Events

QUISS-Symposium – Part 1

Biogeochemical controls on mercury dynamics in contaminated river systems

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Cover photo	Elbe river groyne field km 477, August 2023 (Photo: Jan Wiederhold, BfG)

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Introduction

Mercury (Hg) contamination is a serious problem in many river systems worldwide. Direct releases of Hg into surface waters have been strongly reduced in many countries, but the targeted environmental quality standards for Hg in biota are mostly not reached, likely driven by remobilisation of Hg from contaminated legacy sediments. Biogeochemical transformations of Hg species, such as microbial Hg methylation, demethylation, and reduction, largely control the mobility and bioavailability of Hg in contaminated river systems and trigger its uptake into aquatic food webs.

This publication contains the abstracts of the scientific presentations given at the "QUISS symposium – part 1". The QUISS symposium consists of two parts, an international part held online in English (December 3, 2024) and a German part held at the Federal Institute of Hydrology (BfG) in Koblenz (December 5, 2024). In the international part of the symposium, which is presented in this abstract volume, the state of research on processes and mechanisms controlling Hg dynamics in contaminated river systems is discussed, ranging from analytical method development and application of molecular biology approaches to results of field and laboratory studies. The programme consists of invited keynote lectures and contributed oral presentations, including new results of the research project QUISS.

The QUISS project is an ongoing research project conducted at the Federal Institute of Hydrology (BfG) in Koblenz (Germany) in collaboration with the Technische Universität Braunschweig (Germany), which started in 2022 and is financed by the German Federal Ministry for Digital and Transport (BMDV). The abbreviation QUISS stems from the German title "**Qu**ecksilber **i**n **S**edimenten und **S**chwebstoffen" meaning "mercury in sediments and suspended particulate matter". The full project title is "Fractionation, speciation, transformation, and mobility of mercury in suspended particulate matter and sediments of German rivers".

Five of the abstracts in this volume describe selected results of the QUISS project (see 1.1, 1.6, 1.7, 1.12, 1.13) which are combined in this part of the symposium with two invited keynote presentations (see 1.4 and 1.14) and nine contributed presentations from all over the world. The presentations given at the online symposium originate from ten different countries (in alphabetical order: Belgium, Canada, Czech Republic, France, Germany, Republic of Korea, Slovenia, Russia, Sweden, USA) illustrating the international focus of the first part of the QUISS symposium. In contrast, the second part of the QUISS symposium, held on December 5 as on-site event in German language at the Federal Institute of Hydrology (BfG) in Koblenz (Germany) for which a separate abstract volume is available (see DOI: 10.5675/BfG_Veranst_2024.4), focuses more on applied aspects of the management and monitoring of mercury contaminated rivers in Germany.

1 Biogeochemical controls on mercury dynamics in contaminated river systems

1.1 Investigating the mobility and bioavailability of mercury in sediments and suspended particulate matter of contaminated river systems

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Keywords: legacy contamination, chemical extractions, pyrolytic thermodesorption

The behavior and fate of mercury (Hg) in contaminated river systems strongly depends on the mobility and bioavailability of the chemical forms in which Hg is present. Different Hg species, encompassing different redox states as well as inorganic and organic compounds, occur in environmental samples exhibiting a wide range of physicochemical properties and differing in their ability to enter biological systems. However, most monitoring programs assessing Hg contamination in river systems still focus primarily on total Hg (THg) concentrations, and in some cases monomethyl-Hg (MeHg). Investigations on the mobility and bioavailability of inorganic Hg(II) forms, which commonly make up the majority of THg in riverine sediments and suspended particulate matter (SPM), are less often conducted but relevant for a comprehensive risk assessment of contaminated sites. Different methodological approaches are available ranging from relatively simple selective/sequential chemical extractions and pyrolytic thermodesorption, providing information on operationally defined Hg binding forms, to advanced X-ray absorption spectroscopy methods which may yield quantitative data on Hg redox states and molecular species, but require relatively high THg levels and access to synchrotron facilities. Unfortunately, no simple and unambiguous methods exist to quantify the bioavailable Hg fraction in contaminated sediments or SPM that may, after entering microbial cells, be converted to MeHg and bioaccumulate in aquatic food webs.

