hg. Existing studies rely primarily on sparse field data and models. Mercury to organic carbon ratios (RHgC) are often used to bolster field observations due to relatively more abundant carbon data availability. However, RHgC are highly variable and need to be better constrained for their use to infer across Arctic soil types. Moreover, the extent to which the Hg in Arctic soils is liberated to the environment during permafrost thaw remains unclear.

While a range of processes can release Hg from permafrost, this work focuses on river erosion, which can contribute substantially to permafrost degradation along river corridors and deliver large amounts of Hg-rich sediment into rivers. To better constrain Hg stocks and fluxes in river floodplains, we present a new dataset of Hg measurements in riverbank and floodplain sediments and employ a mass balance approach to evaluate the role of river migration on erosional and depositional Hg sediment fluxes in the Yukon River Basin of Alaska. We find that sediment deposit geomorphology and spatial patterns of river erosion play significant roles in determining mercury content and fluxes, so incorporating such sedimentological controls on Hg contents and RHgC ratios in future models has the potential to improve estimates of Hg stored in permafrost — as well as the likelihood of its environmental mobilization due to river migration in a warming climate.

348

## Remediation of Mercury in Groundwater by In Situ Chemical Fixation: Geochemical Characterization and Modeling Are Keys to Success

Vlassopoulos D<sup>1</sup>, Carey M<sup>2</sup>

<sup>1</sup>Anchor QEA Inc., <sup>2</sup>Anchor QEA Inc.

We present an in situ remediation case study of a Hg plume in a suboxic shallow sandy aquifer downgradient of a former chlor-alkali facility in the northeastern United States. Sodium sulfide injection was used to manipulate geochemical conditions and promote Hg immobilization as insoluble sulfides. The Hg source area at the site was previously addressed by installation of an impermeable barrier wall, however groundwater Hg concentrations downgradient of the source ranged up to 100 µg/L and exceeded the groundwater cleanup level (CUL, 2 µg/L). Higher Hg concentrations are associated with elevated groundwater pH up to 11.5. We developed an iterative approach for remedial design, implementation and performance monitoring including characterization of subsurface hydrologic and (bio)geochemical conditions and mercury concentrations and forms in both dissolved and solid phases. Reagent dose and delivery were optimized considering Hg distribution and aquifer sulfide demand [soil Fe(III) and Mn oxides and reactive Fe(II) which consume sulfide] and injection design was supported by a 3D reactive transport model. Injections were performed in 2017 and 2019 and a tiered, multiple lines-of-evidence approach was adopted to evaluate performance. Quarterly groundwater sampling documented concentration trends, geochemical modeling was used to assess post-injection aquifer conditions with respect to HgS stability, and solids analysis (XRF, XRD, and SEM) was performed to confirm that treatment is occurring. As of 2023, the area of the Hg plume exceeding the CUL has decreased by more than 70%. Dissolved Hg concentrations have decreased in ~80% of the 26 well monitoring network relative to pre-injection baseline with ~70% below the CUL. An additional ~15% are within 5X CUL with generally decreasing trends. Geochemical modeling indicates subsurface conditions remain favorable for precipitation of metacinnabar and solids analyses confirmed in situ precipitation of mackinawite and traces of HgS occurred following injection.

## Mercury Adsorbents for Artisanal Gold Mining

De Resende N<sup>1</sup>, Salim V<sup>1</sup>, Manske Camargo C<sup>2</sup>, Zaroni Megale E<sup>1</sup>, Chaves da Costa L<sup>2</sup>, Martins N<sup>2</sup>  
<sup>1</sup>Programa de Engenharia Química, Universidade Federal Do Rio De Janeiro, <sup>2</sup>Escola de Química, Universidade Federal do Rio de Janeiro

The main source of gaseous elemental mercury emissions in South America is artisanal gold mining, where emissions reach 340 tons/year, which expresses about 70% of the global emissions within this sector [1]. Numerous studies report chronic exposure of the Amazon region's population to mercury through inhalation and ingestion. Furthermore, deforestation and recurrent wildfires increase mercury mobility in that region, magnifying population intoxication [2]. Therefore, technologies capable of mitigating the release of gaseous elemental mercury from artisanal gold mining are urgent and necessary. Hydroxyapatite modified with copper sulfide has been effective as an adsorbent for capturing and immobilizing mercury in gas streams, such as natural gas, characterized by low Hg concentrations (1-200 µg/m<sup>3</sup>) [3]. Conditions involving mercury concentrations in the gas stream of up to 12500 µg/m<sup>3</sup> were studied, with an observed adsorption capacity of 33.9 ± 7 mg/g [4]. Thus, in this work, the adsorbents were improved to suit the conditions applied in artisanal mining, particularly in the chimneys where amalgam burning occurs. In these locations, concentrations are substantially higher and fluctuate according to the processed amalgam quantity. The adsorbents developed in this study are hydroxyapatite modified with copper and iron sulfide, exhibiting promising results in bath adsorption systems at room temperature, yielding equilibrium mercury concentrations at the order of 18000 µg/m<sup>3</sup>. Under these conditions, the adsorption capacity reached 93 mg/g. The current challenge is developing a new technology for controlling mercury emissions in artisanal mining, complementing existing strategies employed by miners to minimize mercury loss, such as the use of retorts for metal recovery.

[1] UN ENVIRONMENT. Global Mercury Assessment 2018.

[2] CRESPO-LOPEZ, Maria. Elena et al., *Ecotoxicology and Environmental Safety*, v. 256, 7, 2023.

[3] SHAFAWI, Azman et al., *Analyst*, v. 124, n. 2, 185, 1999.

[4] CAMARGO, Carla Luciane Manske, et al. *Fuel*, v. 225, 509, 2018.

350

## Dyslipidemia and insulin resistance in individuals exposed to mercury in a riverside city in the Brazilian Amazon

De Jesus I<sup>1</sup>, Faial K<sup>1</sup>, Miranda A<sup>1</sup>, De Jesus I<sup>1</sup>, Pereira J<sup>1</sup>, Miranda J<sup>1</sup>, Carneiro B<sup>1</sup>, Marumoto K<sup>2</sup>, Santos E<sup>1</sup>, Akagi (in memoriam) H<sup>3</sup>

<sup>1</sup>Evandro Chagas Institute, <sup>2</sup>National Institute for Minamata Disease, <sup>3</sup>International Mercury Laboratory

Mercury can cause systemic harmful effects on human health, favoring oxidation or reducing anti-oxidant defenses, inducing inflammation and enhancing the development of metabolic syndrome components such as dyslipidemia, hypertension and insulin resistance. Metabolic changes observed in type 2 diabetes may be associated with increased toxicity from methylmercury which would pose a risk to populations exposed to this organic form of mercury through the fish consumption. This study evaluated the insulin resistance profile and dyslipidemia in individuals exposed to mercury in a city in the Acre state, Brazilian Amazon. Total mercury (T-Hg) analyzes in blood and hair were performed by CVAAS. Lipoproteins and glucose measurements were performed using an automated enzymatic colorimetric method and insulin using a solid phase immunoenzymatic assay. Participants from Manoel Urbano city had T-Hg levels average in blood of 20.53  $\mu\text{g/l}$  ( $\pm 25.57$ ) and in hair of 6.07  $\mu\text{g/g}$  ( $\pm 12.26$ ). Around 35% of individuals had dyslipidemia and 26% had insulin resistance according to the HOMA-IR index. Insulin resistance was associated with BMI ( $p=0.0193$ ), hypertension ( $p=0.0027$ ) and triglycerides (0.0007). Total mercury levels in blood were associated with LDL ( $p=0.0270$ ), T-Hg levels in hair ( $p<0.0001$ ) and fish consumption ( $p=0.0360$ ). Mercury levels in hair were associated with total cholesterol ( $p=0.0459$ ), T-Hg in blood ( $p<0.0001$ ) and fish consumption ( $p=0.0291$ ). Among non-diabetics, 17.2% had insulin resistance. It was not found a direct association between HOMA-IR and mercury exposure, however, factors related to metabolic syndrome that may influence this indicator were associated with mercury levels.

351

## Effect of atmospheric boundary layer height on changes in the vertical distribution of TGM at the continental background site

Vítková G<sup>1</sup>, Komínková K<sup>1,2</sup>, Prokeš R<sup>1,3</sup>

<sup>1</sup>Global Change Research Institute CAS, <sup>2</sup>Department of Geography, Faculty of Sciences, Masaryk University, <sup>3</sup>RECETOX, Faculty of Science, Masaryk University

According to previous studies, it can be assumed that there is a connection between local dispersion conditions, atmospheric boundary layer (ABL) height, meteorological parameters and changes in the mercury concentration gradient.

The Tall tower Křešín u Pacova which is part of the National Atmospheric Observatory Košetice (NAOK) located in the central part of the Czech Republic ensures measurements of total gaseous mercury (TGM) at two altitude levels as a long term continuous observation at the background conditions. The two Tekran 2537X instruments are located at 4 and 240 meters above ground (inlets). The site focuses also on monitoring of the occurrence and long-range transport of greenhouse gases, atmospheric aerosols, selected gaseous atmospheric pollutants and basic meteorological characteristics. With a broad range of measurements like this it is possible to look deeper into the relationship between different pollutants and various parameters. One of these parameters which can significantly affect the vertical distribution of substances is the change in ABL height during a day. To determine the relationship between the ABL height and the change in the vertical mercury concentration gradient in this study two periods were compared - two months in winter (January and February) and two months in summer (June and July) 2023. For each of this period the difference between two levels of TGM measurements was calculated and compared with ABL height development during a day and other meteorological parameters.

It was found that a distinguished diurnal variation of the differences between individual TGM measurement levels appears in summer, while in winter the difference remains almost constant which corresponds to ABL development during this periods.

## Mercury binding in riverine suspended particulate matter and the role of sampling techniques: A mercury thermo-desorption and FTIR-spectroscopy approach

Alten A<sup>1</sup>, Krisch S<sup>2</sup>, Breidenbach A<sup>2</sup>, Gan X<sup>2</sup>, Wiederhold J<sup>2</sup>, Biester H<sup>1</sup>

<sup>1</sup>Technische Universität Braunschweig, <sup>2</sup>Federal Institute of Hydrology (BfG)

Mercury (Hg) uptake from sediment or suspended particulate matter (SPM) is the major pathway for Hg accumulation by fish in river systems, but little is known about how Hg is bound in SPM. This study investigates how Hg binding in SPM differs from that in sediments, and if binding of Hg is changed during sediment resuspension. Using a novel approach combining Hg-Pyrolytic-Thermo-Desorption-AAS (PTD) and FTIR-spectroscopy, we aim to identify Hg binding forms in different fractions (organic vs. mineral) of SPM from the Elbe River, Germany. Samples collected from sedimentation boxes (SB) and on-site flow-through centrifugation (FTC) in various seasons and hydrological conditions were analyzed. Characterization of chemical components by FTIR-spectroscopy allowed to distinguish algae derived and humified organic matter as well as a mineral fraction. The case of SPM being dominated by algae could predominantly be detected in FTC samples. PTD allowed discrimination of Hg fractions based on SPM components revealed by FTIR-spectroscopy, indicating weaker Hg binding to algae compared to degraded organic matter. Laboratory centrifugation separated SPM components by density, revealing highest Hg concentrations in degraded organic matter and lowest in the mineral fraction. Our results indicate that Hg binding in SPM sampled by FTC is different from that by SB, affecting Hg methylation/demethylation processes. Moreover, SPM obtained by FTC is more indicative of the Hg compounds entering the food chain through the water phase, whereas SPM from SB corresponds to very young freshly deposited sediments, playing a key role in the Hg dynamics in fluvial environments (e.g., for methylation). Thus, considering the effect of different SPM sampling techniques is crucial for investigating biogeochemical Hg cycles and uptake pathways in aquatic systems. The work is conducted in the framework of a larger project investigating Hg dynamics in rivers (incl. methyl-Hg, microbial communities, and laboratory resuspension experiments).

## Mercury biomagnification and large-scale distribution using seabirds as innovative samplers

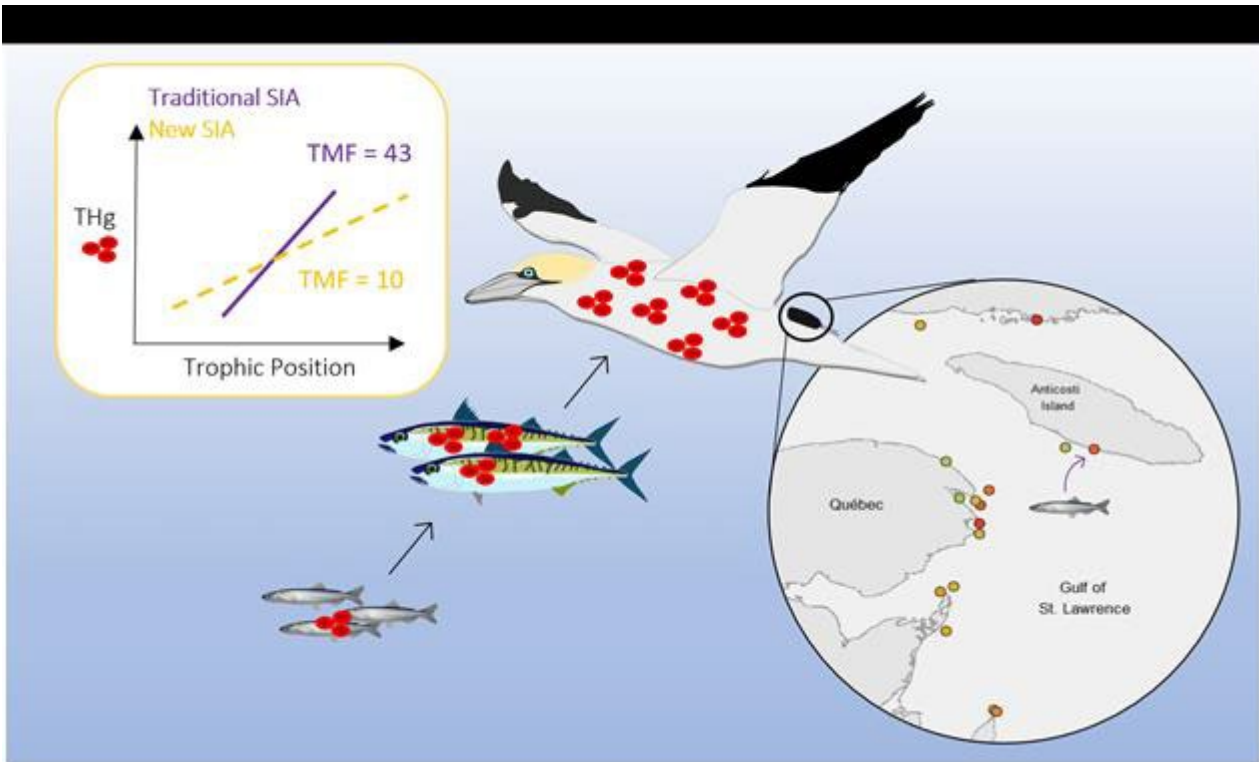
Lacombe R<sup>1,2</sup>, Barst B<sup>3</sup>, Martigny P<sup>4</sup>, Pelletier D<sup>5</sup>, Guillemette M<sup>4</sup>, Amyot M<sup>6</sup>, Elliott K<sup>2</sup>, Lavoie R<sup>1</sup>