Here, we present results of laboratory studies investigating the mobility and bioavailability of Hg in sediments and SPM from contaminated German rivers using different extraction methods (water and glutathione extracts, five-step sequential extraction) and pyrolytic thermodesorption. Oxic and anoxic water extractions conducted with different reactions times and solid-solution ratios confirmed the generally low abundance of water-soluble Hg (<1 % of THg) but also highlighted the dynamic nature of exchange processes between aqueous solution and contaminated solid phases. The thiol-ligand glutathione, which has been suggested to target the bioavailable Hg pool in sediments, extracted up to 8 % of THg from centrifuged riverine SPM samples but only up to 2 % from aged SPM collected in sedimentation boxes. Sequential extraction and pyrolytic thermodesorption data further revealed differences in Hg binding forms between SPM and sediments. No simple relationship between extracted Hg fractions and MeHg concentrations was found, illustrating that the extent of Hg methylation in contaminated sediments and SPM is controlled by a combination of bioavailable THg fractions and the biogeochemical conditions favoring microbial (net) methylation processes.

1.2 Effects of hydrologic regimes on the loading and spatiotemporal variation of mercury in the microtidal river estuary

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Keywords: microtidal estuary, mercury, load, colloidal, typhoon

The influence of hydrological conditions on the distribution and loading of mercury (Hg) species was investigated in the microtidal Hyeongsan River Estuary (HRE). During the post-typhoon period, dissolved Hg (DHg) and dissolved methylmercury (DMHg) from an industrial waste-receiving creek were efficiently settled into the sediment. In contrast, during dry periods, dissolved phase Hg species were transported to the HRE without significant sedimentation. An event-based mean approach was utilized to assess the hydrological impacts on the annual flux of Hg. The highest inputs of DHg and particulate Hg (PHg) were observed in the Hg-contaminated creek, with DHg being predominant during dry periods and PHg during wet periods. Following the typhoon, Hg and methylmercury (MeHg) concentrations in sediments decreased due to surface sediment erosion. Overall, the HRE acts as an effective sink for Hg, mitigating Hg contamination in adjacent coastal waters.

1.3 Mercury in freshwater ecosystems: problems of reliability of results and assessments, national standards of Russia

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Keywords: Mercury, freshwater, maximum permissible concentrations, contamination assessment, accumulation coefficient

The problem of reliability of Hg determination in freshwater really occurs especially at low concentration level. Many countries of the world have established quite strict standards, for example, in Russia, the MAC of dissolved mercury for water bodies used for fisheries is 0.01 µg/dm^3, that requires sensitive analysis methods and control of sample preparation and analysis procedure. At the same time, the Russian Regulatory document on Hg determination in natural waters offers methods with the measurement range of concentration from 0.01 to 1000(2000) µg/l. In accordance with Directive 2009/90/EC the limit of detection must be equal to 30 % (or lower) of the established quality standards, i.e. in our case <3 ng/l. A source of overestimation of concentrations in the laboratory can be chromium mixture or potassium permanganate (not Hg-free quality) used in the mercury analysis or Nessler reagent (K_2HgI_4) widely used in laboratory practice for the photometric determination of ammonium compounds. Water samples filtration (or non-filtration) can also be a source of error in assessment of water body pollution. Therefore, the analysis of real mercury concentrations in freshwater (from < 1 to several ng/l), can be done only by those scientific organizations that use highly sensitive methods such as US EPA 1631 and strict control of all possible Hg contamination and losses during sample preparation and storage.

Hg determination in bottom sediments is easier due to higher concentrations, but approaches to sample preparation and especially assessment of their contamination are also ambiguous. Pollution assessment based on the bottom accumulation coefficient may be incorrect due to the problem of determining the real Hg concentration in water. Guidance document also proposes to compare concentrations in bottom sediment with concentrations in bottom sediments of a background site remote from pollution sources, or with background concentrations in bottom sediment layers collected at the same point, corresponding to pre-industrial times, which doesn't always work. Some researchers use the sedimentary rocks, the earth's crust, regional soils, and MAC for soils as background values.

It is well known that for mercury, not only concentrations in water and bottom sediments are important, but also its bioavailability under current conditions. The determination of physicochemical parameters at the sampling site is required (some of them immediately on-site), which is not always the case.