<sup>1</sup>Environment and Climate Change Canada, <sup>2</sup>McGill University, <sup>3</sup>University of Alaska Fairbanks,

<sup>4</sup>Université du Québec à Rimouski, <sup>5</sup>Cégep de Rimouski, <sup>6</sup>Université de Montréal

Marine organisms are exposed to different mercury (Hg) loads based on their trophic positions and due to spatial heterogeneity of basal Hg contamination. Wildlife that forage over large areas are thus exposed to variable levels of Hg in their diet, discrepancies that must be accounted for in Hg studies. Northern gannets (*Morus bassanus*) forage over long distances, covering large portions of the Gulf of St. Lawrence in Atlantic Canada. Therefore, these seabirds offer a unique opportunity to study the spatial variation of Hg in their fish prey and to assess how feeding in different food webs impacts Hg biomagnification. We used an innovative method, capitalizing on GPS-tracking and on gannets' habits of regurgitating food items, to sample fish from different trophic levels across the Gulf of St. Lawrence, Canada. The "catch location" of the fish, identified through the analysis of the gannet GPS tracks allowed us to map out the spatial trends of total Hg (THg) across the Gulf. From the same fish samples, and from blood collected from the gannets, we examined the effect of different stable nitrogen isotope analysis ( $\delta^{15}\text{N}$ ) methods (emerging and traditional) on THg trophic magnification factors (TMF). Gannets allowed a random sampling of Hg values ( $n = 36$ ) of over 60 000 km<sup>2</sup> of spatial coverage. Amino acid-based  $\delta^{15}\text{N}$  analyses, considered an emerging approach for contaminant studies, yielded a lower TMF (10; i.e., tenfold increase per trophic level) while the TMF obtained through the traditional  $\delta^{15}\text{N}$  method for bulk tissues resulted in one of the highest TMFs (43) recorded yet in the literature. These differences highlight the potential for undetected spatial biases in biomagnification assessments when relying solely on a single method. Our results suggest that previously published studies may have overestimated the biomagnification potential of contaminants in aquatic food webs.

### Abstract Graphics



## Spatio-temporal trends of mercury in eggs of aquatic bird species across the St. Lawrence River and Estuary (Canada)

Lacombe R<sup>1</sup>, Kerric A<sup>1</sup>, Champoux L<sup>1</sup>, Eng M<sup>2</sup>, Lavoie R<sup>1</sup>

<sup>1</sup>Environment and Climate Change Canada, <sup>2</sup>Environment and Climate Change Canada

The St. Lawrence River and its estuary connects the Canadian Great Lakes to the Atlantic Ocean. The St. Lawrence constitutes a vast and intricate ecosystem supporting a rich biodiversity of wild species including marine mammals and seabirds. However, this system faces numerous stressors such as acidification, hypoxia, ship traffic, fisheries, invasive species, warming of the sea surface temperature, and pollution. High contaminant concentrations have been a well-documented issue across the St. Lawrence for many decades. Bird species such as Northern Gannets, Great-blue Herons, and Herring Gulls have been selected as bioindicators to monitor the contamination in the ecosystem. Egg have been collected in the last decades for Northern Gannets (1969 to present) and Great-blue Herons (1991 to present) to measure contaminants, including mercury. Herring Gull eggs were recently collected from multiple colonies across the St. Lawrence from urbanized centers to reference downstream locations for a spatial assessment of contaminants. Mercury concentrations and foraging ecology tracers (stable carbon, nitrogen, and sulfur isotopes) were analyzed. Mercury concentrations in Great-blue Heron and Northern Gannet eggs decreased by 30-60% across the studied region over time. Stable isotopes indicated that foraging ecology did not explain the changes in mercury concentrations. Mercury in Herring Gull eggs decreased downstream of urban sources and re-increased in the marine portion of the estuary. This supports the importance of point sources to explain egg Hg concentration, while also suggesting an impact of the marine food web downstream. This work demonstrates the value of long-term as well as spatial monitoring initiatives in urbanized estuarine ecosystems.

## Movement and foraging ecology affect mercury exposure in breeding seabirds.

Petalas C<sup>1</sup>, Lacombe R<sup>1,2</sup>, Elliott K<sup>1</sup>, Lavoie R<sup>2</sup>

<sup>1</sup>McGill University, <sup>2</sup>Environment and Climate Change Canada

In marine ecosystems, mercury (Hg) concentrations vary widely across different spatial and temporal scales, and trophic levels. Seabirds feed over large distances and can exhibit high intra and interspecific variations in habitats, foraging areas, and diet. A proper understanding of movement and foraging strategies is necessary to link with Hg burdens. Here, we report variation in Hg concentrations among four seabird species, two colonies, and up to five years in the Gulf of St. Lawrence. We also tested the influence of foraging strategies on blood mercury concentrations in seabirds. We equipped seabirds with precise GPS and depth loggers to estimate foraging metrics. We measured blood stable isotopes ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{34}\text{S}$ ) and total Hg concentrations. We found differences in Hg concentrations among species, colonies, and years, with no variation based on sex. Foraging habitat (derived from  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$ ) played an important role in determining blood mercury concentrations, while trophic level (derived from  $\delta^{15}\text{N}$ ) did not have a significant impact. Preliminary findings indicated that mercury burdens were higher in years when foraging trips were significantly farther and longer, and birds foraged closer to coastal riverine outflows. The depth of water columns exploited by foraging seabirds did not influence Hg blood concentrations. By investigating the potential ecotoxicological risks associated with foraging-related contamination at fine scales, our study contributes to the development of robust management plans and conservation strategies.

## Total mercury and methylmercury levels in fish consumed in a city in the Purus river basin, Amazon, Brazil

Carneiro B<sup>1</sup>, De Jesus I<sup>1</sup>, Tavares V<sup>1</sup>, Trindade P<sup>2</sup>, Pereira J<sup>1</sup>, Faial K<sup>1</sup>, Pinheiro S<sup>1</sup>, Santos E<sup>1</sup>, Akagi (in memoriam) H<sup>3</sup>

<sup>1</sup>Evandro Chagas Institute, <sup>2</sup>Biology and Aquatic Resources Management Laboratory/UFPA,

<sup>3</sup>International Mercury Laboratory

Mercury (Hg) is widely recognized as a toxic agent for living organisms, causing significant damage to health, especially to the human nervous system. One of the most relevant routes of exposure is the ingestion of contaminated food like fish. This study evaluated total mercury (T-Hg) and methylmercury (MeHg) levels in fish consumed by residents of the Manoel Urbano city, Acre state, Brazil, considering the most consumed informed in a household epidemiological survey. The fish samples collection was carried out with the support of local fishermen and the species were captured in the Purus River, which borders the city. T-Hg and MeHg analyzes in fish muscle tissue were performed by CVAAS and GC-ECD, respectively. A total of 233 samples of 12 fish species were collected, consumed by residents, with some being mentioned by more than 50% of those interviewed. T-Hg levels in fish differed between groups according to the species' feeding habits ( $p < 0.0001$ ), with higher means  $\pm$  SD in carnivorous such as *Hydrolycus* sp. (cachorro)  $1.648 \pm 0.380$   $\mu\text{g/g}^{-1}$  and *Serrasalmus* spp (piranha)  $0.970 \pm 0.335$   $\mu\text{g/g}^{-1}$  and omnivorous such as *Myleinae* (pacu)  $0.942 \pm 0.149$   $\mu\text{g/g}^{-1}$  and *Hypophthalmus* spp (mapará)  $0.853 \pm 0.061$   $\mu\text{g/g}^{-1}$ . The species *Rhaphiodon vulpinis* (candiru) had the highest mercury content ( $2,922 \pm 1,808$   $\mu\text{g/g}^{-1}$ ), but it was not reported as consumed by the population. The percentage of MeHg present in the species in relation to T-Hg ranged from 90.51% in the omnivorous *Leporinus* spp (aracu) to 43.97% in the carnivorous species *Rhaphiodon vulpinis* (candiru). The most critical T-Hg levels have been found in some carnivorous species with more than 1 ppm Hg in muscle tissue. These results reinforces that the mercury availability in the Amazon environment for aquatic biota has spanned decades, highlighting the importance of environmental health monitoring and exposure prevention.

## Vegetation effects on methylmercury production in saltmarshes of a coastal lagoon

Cesário R<sup>1</sup>, Zilhão H<sup>1</sup>, Hintelmann H<sup>2</sup>, Pereira P<sup>3</sup>, Pereira J<sup>3</sup>, Pacheco M<sup>3</sup>, Canário J<sup>1</sup>

<sup>1</sup>Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, <sup>2</sup>Water Quality Centre, Trent University, <sup>3</sup>CESAM (Centre for Environmental and Marine Studies) & Department of Biology, University of Aveiro

Mercury (Hg) is a recognized global pollutant and its impact in ecosystems can be dramatic. In saltmarshes, recent studies have suggested that the rhizosphere of halophyte plants play an important role in Hg speciation, more specifically in the formation of monomethylmercury (MMHg), the most stable toxic Hg form.

Throughout the seasons, Hg and MMHg natural concentrations were assessed and Hg stable isotopes were used to determine methylation (KM) and demethylation rates (KD), in vegetated and non-vegetated sediments, in order to evaluate the MMHg budget and methylation potential in saltmarshes.

For this study, two saltmarshes in Ria de Aveiro, a Portuguese coastal lagoon, were selected, one Hg contaminated (Laranjo-LAR) and another used as a reference site (Chegado-CHE). Mercury concentrations in sediments ranged between 0.05-6.20 µg/g in CHE and between 0.07-58 µg/g in LAR (Fig.1a). In both saltmarshes, the highest MMHg concentrations were recorded during summer, varying between 2.6-68 ng/g in CHE and between 25-260 ng/g in LAR (Fig.1b), which imply that higher temperatures favor MMHg production. Higher MMHg contents were always recorded in vegetated sediments, suggesting that plant activity potentiates the Hg methylation. This was corroborated by the significant increase of KM during summer with values up to 0.452 day<sup>-1</sup> in CHE and 0.312 day<sup>-1</sup> in LAR (Fig.1c). Moreover, the elevated KD (between 0.48-15 day<sup>-1</sup> in CHE; 1.4-32 day<sup>-1</sup> in LAR) with significant changes between seasons and highly affected by the presence of plants, indicates that demethylation process happens faster than the methylation process. Higher KD values combined with measured half-life of less than 2 days for MMHg (mostly in non-vegetated sediments) is surprisingly short. In these particular cases, it indicates that MMHg is not persistent in aquatic systems and a constant supply of MMHg is necessary to maintain a steady level of MMHg in sediments, making the formation process important.

### Abstract Graphics

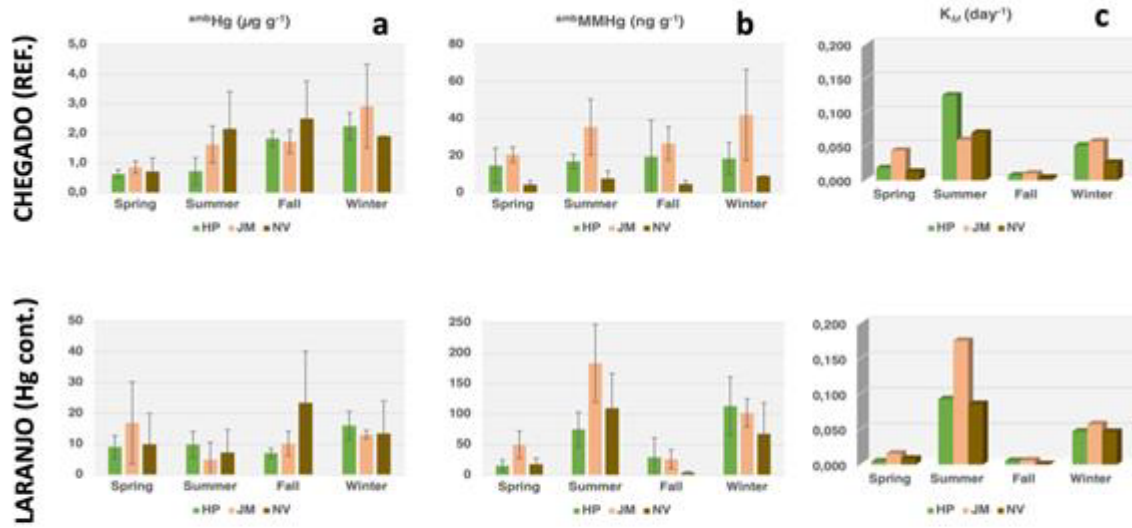


Fig.1: Ambient total Hg (a), MMHg (b) concentrations and rates of Hg methylation ( $K_M$ ) (c) in vegetated sediments with *Halimione portulacoides* (HP) and *Juncos maritimus* (JM), and non-vegetated ones (NV) from the two saltmarshes of Ria de Aveiro: Chegado (CHE-reference site) and Laranjo (LAR-Hg contaminated site), during Spring, Summer, Fall and Winter seasons.

358

## Impact of environmental health research in artisanal and small-scale gold mining sites in Zimbabwe

Bose-O'reilly S<sup>1</sup>

<sup>1</sup>University Hospital, LMU Munich

### Introduction

In Zimbabwe ASGM is one of the only opportunities to earn some dollars. Mercury, a most neurotoxic substance is used.

### Methods

Over the past 20 years, we have studied the health of miners, measured their mercury levels in urine, blood, hair and even in the breast milk of infants. We have determined their health needs, identified the lack of health and safety in the workplace and calculated the high burden of disease. All of these topics can be found in 20 peer-reviewed publications from our research group alone. The question is, what impact has the research had on the real world in a mining town in Zimbabwe?

### Results

Zimbabwe in 2022 artisanal and small-scale gold mining town of Kadoma is busy as usual. In the mining areas on the outskirts of the city, many young miners in particular are digging in small tunnels to get a few sacks of ore out, processing the ore in tiny ball mills and applying mercury to form an amalgam, containing gold and mercury.

At the end of the day the miners heat this amalgam, releasing toxic mercury vapors, until the sponge gold remains, worth a few dollars per miner. It seems this year that there are more young miners, especially female miners, including their little kids.

They are living in unhealthy camps, all exposed day and night to noise, dust and mercury fumes. The reason to be here is the increasing poverty in Zimbabwe.

### Conclusions

Poverty, increased during the pandemic, the lack of alternative livelihoods, the desperate hope to get a bit of money, made people from Zimbabwe and elsewhere to become small-scale miners. Kadoma and elsewhere, mercury exposed children, dry, dusty, unhealthy places for children. For me this is the modern version of Dante's inferno, eternal suffering, no hope, no way out.

359

## The South African Mercury Network: How scientific cooperation can help fill in the data gaps

Martin L<sup>1</sup>, Labuschagne C<sup>1</sup>, Labuschagne P<sup>1</sup>, Setlhare M<sup>1</sup>, Cloete P<sup>1</sup>

<sup>1</sup>SA Weather Service

The Cape Point Global Atmosphere Watch (GAW) Station operated by the SA Weather Service has been conducting continuous mercury measurements on the continent since September 1995 making Cape Point the station with the longest data record in the Southern Hemisphere. The Cape Point GAW Station unique location is however not a true reflection of the current status of mercury in the atmosphere within South Africa as it serves more as a background site. With the need to have a better understanding of the Fate and Transport of mercury within the country, the SA Mercury Network was established to investigate this.

SAMNet started in April 2020 and its aim was to expand the ground-based mercury observation stations in SA. The project is funded by the Department of Science and Innovation, in support of the Global Observation System for Mercury (GOS4M), a GEO flagship program.

The presentation will focus on the data collected at the new established SAMNet stations as well as the Passive Sampling Network that was started in 2021 in collaboration with Environment and Climate Change Canada which also covers sites in Namibia, Ghana, Botswana and Tanzania. Three SAMNet sites also perform monthly sampling using the Gold Amalgamation Manual Method developed by the Ministry Environment of Japan (MOEJ) as part of the MOYAI Initiative that supports developing countries in strengthening their monitoring capabilities as well as implementation of the Minamata Convention

## Mercury stable isotopes as a tool to study the impacts of Artisanal and Small-scale Gold Mining on rivers in the Guianas

Martin L<sup>1</sup>, Maurice L<sup>1</sup>, Laffont L<sup>1</sup>, Sonke J<sup>1</sup>, Bernard C<sup>2</sup>, Landburg G<sup>3</sup>, Williams A<sup>4</sup>

<sup>1</sup>Geosciences Environnement Toulouse, CNRS/IRD/CNES/Université Toulouse III, <sup>2</sup>Faculty of Natural Sciences, University of Guyana, <sup>3</sup>NZCS/CMO, Anton de Kom University of Suriname, <sup>4</sup>WWF Guianas  
Legal and illegal Artisanal and Small-scale Gold Mining (ASGM) is a widespread activity highly developed in Southern countries. This activity uses rudimentary techniques to prospect, extract and process ores, induces deforestation, destruction of habitats, release of mining waste, cyanidation of tailings and amalgamation with mercury (Hg). ASGM accounts for 15 to 25% of the gold production worldwide and 37% of the global Hg pollution. Mercury also poses substantial health effects to miners and communities living in ASGM areas which makes important to understand the cycle of mercury in the environment.

Total mercury and mercury stable isotopes were analyzed in order to assess the sources and the distribution of Hg. Indeed, Hg isotopes present both Mass Dependent (MDF) and Mass Independent (MIF) Fractionations. Anthropogenic and natural sources of mercury highlight contrasted MDF and MIF, both close to zero or poorly negative (in ‰) for the first source and more negative for the latest. Four river systems (Potaro, Mazaruni and Siparuni in Guyana, Suriname in Suriname). For each system, and in collaboration with gold-miners association and with local populations, pristine and mining areas were investigated and also downstream when possible. Various compartments were considered. In aquatic systems, bottom sediments, suspended and dissolved fractions were sampled. In addition, soils, litters, leafs, tailings and parent rock materials were also collected as potential sources of riverborne material. Then, we discuss about the origin of mercury found in river sediments and the potential environmental impacts of ASGM in the Guianas.

361

## Engaging E-Commerce Platforms in Eliminating Toxic Trade in Mercury Added Cosmetics

Bender M<sup>1</sup>, Euripidou, E<sup>1</sup>, Lymberidi-Settimo E<sup>1</sup>, Cheuvart C<sup>1</sup>, MAHAPATRA A

<sup>1</sup>Mercury Policy Project/Zero Mercury Working Group

Despite being banned globally, mercury-added cosmetics (namely skin lightening products (SLPs)) are still being marketed online worldwide based on numerous studies, including a recent Zero Mercury Working Group (ZMWG) report. This online toxic trade perpetuates colorism and presents significant mercury exposure risks to users and household members. Most at risk are pregnant and nursing mothers, and children.

Last year, ZMWG partners from 12 countries sampled 213 suspect SLPs from 23 online platforms, with test results indicating that 90% exceeded the 1 ppm mercury content limit mandated by the Minamata Convention and many governments. Our ZMWG studies highlight the lack of effective controls as many E-commerce giants appear to evade responsibility to prevent unscrupulous merchandising of illicit SLPs.

To address this online toxic trade in SLPs, examples will be presented of 1) online platforms' hazardous policies and procedures designed to prevent such toxic trade, and 2) product safety pledges (PSPs), increasing being developed by governments for online platforms to voluntarily block and/or remove online offerings of hazardous products, among several other related commitments.

PSPs were first adopted in the European Union in 2018 and often go beyond existing regulations. Subsequently, PSPs have been adopted in South Korea, Australia, Japan, and Canada. As of last November, India is reportedly considering the same. On a parallel track, the Organization for Economic Development (OECD) has a working group that promotes and supports the development of PSPs.

In summary, we will describe how the OECD, the World Health Organization and the Minamata Convention, as well as the academic community, civil society and others, can further assist Parties engage online platforms in blocking sales of toxic SLPs. This includes establishing a global SLP database, building on the ZMWG database (with over 1,000 tested products) and other databases, for ferreting out illicit SLPs.

362

## The Journey of Anthropogenically Emitted Mercury to Planktons in South-East Asian Oceans according to Stable Isotopes

Motta L<sup>1</sup>, Lim S<sup>2</sup>, Lee Y<sup>3</sup>, Kang D<sup>3</sup>, Kwon S<sup>2</sup>

<sup>1</sup>Woods Hole Oceanographic Institution, <sup>2</sup>Division of Environmental Science and Engineering, Pohang University of Science and Technology, <sup>3</sup>Korea Institute of Ocean Science & Technology

Mercury (Hg) is known as a global pollutant because, once emitted, gaseous Hg can be disseminated globally, making it difficult to track its origin. All forms of Hg are toxic, but anthropogenic Hg emissions would pose less of a threat if Hg was not converted to methylmercury in marine waters, the neurotoxic form of Hg found in fish at elevated concentrations resulting in public health concern. The journey of anthropogenic Hg(0) to methylmercury remains uncertain, however. Here, we present the measurement of the stable isotopic composition of mercury in surface-dwelling zooplankton from the East China Sea to the Bay of Bengal and a vertical profile from the Philippine Sea. We show a spatial positive increase in  $\delta^{202}\text{Hg}$  and  $\Delta^{199}\text{Hg}$  from the Asian marginal seas to the Central Pacific Ocean (Station ALOHA, and 5 and 8N with 155 W), illustrating a gradient for decreasing contribution of anthropogenic Hg sources with increasing distance from continental Asia. A  $\delta^{202}\text{Hg}$  and  $\Delta^{199}\text{Hg}$  Bayesian isotope mixing model shows that anthropogenic Hg emissions contribute 14% in the Philippine Sea to 40% in the East China Sea of the total Hg in surface zooplankton. The Hg isotopic patterns in zooplankton with depth confirm the propagation of anthropogenic Hg with depth and the strong influence of dissolved Hg from the South China Sea.  $\Delta^{200}\text{Hg}$  values from the coast of the Asian continent and the Pacific Ocean indicate that oxidized Hg via atmospheric deposition is the main source of Hg to pelagic organisms, and atmospheric Hg(0) uptake is not an important source to marine biota. This has critical implications for our understanding of the link between Hg emissions and marine ecosystem loading.

363

## Innovative binding agents: Novel material included in diffusive gradients in thin-films (DGT) technique for mercury assessment in aqueous environments

Diez S<sup>1</sup>, Marrugo-Madrid S, Marrugo-Negrete J, Fontàs C, Kurt G

<sup>1</sup>IDAEA - CSIC

Despite the agreement of the Minamata Convention, artisanal and small-scale gold mining (ASGM) continues to take place mainly in remote and difficult-to-access sites, where the application of a convenient method for sampling, preserving and transporting Hg samples is required. In this study, we evaluated the effectiveness of the Diffusive Gradients in Thin Films (DGT) technique for monitoring and quantifying the bioavailable fraction of Hg in Colombian freshwater ecosystems highly impacted by ASGM. Therefore, various types of materials with proven affinity to Hg were evaluated as potential binding layers for novel DGT devices. In laboratory tests, the effects of key DGT parameters (e.g. sorption capacity at different deployments time, ionic strength and pH) were evaluated and the diffusion coefficients were determined. The DGT devices were deployed along the Atrato and Quito rivers, and abandoned mining ponds, without statistically significant differences were seen between the concentrations of dissolved Hg between the sampling points ( $P < 0.05$ ). In the ponds, no significant differences were found in dissolved Hg related to the abandonment period. This study demonstrates the continuous development of the DGT technique through the use of new and valorized materials with a high affinity for mercury.

364

## Mercury emissions coal from tests in combustion pilot plant

Da Cruz R<sup>1</sup>, Fernandes de Aquino T, Michels Bianchi F, Silva Moura P, da Rocha Silvano Neves J, Luis Zanin T

<sup>1</sup>Beneficent Association Of The Santa Catarina Coal Industry – Satc

The concerns about emissions of polluting gases into the atmosphere from fossil fuels have been discussed for many years. However, the quantification that emissions of such pollutants is necessary to be able to mitigate them while there is energetic transition from fossil fuels to renewables or even efficient abatement technologies that allow us to continue using the mineral. Therefore, the present work aims to quantify mercury emissions in mineral coal on a pilot scale, thus covering the quantification of Hg in coal, limestone, ashes from the process (fly ash, bottom ash) and in gases. Furthermore, two burning temperatures will be evaluated: 815°C and 850°C, these temperatures will be evaluated only using mineral coal, as well as with the desulfurization process. It will still be possible to assess the influence of coal desulphurization and how much it will impact in the mercury emissions, as well as in which matrix the metal will be concentrated associated with sulfur abatement.

### Abstract Graphics



365

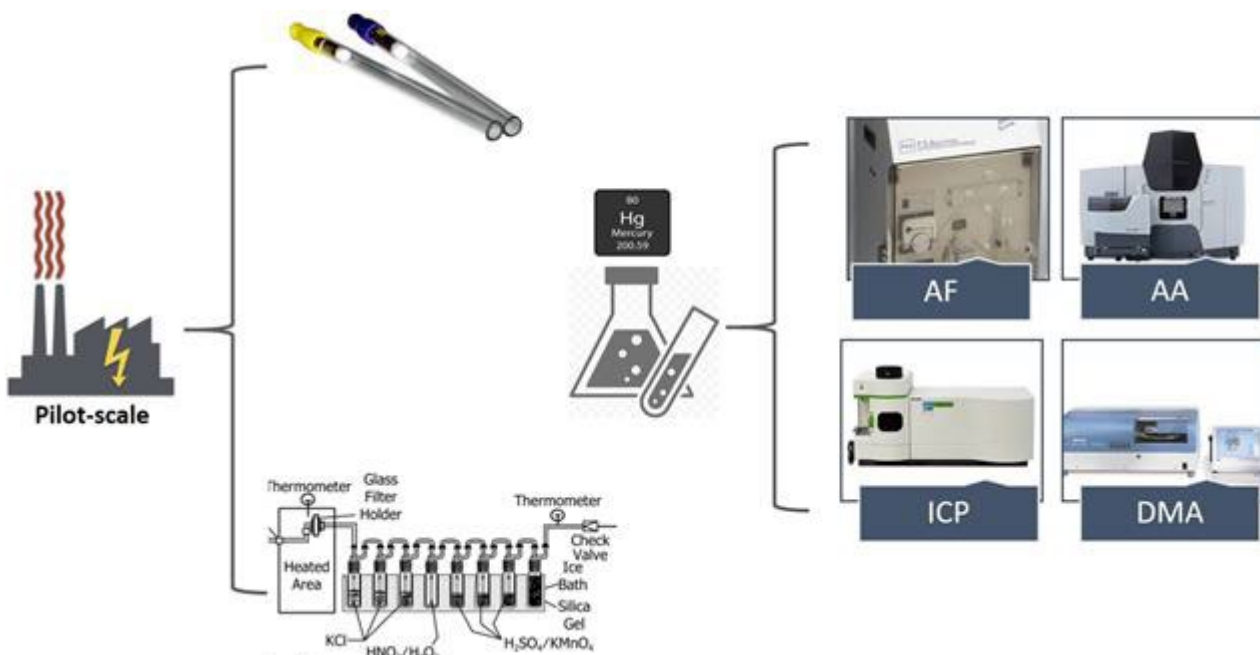
## Sampling methods and techniques for determining mercury in atmospheric emissions

Da Cruz R<sup>1</sup>, Fernandes de Aquino T<sup>1</sup>, Michels Bianchi F<sup>1</sup>, Silva Moura P<sup>1</sup>, da Rocha Silvano Neves J<sup>1</sup>, Luis Zanin T, Malgarise Brolesi T<sup>1</sup>, Mendes de Resendes F<sup>1</sup>

<sup>1</sup>Associação Beneficente Da Indústria Carbonífera De Santa Catarina -sac

Currently, there are several ways of sampling and determining mercury from stationary sources, among them the most discussed in legislation are the methods US EPA Method 29, US EPA Method 101A, ASTM D6784-16, US EPA Method 30b. Furthermore, the advancement of technology in analytical equipment has made it possible to quantify this metal in various determination techniques, from very low concentrations (ppt) to very high concentrations (% m/m or v/v). Thus, it was possible to combine the best quantification techniques with sampling of these emissions, knowing the peculiarities that each one could have. In the case of determining mercury from mineral coal, the following points to be discussed as facilitators or interferers in sampling and determination are: organic matter content, combustion process, abatement or not of acid gases such as CO<sub>2</sub>, SO<sub>x</sub>, NO<sub>x</sub>, quantity of ash, particulate matter abatement system. All of these points mentioned interfere in the sampling and quantification procedure. Therefore, in the present work two sampling methodologies will be discussed (ASTM D6748-16 and US EPA Method 30b), in which their differentiation is in the metal sequestration, in which one considers metal in the particle and gas through filters and absorbent solutions, and the other another in traps with selective adsorbents. The techniques for quantifying these emissions will be DMA-80 (Direct Analyzer Mercury), AA (Atomic Absorption), AF (Atomic Fluorescence) and ICP-OES (Inductive Couple Plasm). It will then be possible to verify, under the same process conditions, which sampling is best for this situation as well as evaluate digestions and quantifications using these techniques.

### Abstract Graphics



## Understanding the Impacts of Mercury Contamination from ASGM in Amazonian Wildlife: A Seven Year Case Study from Madre de Dios, Peru

Fernandez L<sup>1,2</sup>, Vega C<sup>1,2</sup>, Araujo J<sup>1,2</sup>, Pisconte J<sup>2</sup>, Delgado S<sup>2</sup>, Portillo A<sup>3</sup>, Ascorra C<sup>2</sup>, Silman M<sup>1,2</sup>

<sup>1</sup>Wake Forest University, <sup>2</sup>Centro de Innovacion Cientifica Amazonica - CINCIA , <sup>3</sup>Universidad Nacional de San Antonio Abad del Cusco

The impact of extensive artisanal and small-scale gold mining (ASGM) in the Amazon's Madre de Dios region on mercury levels in wildlife and its broader implications for tropical ecosystems poses a critical question. ASGM, a prevalent source of mercury pollution, threatens the region's rich biodiversity, yet the scope of its impact on diverse species across trophic levels is not fully understood.