Assessment of pollution and the state of the environment based on the analysis of mercury in biota and fish, taking into account the physical and chemical conditions at the present time, seems to be the most reliable method.

1.4 Mercury Dynamics in two Canadian River Systems

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Keywords: Hg isotope fractionation, Hg methylation, arctic, rivers, carbon isotopes

This presentation describes the application of mercury isotope tracers and isotope ratio measurements to characterize sources of Hg in the Mackenzie River Basin (MRB) and the formation of methylmercury in the severely contaminated Wabigoon River system in Northwestern Ontario.

Arctic environments are believed to store large quantities of both mercury and organic carbon, which are potentially released during periods of global warming. Especially the mobilization of Hg and its export to arctic aquatic ecosystems may pose as serious threat to both wildlife and northern communities living off the land. The Mackenzie River is the fourth largest source of freshwater and of riverine Hg to the Arctic Ocean. However, sources of Hg across the MRB are uncertain, which leads to a poor understanding of potential future release. Measurements of dissolved and particulate Hg and carbon concentrations were performed, along with Hg stable isotope ratio and radiocarbon analyses. Isotopic ratios of Hg revealed a closer association to terrestrial Hg reservoirs for the particulate fraction, while the dissolved fraction was more closely associated with atmospheric deposition sources of shorter turnover time. There was a positive correlation between the radiocarbon and riverine Hg concentration for both particulate and dissolved fractions, indicating that waters transporting older carbon also contained higher levels of Hg.

The Wabigoon River is known for an historic Hg pollution source, caused by a chlor-alkali facility operating in the 60’s. The legacy Hg contamination persists to current days, adversely affecting the health of local communities. Results show that locations downstream from the pollution source are still elevated in Hg, with concentrations at least five times higher in water and up to 134 times higher in sediments compared to background. The ability of an environment to produce methylmercury from inorganic Hg is important in determining the potential impact of Hg on human health and the environment. To understand which areas within the system are impacting negatively the local communities, Hg stable isotope tracers were used to assess Hg methylation at different locations along the river system, including lake, river and wetland sediments as well as water. Hotspots for methylmercury formation converted up to 4.4 % of the added Hg spike to methylmercury and have the potential to distribute methylmercury throughout the Wabigoon River system.

1.5 Mercury in river system Kössein-Röslau-Eger – 30 years after remediation in Marktredwitz

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Keywords: river contamination, filtered Hg, particulate material Hg, floodplain, sediment

Over a period of four years we monitored the Kössein-Röslau-Eger river system to observe Hg mobility downstream of the abandoned chemical factory in Marktredwitz (CFM). Although part of the former contamination directly in the CFM and on the adjacent banks of the Kössein River was successfully remediated in the period 1986-1993, downstream transport of Hg continues to this day, exporting Hg to the German-Czech border and further downstream. The knowledge of the Hg transport towards the Skalka reservoir in the Czech Republic is essential for future decisions and actions to limit the continuous spread of the contamination. Therefore, we aimed to quantify the contribution of each of the two tributaries, i.e. the Kössein-Röslau and Eger rivers, to the total input of Hg to the Skalka reservoir just downstream of the Eger-Röslau confluence. We assessed monthly changes of filtered concentrations of Hg and MeHg, unfiltered Hg and suspended particulate Hg in the period 2019-2022. Furthermore, we investigated the occurrence of Hg in the pore water of Hg-rich floodplain sediments near the Skalka reservoir and the interaction of vegetation with deposited Hg-rich sediments.

Filtered Hg concentrations just below the former CFM averaged 6.9 ± 4.1 ng/L (n=22), 23 km downstream in the River Röslau, just before the confluence with the River Eger it increased to 9.2 ± 6.5 ng/L (n=31). In the drainage area of the River Eger without any Hg contamination sources, the average concentration was 1.8 ± 1.3 ng/L (n=23). Total unfiltered Hg concentrations at the same sites were much higher in Kössein 35.5 ± 28.6 ng/L (n=12), Röslau 61.1 ± 46.8 ng/L (n=17) and Eger 6.1 ± 5.7 ng/L (n=16). Finally, MeHg concentrations averaged 0.31 ± 0.04 ng/L (n=3), Röslau 0.81 ± 0.48 ng/L (n=6) and Eger 0.29 ± 0.23 ng/L (n=5). Filtered Hg concentrations were positively related to those of DOC at the sampling sites and both (filtered Hg, DOC) increased with increasing discharge. Unfiltered Hg concentrations increased rapidly with increasing discharge, but did not correlate with discharge. Concentrations of MeHg were not related to discharge, suggesting that other factors influence its mobility, such as the occurrence of methylation hotspots within the floodplains.