Addressing this gap, the Center for Amazonian Scientific Innovation (CIN CIA) embarked on a suite of baseline studies 2017 - 2023 to quantify mercury concentrations in a various wildlife species, including fish, birds, and bats, complemented by assessments of mercury in air, sediment, and soils in and around mining areas. Findings reveal significant mercury accumulation and mobility in the ecosystem, notably in piscivorous fish, where concentrations were related with the type of mining technology used on the landscape. Birds in mining-impacted areas exhibited elevated mercury levels across all trophic levels, while in bats, significant mercury presence was detected mainly in frugivores and granivores.

However, considerable knowledge gaps persist, particularly regarding the interactions between mercury accumulated in forest soils from atmospheric deposition and its effects on wildlife, and regarding dynamics of mercury in ASGM impacted forests under changing wildfire regimes, influenced by climate change and anthropogenic ignition sources, remain largely unexplored.

Our research in the Southern Peruvian Amazon shows the pervasive influence of ASGM on mercury distribution within Amazonian ecosystems highlighting a possible need for new conservation strategies that explicitly include mercury-related risks to wildlife tailored to mitigate adverse effects. To explore these questions further, in 2024, CIN CIA is expanding its geographic scope and conduct Hg baselines studies in three river watersheds in the Northern Peruvian Amazon (Nanay, Napo and Putumayo), basins that are only just now becoming heavily impacted by artisanal gold mining and its related mercury pollution.

## Total mercury contamination in neotropical bats of different feeding guilds in the Atlantic Forest

Monteiro-Alves P<sup>1</sup>, Bighetti G<sup>2</sup>, Lino A<sup>2</sup>, Souza T<sup>2</sup>, Lourenço E<sup>1</sup>, Meire R<sup>2</sup>, Bergallo H<sup>1</sup>

<sup>1</sup>State University of Rio de Janeiro, <sup>2</sup>Federal University of Rio de Janeiro

Bats can be used as models for monitoring environmental contamination due to their biological and behavioral characteristics. The presence of mercury in bat tissues has already been evidenced. However, there is a scarcity of data on neotropical bats, an area with a higher occurrence of species and diversity of feeding habits, as well as socio-environmental conflicts. The objective of this study is to present the concentration of total mercury (THg) in different bat species with various feeding guilds in the Atlantic Forest, Brazil and create a baseline information for further studies. Samples were carried out in environmental protection areas from 2021 to 2023 in the state of Rio de Janeiro. Muscles and livers of *Desmodus rotundus* (hematophages), *Tonatia bidens* (carnivores), *Molossus molossus* (insectivores), *Glossophaga soricina* (nectarivores), *Phyllostomus hastatus* (omnivores) and *Artibeus* sp (frugivores) species were analyzed. The Direct Mercury Analysis (DMA-80) equipment was used to measure THg concentrations. The results demonstrated that, when evaluating different matrices, the liver showed higher concentrations than the muscles. When assessing gender, no significant difference was observed. However, when evaluating feeding habits, it was possible to observe a higher concentration in insectivores, followed by a decrease in concentrations for carnivores, omnivores, hematophages, nectarivores, and with the lowest concentrations in frugivores. Nevertheless, it was observed in this study that the location had a greater influence than the feeding habits. This is the first study on neotropical bat species in Brazilian territory, and more information is needed to add details regarding the distribution of mercury in these animals.

368

## Will a Changing Global Sulfur Cycling Affect Mercury Bioavailability?

Hinckley E<sup>1</sup>, Hermes A, Rea L, Driscoll C

<sup>1</sup>University Of Colorado, Boulder

Sulfur (S) is an element whose cycle has dramatically changed from human activities and is inextricably linked to the availability and fate of mercury (Hg) in ecosystems. The nature of human alteration of the global S cycle is changing, with implications for changes in Hg bioavailability through methylmercury (MeHg) production. As atmospheric S deposition declines in response to air quality regulation in the U.S. and Europe, there has been an increase in S fertilizer applications in many large, regional crop systems. In addition, intensification of agriculture has driven increases in other uses of S inputs: as a pesticide, regulator of soil pH, and soil conditioner. Given that excess sulfate is highly mobile in terrestrial ecosystems, transport to adjacent aquatic ecosystems with fluctuating redox conditions can stimulate the production of MeHg, a neurotoxin that biomagnifies and bioaccumulates in the food chain. In this presentation we describe new long-term data analyses over regional crop systems to which S is added; the development of stable isotope and radioisotope methods to trace the “fingerprint” of agricultural S through complex landscapes and the rates of key transformations in the S cycle; and the interactions of S and Hg transformations. Highlights of our findings include a 300% increase in the amount of reactive S applied to major crop systems in the U.S. over the last 30 years; evidence of increased loading of sulfate and organic S from agricultural areas to downstream wetlands; the persistent, anomalous isotopic signature of agricultural S at the watershed scale; and elevated concentrations of MeHg in wetlands receiving agricultural S runoff. Collectively, these data provide motivation to (1) address regulation of S in crop systems and (2) study the fates and consequences of S applications to major agricultural regions due to their role in enhancing the availability of heavy metals like Hg.

## Avian Mercury Exposure in Gold Mining Areas of the Southern Peruvian Amazon

Pisconte J<sup>4</sup>, Sayers II C<sup>2</sup>, Vega C<sup>4,1</sup>, Huaraca-Charca N<sup>5</sup>, Salvador J<sup>6</sup>, Mandujano J<sup>6</sup>, Huamani Valdivia L<sup>4</sup>, Fernandez L<sup>1,4,7</sup>

<sup>1</sup>Wake Forest University, <sup>2</sup>University of California, Los Angeles, Department of Ecology and Evolutionary Biology, <sup>3</sup>Biodiversity Research Institute, Center for Mercury Studies, <sup>4</sup>Centro de Innovación Científica Amazónica - CINCIA, <sup>5</sup>Inkaterra Asociación, <sup>6</sup>Centro de Ornitología y Biodiversidad - CORBIDI, <sup>7</sup>Carnegie Institution for Science, Department of Global Ecology

Artisanal gold mining has expanded across the tropics, clearing extensive forest areas, causing fragmentation, habitat loss, and modifying hydrological systems. Extensive use of mercury for gold recovery contaminates aquatic and terrestrial systems, threatening the wildlife that inhabits them. In the Amazonian region of Madre de Dios, Peru, gold mining primarily uses two mining methods: minimal mechanized (MM), using suction pumps, and highly mechanized (HM), using excavators and front loaders, causing different scales and patterns of landscape alteration and mercury use, the resulting mercury contamination on wildlife from these different methods is poorly understood. This study aimed to assess mercury contamination at different scales of disturbances and identify the association with the body condition of birds that inhabit these sites. We determined total mercury (THg) concentrations in flank feathers of 452 birds captured along disturbance gradients across gold mining sites using minimally mechanized, heavily mechanized, and non-mining control sites. Piscivorous ( $27.19 \pm 17.11 \mu\text{g/g}$ ) and Insectivores ( $2.63 \pm 2.85 \mu\text{g/g}$ ) presented higher Hg-levels and we determined that the highest average THg concentrations in birds were in minimally mechanized mining sites ( $4.41 \pm 6.85 \mu\text{g/g}$ ), compared to highly mechanized sites ( $1.65 \pm 3.15 \mu\text{g/g}$ ) and sites without mining ( $1.03 \pm 0.12 \mu\text{g/g}$ ). Also, individuals inhabiting near mining ponds ( $3.77 \pm 8.80 \mu\text{g/g}$ ) and forested areas ( $2.14 \pm 2.72 \mu\text{g/g}$ ) showed higher concentrations than in non forested areas ( $2.45 \pm 5.96 \mu\text{g/g}$ ). These preliminary results suggest that not only the presence of mining activity but also the method applied for gold extraction and amalgamation process may influence Hg exposure in birds inhabiting and around ASGM sites, which might negatively affect reproductive success and potentially impact regional and global (migratory birds) avian communities .

## Avian Mercury Exposure in Gold Mining Areas of the Southern Peruvian Amazon

Vega Ruiz C

Artisanal gold mining has expanded across the tropics, clearing extensive forest areas, causing fragmentation, habitat loss, and modifying hydrological systems. Extensive use of mercury for gold recovery contaminates aquatic and terrestrial systems, threatening the wildlife that inhabits them. In the Amazonian region of Madre de Dios, Peru, gold mining primarily uses two mining methods: minimal mechanized (MM), using suction pumps, and highly mechanized (HM), using excavators and front loaders, causing different scales and patterns of landscape alteration and mercury use, the resulting mercury contamination on wildlife from these different methods is poorly understood. This study aimed to assess mercury contamination at different scales of disturbances and identify the association with the body condition of birds that inhabit these sites. We determined total mercury (THg) concentrations in flank feathers of 452 birds captured along disturbance gradients across gold mining sites using minimally mechanized, heavily mechanized, and non-mining control sites. Piscivorous ( $27.19 \pm 17.11 \mu\text{g/g}$ ) and Insectivores ( $2.63 \pm 2.85 \mu\text{g/g}$ ) presented higher Hg-levels and we determined that the highest average THg concentrations in birds were in minimally mechanized mining sites ( $4.41 \pm 6.85 \mu\text{g/g}$ ), compared to highly mechanized sites ( $1.65 \pm 3.15 \mu\text{g/g}$ ) and sites without mining ( $1.03 \pm 0.12 \mu\text{g/g}$ ). Also, individuals inhabiting near mining ponds ( $3.77 \pm 8.80 \mu\text{g/g}$ ) and forested areas ( $2.14 \pm 2.72 \mu\text{g/g}$ ) showed higher concentrations than in non forested areas ( $2.45 \pm 5.96 \mu\text{g/g}$ ). These preliminary results suggest that not only the presence of mining activity but also the method applied for gold extraction and amalgamation process may influence Hg exposure in birds inhabiting and around ASGM sites, which might negatively affect reproductive success and potentially impact regional and global (migratory birds) avian communities .

370

## From River to Plate: Tracing Mercury Exposure through Fish and Bushmeat Consumption in the Northern Peruvian Amazon

Valdivia G<sup>2</sup>, Vega C<sup>1,2</sup>, Huamani Valdivia <sup>2</sup>, Puertas P<sup>2</sup>, Ascorra C<sup>2</sup>, Silman M<sup>1,2</sup>, Fernandez L<sup>1,2,3</sup>

<sup>1</sup>Wake Forest University, Sabin Center for Environment and Sustainability, <sup>2</sup>Centro de Innovación Científica Amazónica - CINCIA, <sup>3</sup>Carnegie Institution for Science, Department of Global Ecology

In the Amazonian region of Peru, high fish consumption rate by the population represents a significant exposure route for mercury exposure enhanced by the proliferation of artisanal gold mining (AGM). Gold mining results in the environmental dispersion of mercury, which undergoes conversion to methylmercury and biomagnification/bioaccumulation in aquatic foodwebs contaminating wildlife and consumable fish stocks. Findings from prior studies in Madre de Dios, a region extensively impacted by artisanal and small-scale gold mining (ASGM), have revealed elevated mercury concentrations within indigenous communities, including locales remote from direct mining operations.

The Center for Amazonian Scientific Innovation (CINCIA) is addressing this issue through detailed research on mercury exposure from fish consumption. Preliminary findings from 2023 in Loreto reveal high levels of mercury concentrations in consumable fish species: carnivores, 0.69 ppm, omnivores: 0.27 ppm, detritivores, 0.17 ppm. Given Loreto's significant indigenous demographic, constituting 31.8% of its populace across 32 communities, and the predominant reliance on fish, accounting for nearly 90% of dietary intake, the potential for mercury exposure is markedly high.

This research underscores the critical need to monitor mercury pollution of species consumed by local populations, and possibly for assessments to include a variety of species consumed by local communities, including bushmeat such as lizard, caiman, turtle, agouti, and peccary. This would more accurately assess the risks associated with mercury exposure in Loreto and, where needed, inform the development of dietary intake guidelines for at-risk communities in the region.

371

## Catalytic oxidation of Hg<sub>0</sub> over Co-based mixed metal oxides catalyst

Chang H<sup>1</sup>, Qiu L, Xiao R

<sup>1</sup>Renmin University Of China

In this work, a series of modified Co<sub>3</sub>O<sub>4</sub> metal oxides catalysts were synthesized by coprecipitation method. The Co-Cu-Ox catalysts exhibited nearly 100% Hg<sub>0</sub> oxidation efficiency at 100-400 °C. The BET specific surface area of Co-Cu-Ox catalyst increased to 26 m<sup>2</sup> g<sup>-1</sup>. The H<sub>2</sub>-TPR and O<sub>2</sub>-TPD demonstrated that the catalyst exhibited optimal redox performance (192 °C) and migration activity of oxygen species (203, 382 and 610 °C), resulting in its highest O<sub>α</sub>/ (O<sub>α</sub> + O<sub>β</sub>) ratio (56.4%). In addition, in-situ DRIFTS of NO adsorption indicated that the band at 1390 cm<sup>-1</sup> disappeared after the pretreatment of Hg<sub>0</sub>. And the Hg<sub>0</sub> could also be extruded from the surface of the catalyst after the introduction of NO. It was proved that there was competitive adsorption between Hg<sub>0</sub> and NO over Co-Cu-Ox catalyst. And sufficient O<sub>2</sub> could offset the competitive adsorption of NO with Hg<sub>0</sub>. Finally, the simultaneous oxidation of Hg<sub>0</sub>-NO over Co-Cu-Ox catalyst was investigated by the XPS before and after reaction. It was deduced that O<sub>α</sub> would be consumed and there was the redox cycle of Co<sup>3+</sup> + Cu<sup>+</sup> ↔ Co<sup>2+</sup> + Cu<sup>2+</sup> in Hg<sub>0</sub>-NO simultaneous oxidation.

## A complete understanding of the sources and pathways of mercury deposited to lake ecosystem using a stable mercury isotope mass balance model

Zhang H<sup>1</sup>

<sup>1</sup>Institute Of Geochemistry, Chinese Academy Of Sciences

Mercury (Hg) pollutions in lake ecosystems are of particular concerns of environmental and human health. To date, however, there are incomplete understanding of the sources and transport pathways of Hg deposited to the lake ecosystems. Here we measured the isotopic compositions of Hg in various environmental media at Hongfeng Lake (HFL), southwestern China, and quantify the contributions of six potential sources of Hg deposited to the lake using a stable Hg isotope mass balance model. The  $\delta^{202}\text{Hg}$  variation in lake dissolved Hg (DHg) ranged from -2.11 to 0.33‰, with a mean of  $-0.89 \pm 0.43\text{‰}$  ( $\pm 1\sigma$ ,  $n = 60$ ). Overall, DHg samples had positive  $\Delta^{199}\text{Hg}$  (varied from 0.03 to 0.56‰) and slightly positive  $\Delta^{200}\text{Hg}$  values (varied from -0.02 to 0.14‰) during winter, spring and winter sampling period, with average values of  $0.19 \pm 0.10\text{‰}$  and  $0.04 \pm 0.04\text{‰}$ , respectively. The lake water particulate Hg (PHg) samples generally exhibit a slightly lower  $\delta^{202}\text{Hg}$  (mean  $\pm 1\sigma$ :  $-1.55 \pm 0.42\text{‰}$ ,  $n = 62$ )  $\Delta^{199}\text{Hg}$  (mean  $\pm 1\sigma$ :  $-0.03 \pm 0.06\text{‰}$ ) and  $\Delta^{200}\text{Hg}$  (mean  $\pm 1\sigma$ :  $0.00 \pm 0.03\text{‰}$ ) than DHg samples. The precipitation and particulate bound Hg (PBM) samples had moderately positive  $\Delta^{199}\text{Hg}$  and slightly positive  $\Delta^{200}\text{Hg}$  values. In contrast, the atmospheric Hg(0) and runoff Hg isotope composition samples in this study had negative MIF values for both odd and even Hg isotopes. Based on the input fluxes and Hg isotopic signatures of the end-member at HFL, we calculated the atmospheric Hg(0), rainfall, atmospheric gaseous oxidized Hg (GOM), PBM, riverine, and surface runoff loads of  $4.7 \pm 1.4\%$ ,  $6.4 \pm 2.3\%$ ,  $1.0 \pm 0.1\%$ ,  $4.4 \pm 0.1\%$ ,  $11.7 \pm 0.11\%$ , and  $71.9 \pm 0.11\%$ , respectively. Our study showed and emphasized that GEM deposition to the watershed followed by surface runoff transport is the largest source of Hg to lakes.

373

## Adsorption mechanism of gaseous elemental mercury on carbon nanotubes with typical functional groups

Luo J<sup>1</sup>, Jin M, Ye L, Zhou S

<sup>1</sup>Xiamen University

The effect of physicochemical properties of carbon nanotubes on adsorption of elemental mercury (Hg<sup>0</sup>) was investigated in this study. Non-thermal plasma pre-treatment was conducted to introduce typical functional groups (O, S, Cl) on carbon surface. Hg<sup>0</sup> adsorption experiments were run in a fixed-bed reactor with nitrogen as the carrier gas. Surface characteristics of samples were studied by the method of N<sub>2</sub> adsorption, scanning electron microscope with energy dispersive spectrometer (SEM-EDS), transmission electron microscope (TEM), Fourier transform infrared reflection (FTIR), diffraction of x-rays (XRD), Hg-temperature programmed desorption (Hg-TPD), X-ray photoelectron spectroscopy (XPS), X-ray absorption fine structure (XAFS), thermogravimetric analysis (TA), respectively. Experimental results showed that plasma modification successfully increased active sites (O, Cl, S) on carbon nanotubes and greatly increased its mercury removal efficiency, although the surface structure of the carbon nanotube wall was altered and surface area was slightly reduced. The predominant mechanism of Hg<sup>0</sup> removal was the formation of chemical bonds between Hg and the functional groups. Both XPS and XAFS analysis revealed that mercury bound on the surface was mainly in oxidation state. HgO was the main product when Hg<sup>0</sup> was absorbed on the air plasma modified carbon nanotube. The adsorbed-Hg on HCl-treated / H<sub>2</sub>S-treated carbon nanotube wall mainly in the form of Hg<sup>+</sup>. Gaseous Hg<sup>0</sup> was believed to heterogeneously react with chlorinated / sulphuration sites through electron-transfer and formed Hg<sub>2</sub>Cl<sub>2</sub> / Hg<sub>2</sub>SO<sub>4</sub> compounds.

## KAZAKHSTAN'S EXPERIENCE OF ELIMINATING MERCURY POLLUTION IN TWO INDUSTRIAL CENTERS AND POST-DEMERCURIZATION MONITORING OF THE ENVIRONMENT

Kamberov I<sup>1</sup>, Duisebayeva T<sup>2</sup>, Sultanbekov S, Ilyushchenko M, Nussbaumer M

<sup>1</sup>The National Centre for Research, Training and Education in Civil Protection, <sup>2</sup>«Volkovgeology» JSC branch of CEME

Keywords: central Kazakhstan, industrial centers, PA "Khimprom" and "Carbide" factories, "Irtys" and "Nura" rivers, landfill, burial ground, environment monitoring, cleanup of the river bank, bottom sediments, groundwater, industrial pollution.

After the collapse of the Soviet Union to Kazakhstan were inherited the sources of technogenic mercury pollution that located within two large industrial centers. The mercury pollution in Pavlodar was associated with the production activities between 1975-1993 years of the chemical plant Production Association (PA) "Khimprom" which included chlorine-alkaline production by the electrolysis method with a mercury cathode with a capacity of 100,000 tons of chlorine per year [1]. The activity of acetaldehyde production of the "Carbide" JSC plant was a source of extensive mercury pollution within 1950-1993 years in the area of Temirtau city [2,3]. The main environmental risks in the industrial zone of Pavlodar city were due to the emissions of mercury in to the atmosphere from mercury-contaminated dilapidated buildings and topsoil, as well as the possibility of the spread of mercury-contaminated groundwater to the floodplain of the "Irtys" river in 5 km west from the plant. The risks to health for continue working staff and people living near the plant were contaminated by mercury vapor and mercury poisoned fish that fishermen were caught from the storage of sewage. The groundwater pollution could also reach the water wells of a large settlement located 4 km from a chemical plant between the plant and the "Irtys" river. The long-term releases of mercury to the environment of Temirtau city were carried out during accidents, as well as due to imperfection of technologies in the thermal regeneration of mercury from sludge, discharge of mercury-containing wastewater into the "Nura" river and the accumulation of mercury wastes in the enterprise and beyond.

375

## Latest trends and findings from ground based sites within the SA Mercury Network

Martin L<sup>1</sup>, Labuschagne C<sup>1</sup>, Labuschagne P<sup>1</sup>, Setlhare M<sup>1</sup>, Cloete P<sup>1</sup>, Mkololo T<sup>1</sup>

<sup>1</sup>SA Weather Service

The Cape Point Global Atmosphere Watch (GAW) Station operated by the SA Weather Service has been conducting continuous mercury measurements on the continent since September 1995 making Cape Point the station with the longest data record in the Southern Hemisphere. The Cape Point GAW Station unique location is however not a true reflection of the current status of mercury in the atmosphere within South Africa as it serves more as a background site. With the need to have a better understanding of the Fate and Transport of mercury within the country, the SA Mercury Network was established to investigate this.

SAMNet started in April 2020 and its aim was to expand the ground-based mercury observation stations in SA to have better coverage.

The presentation will focus on the data collected since 2021 at the new established SAMNet stations in the N-Cape, Gauteng, Mpumalanga and Kwazulu-Natal provinces. Comparisons studies with the MerPas at the Witbank Air Quality station where a Lumex RA 915-AM analyzer is operational will also be presented.

376

## Towards a Mercury-free Artisanal and Small-scale Mining Regime in a Just Energy Transition

Munakamwe J<sup>1</sup>

<sup>1</sup>Wits Mining Institute, University Of The Witwatersrand

This paper focuses on transitioning towards a mercury-free approach in artisanal and small-scale mining (ASM) within the context of a just energy transition. ASM in Africa is a contentious issue characterised by conflicting interests between powerful stakeholders and vulnerable communities. The sector is often marred by 'criminalisation', notably in the extensive use of mercury, causing significant harm to the environment, land, and water bodies. Despite these challenges, ASM serves as a vital source of livelihood for impoverished individuals. Globally, an estimated 100 million workers and their families rely on income from artisanal mining, surpassing the 7 million employed in large corporate mining. In South Africa alone, 16,000 to 30,000 artisanal miners, benefiting nearly 100,000 families, underscore the socio-economic importance of ASM. However, the unregulated and informal nature of these activities pose potential health hazards and threatens food security if not properly managed. The paper will draw from documentaries including first-hand testimonies, as it seeks to elucidate the adverse effects of mercury on humans, fauna, flora, and the broader environment. Given the central role played by the ASM sector in alleviating poverty, the session aims to explore alternatives to mercury usage, offering strategies to mitigate identified social and ecological impacts.

377

## A global model for marine mercury cycling and bioaccumulation

Bieser J<sup>1</sup>, Amptmeijer D<sup>1</sup>, Soerensen A<sup>1</sup>, Daewel U<sup>1</sup>, Logemann K<sup>1</sup>

<sup>1</sup>Helmholtz-zentrum Hereon

We present our newest development: The global marine mercury cycling model ICON-MERCY. It is the first hydrodynamic biogeochemical model to include a complete mercury cycle up to the bioaccumulation into higher trophic levels. The model was developed to answer the question how Hg and MeHg levels in fish react to changes in anthropogenic Hg emissions.

The model is part of the multi compartment Hg model ensemble study (MCHgMAC) to support the effectiveness evaluation of the Minamata Convention. Besides the model itself and our first results, we will present the model studies planned for the ocean model ensemble within the MCHgMAC.

378

## The Caribbean Region Mercury Monitoring Network

Christian L<sup>1</sup>

<sup>1</sup>Department Of Analytical Services

Antigua and Barbuda acceded to the Minamata Convention on Mercury in September 2016 and remains committed to its implementation. The Specific International Programme (SIP) supports implementation through capacity building and Technical Assistance to Parties as a core component of the financial mechanism of the Convention.

In collaboration with the Biodiversity Research Institute (BRI), the Department of Analytical Services as Focal Point of the Convention successfully received funding through the SIP to execute a country-led initiative to establish a regional mercury monitoring network.

The Caribbean Region Mercury Monitoring Network (CRMMN) was officially endorsed by seven (7) countries within the wider Caribbean Region in 2022. Since its inception, the Network has established air monitoring sites in member countries and has been engaged in Hg monitoring in fish, birds, bats, human hair, and cosmetics.

In partnership with Environment and Climate Change Canada, atmospheric air monitoring has proceeded for approximately one year and spatial relations have been observed. The main objective is to establish temporal trends to facilitate reporting and to support the effectiveness evaluation process of the Convention.

Total Hg (THg) levels in marine fish tissue samples (n=265) ranged from 0.00 to 5.71 ug/g wet weight, and thirty-four percent (34 %) of human hair samples (n=130) exceeded 1 ug/g THg. Additionally, several brands of skin-lightening cream samples (n=154) exceeded 1000 mg/kg with maximal values exceeding 5000 mg/kg. Blood (n=9) and feathers (n=20) from passerines were generally unremarkable except for a single species that possessed an exceptionally high THg level (14.9 mg/kg).

The CRMMN seeks to contribute to current science, address gaps in global mercury data sets, advise policy, and thereby strengthen the science-policy interface. Furthermore, the network recognizes the need and opportunities for collaboration with other networks and entities to strengthen Hg monitoring globally.

379

## Supercritical CO<sub>2</sub> coupled with mechanical force to enhance carbonation of fly ash, stabilization of mercury and other heavy metals in lab and a pilot

Zhang Y<sup>1</sup>

<sup>1</sup>North China Electric University

Accelerated carbonation of fly ash is a potential way to achieve CO<sub>2</sub> emission reduction and heavy metal solidification. Slow conversion in the diffusion control stage is the bottleneck of the carbonation technical route. Based on the strong diffusion and permeability of supercritical CO<sub>2</sub>, and the modification of mechanical force to produce more fresh surfaces and pores, a method consisting of supercritical CO<sub>2</sub> coupled with mechanical force was carried out to strengthen the carbonation of fly ash. Research results show that the carbonation efficiency of fly ash under supercritical CO<sub>2</sub> is higher than under low-pressure conditions, and carbonation under supercritical CO<sub>2</sub> can effectively stabilize heavy metals in fly ash. The supercritical mineralization efficiency at 8 MPa was 55.27%, a factor of 2.09 larger than for non-supercritical mineralization at 3 MPa (26.39%). In the pilot experiment of coal-fired power plant, in which the fly ash carbonation capacity is 1t/d, its carbonation efficiency can reach 81.3%. Additionally, carbonation has an obvious inhibitory effect on the leaching of Hg, As, Cr and Cd from fly ash, and the leaching concentration decreased by 9.05%, 57.78%, 47.97%, and 10.64%, respectively.

## An insight into the distribution and abundance of bacterial species along different size fractions of the suspended particulate matter and their correlation with mercury levels

Kerševan T<sup>2</sup>, Rijavec T<sup>1</sup>, Živković I<sup>1</sup>, Kotnik J<sup>1</sup>, Horvat M<sup>1</sup>, Lapanje A<sup>1</sup>

<sup>1</sup>Jozef Stefan Institute, <sup>2</sup>Jožef Stefan International Postgraduate School

This research delves into the interplay between bacterial communities' development and the size of suspended particles present in freshwater. The aim is to unravel bacteria's natural distribution and abundance along size fractions ranging from 0.2 to 180.0 micrometres ( $\mu\text{m}$ ), gaining insight into the relationship dependent on particle size.

Particle size influences the surface area for bacterial colonisation as increased surface area can promote bacterial growth and activity. Particle size also influences the dispersion in aquatic environments – the size of particles to which bacteria attach can dictate the dispersal patterns in the water column. Furthermore, particle surfaces serve as attachment sites for bacterial biofilm formation and their size dictates the complexity and stability of biofilms.

The subject of the study is a freshwater ecosystem, specifically a river, which is characterised by a strongly present pollutant, mercury. Thus, the research extends beyond bacterial characterisation, seeking to understand how a potent pollutant affects bacterial communities, focusing on size-dependent dynamics. Water samples will be subjected to size fractionation via filtration, and DNA will be isolated. Subsequent polymerase chain reaction (PCR) amplification and sequencing facilitate the targeted assessment of the genetic information in the microbial communities within size fractions. Furthermore, by gaining information on the concentration and distribution of mercury along size fractions, we expect to reveal size-specific adaptations and preferences of bacteria in response to varying pollutant levels as well as identify possible bioaccumulation patterns.

This unique focus on size-dependent dynamics provides novel insights into microbial communities in polluted environments, where implications of the research could extend to the realm of bioremediation. Especially in the context of pollutant stress, certain size fractions may carry communities with enhanced ability to accumulate or metabolise mercury, providing potential bioindicators for pollution levels and unveiling potential candidates for bioremediation strategies.

381

## Mercury transport in the terrestrial ecosystem in the Ussuri broadleaf and mixed forests ecoregion

Ulianova M<sup>1</sup>, Poddubnaya N<sup>1</sup>

<sup>1</sup>Cherepovets State University

Many mammal species in the Far East are predicted to be at significant future risk from anthropogenic environmental change and long-term climate change. One of the priority areas in need of special attention is the Ussuri broadleaf and mixed forests ecoregion (Primorsky Krai and Khabarovsk Krai, Russia), which is the most biologically diverse in North Asia. The total mercury (Total Hg, THg) concentration was analyzed in samples collected from animals obtained by state license and from the traps of fur. The analysis was carried out on a RA-915M mercury analyzer (Lumex). THg in the muscles of young *Rana amurensis* (n=12) is  $0.055 \pm 0.018$  mg/kg DW; in the muscles and fur: *Apodemus peninsulae* (n=75) are  $0.051 \pm 0.074$  and  $0.118 \pm 0.020$  mg/kg DW; *Crocidura shantungensis* (n=23)  $0,386 \pm 0.038$  and  $0,871 \pm 0.057$  mg/kg DW; *Crocidura lasiura* (n=13)  $0,426 \pm 0.073$  and  $1,988 \pm 0.097$  mg/kg DW; in fur: *Hydropotes inermis argyropus* (n=7)  $0,008 \pm 0,003$  mg/kg; *Lynx lynx* (n=3)  $0,206$  mg/kg; *Panthera tigris altaica* (n=12)  $0.239 \pm 0.075$  mg/kg; *Prionailurus bengalensis euptilurus* (n=14)  $1,736 \pm 0,351$  mg/kg; *Ursus thibetanus* (n=22)  $0,336 \pm 0,056$  mg/kg. In the trophic chain, THg content increases by 4 – 34. The leopard cat *P.b. euptilurus* and *Cr. lasiura* that eat terrestrial, aquatic and near-aquatic animals have the highest levels of mercury. THg content in fur of *P.b. euptilurus* is higher by 15 times than THg content in fur *A. peninsulae* – its main prey. Additional research is needed in regions which are unique in the number of Mesozoic relics, species that require special conservation measures.

## Assessment of mercury content in tree plants in the industrial area of North-West of Russia

Ulianova M<sup>1</sup>, Rumiantseva O<sup>1</sup>, Ivanova E<sup>1</sup>

<sup>1</sup>Cherepovets State University

Plants are able to accumulate various pollutants, including mercury. Therefore, plants can be used as bioindicators of the level of environmental pollution with this toxicant. The total mercury (THg) concentration in the aboveground organs of different plant species was measured using a mercury analyzer RA-915M (Lumex). Plant organs were sampled in the industrial area of Cherepovets city, North-West of Russia. It was noted that the branches of the current year have THg concentrations by 3-4 times lower than in leaves. The average THg concentration of the current year escapes of different plant species was: a minimum of  $2.58 \pm 0.08$  ng/g (*Quercus robur*) and a maximum of  $10.08 \pm 0.81$  ng/g (*Thuja occidentalis*) and in leaves/needles: a minimum of  $6.66 \pm 0.97$  ng/g (*Cornus alba*) and a maximum of  $26.34 \pm 3.28$  ng/g (*Larix* sp.). The absorption of mercury by the tree and shrub leaves decreases: *Larix* sp. (26.34 ng/g) > *Tilia platyphyllos* (25.41 ng/g) > *Tilia cordata* (21.58 ng/g) > *Malus* sp. (17.70 ng/g) > *Acer negundo* (17.18 ng/g) > *Acer platanoides* (16.46 ng/g) > *Quercus robur* (15.83 ng/g) > *Crataegus* sp. (15.33 ng/g) > *Sorbus aucuparia* (15.17 ng/g) > *Populus balsamifera* (14.96 ng/g) > *Symphoricarpos albus* (14.25 ng/g) > *Lonicera tatarica* (13.10 ng/g) > *Betula pendula* (12.72 ng/g) > *Thuja occidentalis* (12.46 ng/g) > *Pinus sylvestris* (10.35 ng/g) > *Picea pungens* (7.05 ng/g) > *Cornus alba* (6.66 ng/g).

383

## Mercury and stable isotopes of nitrogen and carbon in the hair of wild mammals of the Northwest of Russia

Eltsova L<sup>1</sup>, Ivanova E<sup>1</sup>, Komov V<sup>2</sup>

<sup>1</sup>Cherepovets State University, <sup>2</sup>Papanin Institute for Biology of Inland Waters Russian Academy of Sciences

This study is devoted to the analysis of the relationship of mercury and the ratio of stable isotopes of carbon ( $\delta^{13}\text{C}$ ) and nitrogen ( $\delta^{15}\text{N}$ ) in the hair of wild mammals of the orders: Carnivore (Carnivora, n=94), Rodents (Rodentia, n=28), Artiodactyls (Artiodactyla, n=32). The collection of mammalian hair was carried from 2015 to 2021 in the zone of the southern and middle taiga in the Northwest of the Russian.

The mercury content was measured using a mercury analyzer RA-915M, the isotopic composition using Thermo Delta V Advantage isotope mass spectrometer at the Cherepovets State University. To statistical analyze the data, used: Kruskal-Wallis test and Spearman's correlation coefficient, in which the differences were considered significant at  $P \leq 0.05$ .

The concentration of mercury in animal hair varies from 0.001 to 7.85 mg/kg. The isotopic signature of carbon varies from -29.8‰ to -21.0‰, nitrogen – from 2.0‰ to 14.5‰.

The concentration of mercury in the hair of mammals of the carnivore order (n=94) is statistically significantly higher than that of rodents ( $P=0.00$ , n=28) and artiodactyls ( $P=0.00$ , n=32).

A statistically significant correlation was established between the level of mercury and  $\delta^{15}\text{N}$  ( $P=0.00$ , n=154) for the sample as a whole and for each individual order (carnivore:  $P=0.00$ , n=94; rodents:  $P=0.00$ , n=28; artiodactyls:  $P=0.04$ , n=32). A statistically significant correlation was established between the level of mercury and  $\delta^{13}\text{C}$  ( $P=0.00$ ) for the sample as a whole and for each individual order (carnivore:  $P=0.00$ ; rodents:  $P=0.00$ ; artiodactyls:  $P=0.03$ ).

384

## Production and Challenges - A High-Level Synopsis of Mercury Across the Global Oil and Gas Value Chain

Kirby M

<sup>1</sup>Qa3 Limited

This presentation aims to provide a high-level overview of (i) how and where mercury exists in the value chain, (ii) estimations on the global mercury production and emissions from the industry and (iii) current challenges faced by the industry as a result of the presence of mercury.

It is generally understood that concentrations of mercury are higher in certain areas of the world, for example, SE Asia; however, many are under the misconception that some regions do not produce mercury. Data from extensive on-site projects undertaken around the world will be presented, demonstrating that significant variation in the produced mercury concentrations have been observed in the same region and even within the same field.

Mercury exists in a number of forms in the industry. It is widely accepted that mercury in natural gas will only exist in the elemental form whilst in liquids, can exist in a number of forms both soluble and insoluble. Data will be presented from across the entire value chain, highlighting what forms mercury can be present in as well as common mechanisms for losses of mercury and also releases to the environment.

Mercury removal from natural gases is mature technology and most recently advances have been made to allow for removal from liquids and wet gases; however, there are a number of routes for mercury emissions into the environment which have not been previously considered. Qa3 have estimated the mass of mercury which is being emitted to the environment is in the range 60 – 150 tonnes, which significantly exceeds previous published estimates.

There are a number of challenges facing the industry with regards to mercury. The current, major industry challenge is linked to the fate of mercury contaminated steel arising from the decommissioning of oil and gas assets.

385

## The Assessment and Impact of Mercury on Asset Decommissioning.

Stewart K

<sup>1</sup>Qa3 Limited

One, often overlooked consideration, during decommissioning of assets within the oil and gas industry, is the deposition of contaminants within the scale that builds up on the internal surfaces of pipelines and vessels. Whilst some natural contaminants may be present at only trace concentrations, over decades of operational lifetime, the total mass of harmful material that may accumulate can be considerable.

Currently, there is no legislation in most global locations that prescribes acceptable mercury concentrations for steel being sent for smelting. In many countries, the only stipulation for such steel is that it is free of hydrocarbons and NORM.

From extensive experience of on-site sampling and analysis campaigns undertaken internationally, Qa3 chemists have seen that the rate of mercury deposition may vary significantly and is dependent on a number of factors. Qa3 will present data from a case study which identified the primary mechanism of loss to be via reaction with iron sulphide.

The fate of the contaminated steel must be considered. Is the steel to be lifted and sent for recycling via smelting leading to potential worker exposure and significant environmental release? Most smelters stipulate steel must have zero mercury. Or is the steel, such as sub-sea pipelines, being left in situ, presenting a potential for release of mercury into aquatic ecosystems.

A pre-cessation investigation will provide information on the mercury content of the fluids and identify where mercury is likely to have accumulated across a process. Post cessation, studies can be undertaken to quantify the concentration of mercury within vessels and on internal surfaces of pipelines and other infrastructure and, where necessary, suitable decontamination programmes can be planned. We will discuss current practices for the semi-quantitative assessment of contamination as well as procedures for accurate total mercury determinations.

386

## Characterization of mercury sorption on hydroxylapatite: Batch studies and microscopic evidence for adsorption

Kim Y<sup>1</sup>

<sup>1</sup>Pukyong National University

Although previous studies have investigated Hg sorption on various common minerals, there has been limited study of Hg interaction with apatite. In this study, systematic experiments regarding Hg sorption on HAP were performed over a wide range of physicochemical conditions. In the sorption edge experiments, Hg uptake by HAP exhibits a maximum sorption (~90%) at pH 6.0, which rapidly decreases at pH > 6.0. Sorption isotherms are fitted well by Freundlich equations, and the distribution coefficient (KD) increases in the order of pH 5 > 7 > 9. In both the sorption edge and isotherm experiments, sorption patterns and quantities are minimally influenced by variations in the ionic strength. The results from the kinetic experiments are in good agreement with the pseudo-second-order rate law. The initial sorption rate at pH 9 is much slower than that at pH 5 and 7. During desorption, ~90% of the sorbed Hg is retained at both pH 6.0 and 9.0, which indicates strong bonding of Hg to the HAP surface. Our results suggest that adsorption plays an important role in controlling the initial stage of interactions between Hg and HAP.

## Revealing the fate of industrial-era mercury in peatlands with micrometeorology, isotopes, paleoecology, genomics, and an ice-age2

Bishop K<sup>1</sup>, Li C<sup>2</sup>, Osterwalder S<sup>3</sup>

<sup>1</sup>Swedish University of Agricultural Sciences Dept. of Aquatic Sciences and Assessment, <sup>2</sup>Institute of Geography and Oeschger Center for Climate Change Research, University of Bern, <sup>3</sup>Department of Environmental Systems Science, ETH Zurich

Since humans began utilizing mercury, pollution has increased atmospheric Hg seven-fold. Mercury (Hg) contamination is the single largest cause of waters in the European Union failing to meet the standards of the EU Water Framework Directive. Peatlands, which have accumulated a legacy of past atmospheric Hg pollution, are major sources of Hg contamination in downstream aquatic ecosystems. Despite peatlands having accumulated Hg for millennia, independent lines of research indicate that some northern peatlands are now returning Hg to the atmosphere. This raises questions about what controls the fate of the pollution legacy Hg stored in peatlands. We hypothesize that legacy Hg accumulated in peat during earlier periods of higher atmospheric Hg pollution is no longer in balance with the lower Hg levels of the contemporary atmosphere, leading to net Hg evasion. Several methodological advances were applied to test this hypothesis on a 2000-year chronosequence of mires created by isostatic uplift along the northern coast of Sweden as well as the nearby Degerö peatland that is even older. Despite uniform climate and atmospheric Hg concentrations across the 15 km extent of the chronosequence, the stock of Hg differs by a factor of two. Novel Hg eddy covariance quantified the Hg exchange between the land and atmosphere. Distributed measurements of dissolved gaseous elemental mercury (GEM) in shallow peat groundwater quantified seasonal variation in a potential source of the evading Hg. Natural abundance of Hg isotopes and community-level expression profiling of microbial metabolisms identified the role of specific processes in the transformation of Hg within peat profiles along the chronosequence. This paper reports on puzzle pieces that have fallen into place, such as isotopic evidence for the role of photoreduction in producing GEM, and the challenges that remain to complete the picture.

Keywords: Peatlands, natural abundance isotopes, mercury reduction, net ecosystem exchange

## Assessment of the consumptive safety of mercury in fish from the surface waters in northwestern Russia

Ivanova E<sup>1</sup>, Bazhenova D<sup>1</sup>, Komov V<sup>1,2</sup>, Rumiantseva O<sup>1</sup>, Borisov M<sup>3</sup>, Tropin N<sup>3</sup>

<sup>1</sup>Cherepovets State University, <sup>2</sup>Papanin Institute for Biology of Inland Waters Russian Academy of Sciences, <sup>3</sup>Vologda Branch of the Federal State Budget Scientific Institution «Russian Federal Research Institute of Fisheries and Oceanography»

The fish consumption is the main source of mercury intake in human body. The content of mercury was evaluated in muscle samples from 10 different species fish (*Carassius carassius*, *Abramis brama*, *Leuciscus leuciscus*, *Rutilus rutilus*, *Ballerus sapa*, *Blicca bjoerkna*, *Leucis idus*, *Sander lucioperca*, *Perca fluviatilis*, *Esox Lucius*). These species predominate in commercial and recreational catches and are most frequently used in the diet of the population. Total mercury content in the samples was measured on a mercury analyzer (RA-915, Lumex, Russia) without additional sample preparation. The mercury level in fish muscle varied from 0.01 µg/g to 1.68 µg/g wet weight. The mercury content is statistically significantly higher in the muscles of predominantly predatory species of fish (*Perca fluviatilis*, *Esox lucius*, *Sander lucioperca*). The relationship between the amount of mercury in fish muscles and morphometric indices has been established. In 7% of fish studied, mercury concentrations exceeding regulatory levels of the Russian Federation were noted. The proportion of examined fish, the consumption of which will lead to an excess of the permissible weekly intake of mercury in the individual, is 44% for children 2-5 years old, 34% for children 6-10 years old, and 17% for adults. The mercury content in fish that does not exceed the sanitary and hygienic standards (normative levels) of the Russian Federation may still be unsafe for the health of the population, especially children.

The study was supported by the Russian Science Foundation, grant no. 23-24-00385 (<https://rscf.ru/project/23-24-00385/>)

## Mercury point source emissions in South Africa: Developments in the Energy and Petrochemical sector

De Vos S<sup>3</sup>, Breet L<sup>1</sup>, Vilakazi L<sup>2</sup>, McCourt B<sup>2</sup>, Pillay S<sup>1</sup>, Ngubeni Z<sup>2</sup>

<sup>1</sup>Sasol, Energy Business, Strategy and Sustainability, <sup>2</sup>Eskom Research Testing and Development,

<sup>3</sup>Sasol, Energy Operations, Research and Technology

Mercury (Hg) release from coal processing is a local and global concern with a heightened interest by environmental activists, scientific groups, policy makers and coal users. In South Africa, coal has been used as a feedstock to both power the country and to produce petrochemical products.

Eskom, established in 1923 is still the largest power supplier in the country with Sasol, established in 1950, being the only coal based petrochemical plant. To understand mercury (Hg) releases associated with coal combustion, Eskom and Sasol established a technical collaboration in 2008 to investigate mercury emissions within their respective operations.

Eskom's coal fired power stations are supplied from coal fields containing varying levels of mercury. The associated emissions are currently calculated based on outdated mercury content, the amount of coal burnt and using US EPA Emission Reduction Factors (ERF's) reflecting the co-benefit received from abatement technologies employed at Eskom's respective stations.

While Mercury reduction can be achieved as a co-benefit of installed pollution abatement technologies, future mercury emission regulations may require further investment of targeted reduction technologies. It is therefore important to be in a position to make accurate calculations of mercury emissions per power station by measuring the mercury content of more recent coal samples from the different coal fields, and developing power station-specific ERF's. An updated baseline of mercury content in Eskom coals has been established for the Eskom fleet and initial mass balance studies have been completed on four stations employing specific pollution abatement technologies.

Mercury speciation analysis, conducted within Sasol's South African operations on a commercial scale from 2020, is an important step to inform the selection of the most effective mercury solution while considering the overall cost and benefits. Various abatement technologies are also being rolled-out as part of industries compliance roadmaps.

## MERCURY CONTENT AND STABLE ISOTOPES RATIO OF NITROGEN AND CARBON IN THE HAIR OF THE POPULATION OF NORTH-WEST RUSSIA

Rumiantseva O<sup>1</sup>, Ivanova E<sup>1</sup>, Komov V<sup>2</sup>

<sup>1</sup>Department of Biology, Cherepovets State University, <sup>2</sup>Papanin Institute for Biology of Inland Waters, Russian Academy of Sciences

Mercury is a toxic metal. The main source of mercury ingestion to humans is food-borne fish. The purpose of this study was to determine the relationship between the amount of mercury in the hair of people with different amounts of fish in their diets and the  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  isotopes composition of their hair.

The mercury content in the hair samples was measured on a mercury analyzer RA-915M (Lumex). The isotopic composition of the hair was measured on an isotope mass spectrometer Thermo Fisher Delta V Advantage. The mercury content in the hair of the population of North-west Russia ranged from 0.01 to 6.80 mg/kg, the average value was  $0.46 \pm 0.04$  mg/kg. It was found that the mercury content in the hair of the population living in the western districts near the lakes (1.03 mg/kg) is higher than the metal content in the hair of the populations from the eastern districts (0.43 mg/kg) and the industrial area (0.31 mg/kg).

The high values of  $\delta^{15}\text{N}$  were detected in people living in the western districts. The high value of  $\delta^{15}\text{N}$  in the hair of the population of the western districts confirms the previously established pattern that the main source of mercury in the human body is fish, primarily predatory fish species. It was noted that people with high mercury values had low  $\delta^{13}\text{C}$  values in their hair. Low values of  $\delta^{13}\text{C}$  in the hair of residents of western districts indicate a significant amount of freshwater fish in the diet. Isotopic analysis of nitrogen and carbon in human hair confirms the assumption that freshwater and predatory fish are the main source of mercury in the human body.

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391

## Compound Facilitating Unabated Global Trade and Sales of Mercury-added Skin Lightening Products (SLPs)

Mahapatra A<sup>1</sup>

<sup>1</sup>Environmental Investigation Agency

Background:

The persistent prevalence of mercury-added skin lightening products (SLPs) in global markets poses a significant public health and environmental concern, despite international efforts to curb their production and trade. The sale of mercury-added SLPs have continued unabated despite widespread reporting, awareness campaigns, and legal prohibitions, including a global treaty ban. However, limited information exists regarding the methodologies employed.

This study investigates the tactics and practices underlying the continued circulation of these products, shedding light on the extent of non-compliance with the Minamata Convention on Mercury.

Methods:

We carried out undercover investigations in three different regions (Asia, North America, and Europe) and confirmed the continued production, trade, and sale of mercury-added SLPs. Compelling evidence from seven companies in three countries showed intentional addition of a mercury compound into SLPs, in violation of the Minamata Convention on Mercury.

Findings:

Our investigation revealed it is common practice for SLP producers across the globe to formulate creams consisting of 3-4% of a particular mercury compound. Discussions with company executives emphasize that these are not isolated incidents but representative of widespread industry practices. Those who trade in mercury compounds are able to operate with impunity across jurisdictions. The results of our investigation examine the tactics and systems of SLP producers, sellers, and traders, and some of the sources of the mercury that contaminate them.

Conclusion:

Our findings underline the need for the scientific community to inform improvements to the Minamata Convention to prevent the proliferation of toxic skin creams, and strengthening the enforcement and compliance mechanisms for online and on-the-ground sales. Additionally, combating the intentional addition of mercury in SLPs necessitates scientifically informed support for national regulatory measures that align with the Convention's objectives. This study underscores the urgency of collaborative efforts to safeguard public health and environmental integrity from mercury exposure through SLPs.

392

## Direct detection of dissolved aqueous mercury with gold nanoparticle based plasmonic sensor

James J<sup>1</sup>, Triana C, Crosby J

<sup>1</sup>Picoyune

We demonstrate direct measurement of dissolved aqueous mercury with a highly portable plasmonic mercury sensor. The sensor uses a film of gold nanoparticles mounted in a flow cell. Dissolved mercury is collected by the nanoparticle film directly from the aqueous phase without reagents. The mercury concentration is quantified using the plasmonic signal of the adsorbed mercury on the amalgam nanoparticles. The measurement relies on changes on transmitted visible light while the film is heated to release the adsorbed mercury as vapor. The monitor is battery powered, 0.75 kg, and packaged in a waterproof 10 x 15 x 22 cm case. The films are reusable for > 200 samples. In this study we found the device limit of detection to be 100 ppt for dilute mercury standards in water in a 5 minute sampling period. We tested 0.5 ppb to 250 ppb of dilute mercury standards and natural waters.

Aqueous field measurements face difficulties due to complexity of equipment and methods. The presented approach addresses these challenges with a simple method and highly portable device capable of screening samples in the field.

393

## Direct measurement of mercury in natural gas with plasmonic sensors.

James J<sup>1</sup>, Crosby J

<sup>1</sup>Picoyune

Plasmonic mercury sensing is shown to be highly sensitive and free from critical interferences for natural gas applications. The standard atomic spectroscopy methods, absorption or fluorescence, have strong interferences from hydrocarbons and other common contaminants. Mercury vapor, at concentrations typical to natural gas, is deleterious to plants and workers. Aluminum heat exchangers, often used in cryogenic processes, are particularly susceptible to corrosive attack from mercury. Awareness on the part of gas processors is necessary to protect equipment, processes, and human health. A plasmonic sensor, operating on the unique optical and physical properties of amalgam nanoparticles, has demonstrated resistance to interferences and high sensitivity to mercury vapor in natural gas. Plasmonic mercury sensing relies on two key physical phenomena, the selective adsorption of mercury vapor by gold surfaces and the powerful and unique response of the surface plasmon resonance to mercury adsorption. This technique has been used to measure attograms of mercury, less than a single atom of mercury per nanoparticle is easily measured in the visible light absorption signal of the film. Plasmonic mercury sensing has been demonstrated to be free of interferences from hydrocarbons, water vapor, oxygen, CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub>, and other common contaminants. Small size, low power requirements, and robust components have allowed the plasmonic sensor to meet the requirements of Class I Division 1 certification.

394

## GOVERNANCE STRATEGIES FOR MERCURY USE AND REDUCTIONS: NIGERIA CASE STUDY

Alo B<sup>1</sup>

<sup>1</sup>University Of Lagos, Nigeria

The development of the Mercury Initial Assessment report for Nigeria (the first to be developed under the Convention by any country) highlighted that the Artisanal and Small-scale Gold Mining (ASGM) Sector as a major focal area to reduce and eventually phase out mercury use in Nigeria. The overall goal of the Nigeria's NAP for ASGM and overall Mercury use is to reduce, and where feasible eliminate, the use of mercury and mercury compounds in, and the emissions and releases of mercury to the environment from ASGM.

This paper will be presenting and interrogating the governance strategies (including legal and institutional) for meeting with the goals and mandate of the Minamata Convention in Nigeria and its impact on in-country mercury research.

395

## Citizen's perception and participation in E-waste management in North East India

Yasmin F<sup>1</sup>

<sup>1</sup>Nowgong College (Autonomous)

Electronic waste or E-waste contains toxic elements like lead, cadmium, mercury and nickel. In the Gazette notification released on November 2, 2022, as E-Waste (Management) Rules, 2022, the Government of India emphasizes the restrictions on the use of lead, mercury and cadmium in manufacturing electrical and electronic equipment. The responsibilities of Local Bodies (Urban and Rural) are also listed in Schedule V, SI No 3 of this Rule.

The success in minimizing the hazardous impacts of global pollutant mercury through an E-waste management policy can be quickened by taking a strategic approach to educate people about the 4Rs of waste management. Awareness through education is essential for citizens to know and understand the adverse impacts of E-waste with special reference to mercury contamination on biota and the environment, their role in proper eco-friendly E-waste management and the benefits of the circular economy. It is also necessary to identify the intrusions of citizen participation in policy recommendations.

The Central Pollution Control Board (CPCB) of India estimates the E-waste generation at national level during 2021-22 is more than 1.6 million tonnes. E-waste is the fastest growing problem in North Eastern states of India. Increased usage of new electrical and electronic equipment over repairing equipment is a concern that results in a significant amount of E-waste. Using semi-structured questionnaires for data collection, a study is being performed to investigate the reasons why the initiatives taken by different agencies like ENVIS-RP Centres, NGO's and educational institutions to aware citizens about E-waste appear insufficient to spark a revolutionary movement among people of the region.

The study aims to inform people about E-waste for proper implementation of rules and regulations. The study highlights the need to gather grassroots information on citizen's participation in preparing an effective policy framework for environmentally sound management of E-waste.

396

## Supporting the phase out of mercury-added skin lightening products across the African, Asian, and Caribbean regions.

Ali Shah T<sup>1</sup>, Burton M<sup>1</sup>, Evers D<sup>1</sup>, Stylo M<sup>2</sup>, Davis K<sup>2</sup>, Dossou Etui I<sup>2</sup>

<sup>1</sup>Biodiversity Research Institute, <sup>2</sup>UNEP Global Mercury Partnership

The use of products to lighten the skin is a trend in many parts of the world and has deep-rooted cultural and social stigmas attached to its continued popularity. Due to the effectiveness of mercury in blocking melanin production, inorganic mercury compounds have been used in the production of skin lightening products found across the globe. Under the Minamata Convention on Mercury, the phase out of the manufacture, import and export of skin lightening products with mercury concentrations over 1 part per million (ppm) by 2020 was mandated and has since been updated to include all skin lightening products with mercury by 2025. Implementation of this phase out has been difficult for many Parties, due in part to the lack of understanding on the presence of mercury in skin lightening products, as many are sold informally and are often unlabeled or mislabeled with mercury concentrations being unclear and varying amongst batches.

As part of the ongoing Global Environment Facility (GEF) project, “Eliminating mercury skin lightening products”, efforts are being made to address the regulatory, analytical and awareness raising needs to successfully phase out mercury-added skin lightening products in the project countries: Gabon, Sri Lanka, and Jamaica. Each of the project countries selected are Party to the Minamata Convention and have expressed serious concerns about the use and cultural promotion of skin lightening products within their countries.

Biodiversity Research Institute (BRI) is co-executing the project with the World Health Organization and is developing a global database that collates new and existing analytical data on skin lightening products with known mercury concentrations. This database will be developed in coordination with the UNEP Global Mercury Partnership and used to support governments and relevant stakeholders in the enforcement and monitoring of these products in their local markets and globally.

397

## Effective implementation plan for the Minamata COP5 ban on fluorescent Lighting in Africa

Kamande R<sup>1</sup>

<sup>1</sup>CLASP

### Background

In November 2023, the Minamata convention on mercury decided to phase out mercury-added fluorescent lighting. This decision in addition to the Minamata COP4 decisions on lighting, will result in significant climate benefits.

All fluorescent lighting contains mercury. Mercury exposure when a bulb breaks poses health risks to vulnerable populations, particularly children, pregnant women, and workers who handle fluorescent lamps at manufacturing and recycling facilities, as well as maintenance workers in commercial and institutional buildings. However, mercury-free alternatives (i.e., LED lighting technology) are widely available and accessible and can cost-effectively replace fluorescents in virtually all applications.

### Methods:

Between 2021 and 2023, the CLiC campaign conducted flagship research assessing the technical and economic feasibility of phasing-out fluorescent lighting globally. This research mapped the global presence of LED manufacturers and assemblers, including in Africa where more than 10 countries have an LED assembling presence. We calculate that the Minamata decision will eliminate 193 tonnes of mercury pollution; avoid 2.9 gigatonnes of CO<sub>2</sub> emissions and save US\$1.23 trillion on electricity bills (cumulatively from the implementation dates through 2050).

### Findings:

This research demonstrated that markets around the world are prepared to take quick action to comply with the COP decisions and turn off the toxic mercury lighting tap, ushering in a new era of equitable and energy efficient LED lighting.

### Conclusion:

To comply with the COP5 ban on fluorescent lighting in Africa, countries can design effective implementation plans that engage stakeholders in the energy departments and standards bureaus to roll out low hanging strategies such as lighting MEPS adoption, private sector to promote local LED manufacturing, and employ best practices for hazardous waste management to handle fluorescent bulbs at their end-of-life. Border control to curtail fluorescent lamps influx and dumping will be a key strategy to ensure the success of the implementation plan.

## A Call for Comprehensive Policy Integration to Managing Contaminated Sites in India

Biswakarma J<sup>1</sup>, Sambasivam K<sup>2</sup>, Kumar A<sup>3</sup>, Mittal V<sup>4</sup>, Qureshi A<sup>5</sup>, Naidu R<sup>6</sup>

<sup>1</sup>School of Earth Sciences, University of Bristol, <sup>2</sup>Division of Energy, Vellore Institute of Technology University, <sup>3</sup>Centre for Converging Technologies, University of Rajasthan, <sup>4</sup>Industrial Engineering and Operations Research, Columbia University, <sup>5</sup>Department of Civil Engineering, Indian Institute of Technology Hyderabad, <sup>6</sup>Global Centre for Environmental Remediation, The University of Newcastle

Contaminated sites (CS) pose a significant threat to public and environmental health, as they often contain a complex mixture of harmful inorganic and organic chemicals such as mercury, lead, brominated compounds, and industrial wastes. The management of CS is a critical issue that requires urgent attention, particularly in the Global South countries like India. The Central Pollution Control Board in India listed less than 500 CS, in contrast to many countries in the non-Global South that have identified thousands of CS through tailored contaminated site monitoring, assessment, and remediation (CS-MAR) strategies over a prolonged period. We will describe the challenges associated with CS management in India, mainly due to various fragmented and overlapped environmental policies. This presentation highlights the urgent need for comprehensive reform in CS management strategies in India by integrating various existing environmental policies at the sectoral, organizational, and institutional levels. The suggested integration amongst various policies can lead to the efficient collection of data on sites, the development of a centralized database of reported chemicals, and the development of a user-friendly portal for CS. The proposed steps for moving forward also emphasize the importance of public engagement and capacity-building initiatives, which can help raise awareness and promote community-based monitoring. The successful implementation of the proposed reform will require robust financial support from governmental, public, and private entities, and innovative funding mechanisms can help address the financial challenges associated with CS-MAR. Therefore, we call for an urgent integration of fragmented policies to enhance the overall efficiency and transparency of CS-MAR steps, contributing to global sustainability objectives.

399

## Decontamination of Decommissioned Mercury Contaminated Subsea Pipeline Infrastructure

Hunter Jnr L

<sup>1</sup>Total Hazardous and Integrated Solutions

Mercury present in produced all oil and gas will deposit onto the internal process infrastructure via a number of mechanisms, the primary mechanism is through reaction with iron sulphide to form mercury sulphide. These mechanisms occur even if produced fluids contain relatively low levels of mercury. Over the lifetime of facilities, this can equate to pipeline scales containing % levels of mercury.

Aged facilities and infrastructure that have reached the end of their operational life and are selected for either recycling or abandonment, may pose a serious risk to health and the environment if the decommissioning process is not managed correctly. Smelting for example, can lead to significant release of mercury, and worker exposure hazard. Alternatively, if sub-sea pipelines are abandoned in-situ, all mercury present will ultimately be transferred to the local ecosystems.

Consequently, the oil and gas industry have the requirement for a complete mercury decontamination solution from initial evaluation, demonstrable cleaning efficacy through to a guarantee for the environmentally-friendly treatment and disposal of the mercury waste generated.

In order to decide upon the most appropriate decontamination solution, an evaluation of the extent of mercury contamination should be undertaken. A recent, successfully implemented technique involved analysis of pipe sections by multiple analytical techniques, providing the mercury concentration in the scale/steel. From this, the total mass of mercury across the process or pipeline can be approximated.

Laboratory based evaluation of chemical treatment of pipe sections can evaluate the efficacy of chemical to remove mercury from the internal surfaces of the process.

In situ decontamination can be performed by a number of applications, including, the use of chemical pig trains in pipelines and closed loop circulation of chemical around topside process equipment. The mercury waste generated is treated to minimise the volume and disposed of through internationally recognised channels.

400

## Innovative Strategies for Mercury Decontamination of Oil and Gas Process Equipment: Ensuring Environmental Safety and Compliance

Hunter Jnr L

<sup>1</sup>Total Hazardous and Integrated Solutions

Mercury contamination in oil and gas process equipment, including topsides and subsea structures poses unique challenges due to their complex geometries and the difficulty in accessing these components for decontamination. Mercury, primarily deposited through chemisorption and adsorption on metal surfaces, presents significant environmental and health risks during decommissioning. This study aims to provide a comprehensive solution for the evaluation and removal of mercury from process equipment and subsea structures such as vessels, Christmas trees, heat exchangers, flow bases, and flexible lines, ensuring their safe decommissioning or recycling.

The study introduces a novel, integrated approach to mercury decontamination, highlighting the importance of tailored solutions that address the unique challenges of the structure requiring decontamination. The successful implementation of these techniques represents a significant advancement in ensuring the safe and environmentally responsible decontamination of oil and gas infrastructure.

After the subsea assets are transferred to an onshore facility, assessment of mercury contamination utilising advanced sampling techniques and analytical methods is used to determine the extent of contamination. The chemical decontamination process is then implemented and conducted in a controlled onshore environment, allowing for the meticulous application of the chemical treatment to each structure. The effectiveness of the mercury removal is verified through detailed post-treatment assessments, ensuring that the decontaminated structures meet all environmental safety standards before disposal or recycling. Targeted chemical treatments, combined with mechanical cleaning methods, can effectively remove up to ~97% of mercury from subsea structures.

After successful decontamination, the minimization and optimization of waste generated from the decontamination process is discussed, including neutralization and filtration of the chemical. Subsequently, the stabilised waste is disposed of adhering to best practices, compliance with Australian Law, and the Basel Convention guidelines. This ensures that the disposal of decontaminated materials and residual waste minimizes environmental impact and aligns with international waste management standards.

401

## Mercury Contamination: The Threat that Entwines People and Biodiversity

Aldous A<sup>1</sup>, Tear T<sup>2</sup>, Escobar-Camacho D<sup>3</sup>, Rosero-López D<sup>3</sup>, Ruiz-Urigüen M<sup>3</sup>

<sup>1</sup>The Nature Conservancy, <sup>2</sup>Biodiversity Research Institute, <sup>3</sup>Universidad San Francisco Quito

The Amazon River Basin in Latin America and the Ogooué River basin in Gabon are globally recognized for their diversity of freshwater fish species and habitats, and for high rates of freshwater species endemism. This diversity of fish is closely linked to the nutritional needs of the millions of people who live along these two rivers and their networks of lakes and tributaries, and who fish for subsistence and small-scale livelihoods. It is therefore troubling that freshwater fish in the Amazon and the Ogooué currently face a suite of stressors, top of which is unregulated gold mining and the associated release of mercury. Mercury contamination in fish has garnered particular interest since fish consumption is the primary pathway for mercury exposure to humans. Here we highlight the work we are currently undertaking in Latin America and Africa, in collaboration with university, government, and community partners. This includes three pathways: (1) collaboratively building data and information related to mercury contamination of freshwater biodiversity and people, using both traditional and western scientific methods; (2) working with communities to secure resource tenure and build leadership to address the threat of mercury contamination; and (3) strengthening access to decision-making platforms, including the Minamata Convention. We illustrate these three pathways with data from Ecuador, Colombia, Brazil, and Gabon where concentrations of mercury in people and fish is elevated.

## Modelling the spatial variation in mercury concentrations over the South African Highveld region

Belelie M<sup>1</sup>, Ayob N<sup>2</sup>, Burger R<sup>3</sup>, Piketh S<sup>3</sup>

<sup>1</sup>Geo & Spatial Sciences, North-West University, <sup>2</sup>Geo & Spatial Sciences, North-West University, <sup>3</sup>Geo & Spatial Sciences, North-West University

Coal-fired power plants, the primary source of mercury (Hg) emissions in South Africa, are predominantly located in the South African Highveld area, a region known for its poor air quality. The exact state of Hg emissions from the power sector in this area remains unclear. Given that this region is one of the world's most concentrated sources of Hg, it is crucial to understand the emissions better. This study is the first to use dispersion modelling (CALPUFF) to examine Hg concentrations and their wet and dry deposition in the Highveld area. The study focused on the atmospherically significant forms of Hg (Hg<sup>0</sup>, Hg<sup>2+</sup>, and HgP) emitted from coal-fired power plants between 2011 and 2014. Among these, Hg<sup>0</sup> is the only species identified as posing an inhalation threat, prompting a brief health risk assessment to contextualize the modelling results. The highest concentrations of Hg species were found over the central cluster of power plants. The results indicate that these species are accumulating in an area already high in concentrations, particularly over two of the plants. This area also showed the highest levels of wet and dry deposition, suggesting that the proximity of the power plants leads to increased deposition. The health risk assessment indicates that individuals working and living near these power plants may face acute adverse health impacts due to inhalation

## Monitoring of mercury in various mineral ores processing and assessment of its potential impacts on the environment

Letsoalo R<sup>1</sup>, Mkhohlakali A<sup>1</sup>, Ntsasa N<sup>1</sup>, Tshilongo J<sup>1</sup>

<sup>1</sup>Mintek

The abundance of mineral resources in South Africa is remarkable for promoting and regulating the minerals and mining for transformation, growth and development. The wealth of minerals is typically found in the well-known geological formations. The Council for Mineral Technology (Mintek) is tasked with ensuring the sustainability of the mining industry by implementing the innovative technological advancements and mineral processing techniques while also limiting emission of hazardous chemicals into the environment. Mining and processing of mineral ores may elevate the mercury (Hg) pollution in the environment. Mercury is one the most toxic elements having detrimental effects on the environment and human health, its presence requires a constant monitoring to implement measures for pollution control. In this study, Hg content in the range of 41.1 – 167 µg/L were quantified using inductively coupled plasma – mass spectrometry (ICP-MS) from the concentrates of platinum group metals (PGMs) bearing ores obtained by flotation flowsheet mineral processing. These low Hg concentrations were expected because the PGMs occurred in the magmatic sulphide mineral ores with less Hg. In the perspective of environmental monitoring, Hg was quantified in the concentration range of 0.04 – 0.09 µg/L and 130 – 200 µg/Kg in water and sediments, respectively, in the selected river streams during high rainfall season. These concentrations were below maximum permissible levels of Hg in water and sediments as stipulated by water quality standard guidelines. Analytical figures of merit such as detection limits, linearity, precision and accuracy for quantification of Hg in mineral ores and environmental samples were within the acceptable ranges that confirmed the method's validity for Hg monitoring.

406

## Determination of Mercury isotopes in mineral sulphides deposits from Southern African carbonatite (Palaborwa) complexes using Inductively Coupled Plasma Mass Spectrometry

Mkhohlakali A<sup>1</sup>, Letsoalo M<sup>1</sup>, Mabowa H<sup>1</sup>, Ntsasa N<sup>1</sup>, Tshilongo J<sup>1</sup>

<sup>1</sup>Mintek

Mercury, carbonatite, Mineral sulphide, Inductively Coupled Plasma Mass Spectrometry

407

## Interactions between Microplastics, Hg and Microorganisms with environmental impacts – Major findings of PlasticHg Project

Motubane N<sup>1</sup>

<sup>1</sup>FCT

Microplastics ( $\varnothing < 5$  mm, MPs) and mercury (Hg) problematic aquatic pollutants, which undergo bioaccumulation and biomagnification and cause toxic effects. Microorganisms are the key players in the biogeochemical cycle of Hg, performing Hg-reduction, Hg-methylation (formation of the neurotoxic methylmercury), and methylmercury-demethylation. Microorganisms isolated from Tagus estuary, one of the most important wetlands of Europe, were found to be involved in these processes. Thus, this study aims to assess the complex interactions between MPs, Hg and Hg-resistant microorganisms to disclose the impacts of MPs on the biogeochemical cycle of Hg and toxicity.

To accomplish this, an urban area of Tagus estuary with port and industrial activities was selected as study case. Sediment and water samples were collected for: (1) MPs isolation and characterization; (2) total Hg concentration determination, and (3) Hg-resistant microbial communities' isolation. DNA was extracted from the MPs and sediment samples to assess the presence of Bacteria and Archaea via taxonomic analysis. Suspension and microcosms experiments with several MPs polymers ( $\varnothing > 1$  mm) were performed to evaluate the interactions between MPs:Hg:Microorganisms.

The results showed the presence of MPs ( $109 \pm 71.6$  to  $52.0 \pm 8.70$  particles/kg of dry sediment), especially fibers and fragments of polypropylene, polyethylene, expanded polystyrene and polyester polymers. Hg concentration above Effects Range Medium ( $0.71 \mu\text{g/g}$ , dry wt) was found ( $3.08 \pm 0.93 \mu\text{g/ml}$ ) and resistant microbial community (MIC Hg<sup>2+</sup> =  $125.0 \pm 0.00 \mu\text{M}$  and MIC CH<sub>3</sub>Hg =  $0.4638 \pm 0.00 \mu\text{M}$ ) was isolated. Taxonomic analysis indicated the presence of Bacteria and Archaea associated to MPs, including pathogenic bacteria. Interactions between MPs and Hg and between MPs and microorganisms with effect on Hg biotransformations was observed. Thus, this study showed that MPs and Hg coexist in Tagus estuary and that MPs affects the natural occurring biotransformation of Hg via interactions with Hg and microorganisms.

## Reduction of Mercury in crude oil using Thermal Heating Technology: A case study from a Libyan Oilfield

Abulgam M<sup>1</sup>, Madi M<sup>2</sup>, Alwaer A<sup>2</sup>

<sup>1</sup>National Oil Corporation, <sup>2</sup>Mellitah Oil and Gas B.V

In response to the global need to mitigate mercury contamination in crude oil within oilfields, an innovative thermal heating technology was implemented. This approach utilized 175°F steam heating within a separator to facilitate the efficient liberation of elemental mercury from the liquid phase. This applied technology proved very efficient at partitioning elemental mercury dissolved in the oil into the gaseous phase. Subsequently, the mercury-laden gas was conveyed to a dedicated mercury removal unit at the Natural Gas Liquids (NGL) plant for comprehensive removal and internationally accepted means of safe disposal.

Through standard testing and analysis of total mercury in crude oil, this thermal heating technology demonstrated remarkable efficacy in significantly reducing total mercury levels in crude oil. Prior to its application, crude oil samples showed total mercury concentrations exceeding 100 parts per billion (ppb), posing quality, operational and environmental issues. However, following the implementation of the thermal heating process, total mercury levels were successfully reduced to less than 30 ppb, marking a substantial decrease in mercury contamination.

The success of this technology ensured that the treated crude oil met regulatory standards and environmental requirements, further enhancing operational efficiency and sustainability.

By showcasing the successful application of thermal heating technology for mercury reduction in an oilfield setting, this case study contributes valuable insights to the petroleum industry's efforts to address mercury contamination challenges. The findings underscore the feasibility and efficacy of innovative technologies in enhancing best operational methodologies, environmental, and regulatory compliance within the oil and gas sector. Further investigation of mercury speciation in Libyan oil and gas streams is recommended to address further details for controlling the distribution of mercury in oil and gas fields.

419

## Tropical peat: a highly vulnerable global mercury sink

Driscoll C

Peat is an important mercury (Hg) sink, but concentration measurements are limited and prevent accurate estimations of global storage across tropical peatlands. Tropical peatlands contain ~30% of global peat reserves and are under severe pressures from conversion to agriculture and gold mining. Here we quantify the Hg content of tropical peat forests from a global archive, provide a first estimate of Hg stored for several tropical peatlands, and use Hg stable isotopes to describe sources and patterns with covariates. We found a range of total Hg concentrations (15 – 912 ng/g dry weight (dw), mean = 200 ng/g dw, n = 295). The highest concentrations occurred at sites proximate to a volcanic point source (204 – 912 ng/g dw, mean = 547 ng/g dw, n = 18, Hawaii, USA) and potential gold mining activities (283 – 566 ng/g dw, mean = 363 ng/g dw, n = 16, Bonzale, Republic of Congo).  $\delta^{202}\text{Hg}$  and  $\Delta^{199}\text{Hg}$  were regionally distinct suggesting differences in atmospheric Hg sources or preservation. Ombrotrophic peatlands had significantly higher concentrations of both total Hg and  $\delta^{202}\text{Hg}$ . Across all sites, percent sulfur explained variation in  $\delta^{202}\text{Hg}$  while percent nitrogen explained variation in  $\Delta^{199}\text{Hg}$ . Other trace metals including lead and cadmium were positively related to total Hg concentrations. A decrease of 0.20 to 0.40‰ in  $\delta^{202}\text{Hg}$  from 70 cm to surface samples was consistently found at two undisturbed peatland sites in Indonesia and Brunei, suggesting a possible modern atmospheric signal from forest fires. We found a wide range in Hg stocks (6 – 52 mg/m<sup>2</sup>) in the upper 70 cm across sites, with estimates equivalent or higher than values reported for Canadian boreal and Western Siberian peatlands. This work demonstrates that loss of tropical peat forests has important implications for global Hg releases and ecosystem health.