Previous work identified suspended particulate matter (SPM) as the main transport medium of Hg to the Skalka reservoir. The SPM was high in Hg: 4-11 mg/kg at Kössein and 8-16 mg/kg at Röslau; for reference, the SPM of the Eger River averaged 0.6 mg/kg Hg. Using discharge and turbidity data from the Bayerisches Landesamt für Umwelt - Gewässerkundlicher Dienst, we estimated that the annual input of filtered Hg from the Röslau River to the Skalka Reservoir averaged 1.1 kg/yr, while the Eger River contributed 0.2 kg/yr in the period 2020-2022. Nevertheless, the mean annual mass of SPM transported by the Röslau River at Arzberg was 2 200 t, and assuming a mean SPM Hg concentration of 13 mg/kg, the mass of Hg transported by SPM to the Skalka Reservoir would reach up to 30 kg.

1.6 Methylmercury Dynamics in Riverine Suspended Matter: Comparison of Sampling by Continuous Flow Centrifugation and Sedimentation Boxes

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Keywords: Suspended particulate matter, methylmercury, continuous flow centrifuge, sedimentation box, seasonal variations

In Germany most water bodies continue to be classified as failing to achieve "good chemical status," mainly due to high methylmercury (MeHg) levels in fish (EU Water Framework Directive). Despite extensive research the formation and fate of MeHg in fluvial systems, especially the role of suspended particulate matter (SPM) is not fully understood.

SPM from the German Elbe River and its tributaries, Mulde and Saale, known for industrial legacy mercury (Hg) pollution was collected by continuous flow-through centrifugation (several hours) and sedimentation boxes (several weeks). Hence, two completely different sampling principles (active and passive) were compared across various seasons to assess the temporal variability in MeHg formation.

Mean concentrations of MeHg were 5 µg kg^{-1} in centrifuge samples and 7 µg kg^{-1} in sedimentation box samples (max. 11 µg kg^{-1} and 20 µg kg^{-1}, respectively). Although Saale River shows the highest overall total Hg (THg) concentrations in both SPM sampling types, highest average MeHg concentration of 11 µg kg^{-1} and the highest average MeHg/THg proportion of 1.1 % (max. 2.5 %) were found in Elbe River sedimentation box samples, indicating site-specific differences in Hg methylation.

The SPM collected with the centrifuge exhibited significantly higher total organic carbon (TOC) values across all sites, particularly aligning with periods of high biological productivity. Thus, SPM sampling by flow-through centrifugation delivered a snap-shot of the SPM composition (including fresh algae), whereas sedimentation boxes showed lower and less variable TOC levels by generating mixed samples over weeks. Additionally, an incomplete capture of low density (organic) particles as well as in-box decomposition processes during the longer sampling period must be considered.

These considerations are supported by stronger seasonal variations in MeHg concentrations and consistently the highest MeHg/THg proportions during warm periods with high productivity indicating in-box Hg methylation most likely fueled by repeated addition of easily degradable particles under static conditions. Thus, sedimentation box derived SPM may suffer from MeHg formation artefacts under reducing conditions which are more comparable to recently deposited bottom sediments than to SPM in the river flow.

The differences between the two methods highlight the importance of method selection in environmental Hg species monitoring and the need for precise understanding of the limitations of individual methods.

1.7 Seasonal variations of mercury and methylmercury in freshly deposited suspended particulate matter samples of the Danube, Mulde, Saale and Elbe Rivers

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Keywords: Methylmercury; suspended particulate matter; river monitoring, seasonal variations, climate change

Archived samples of suspended particulate matter (SPM) from the years 2016-2024 were provided by the German Environmental Specimen Bank and analyzed for total mercury (THg) and methylmercury (MeHg). The analysis comprised monthly mixed samples collected with sedimentation boxes from the river monitoring stations Jochenstein (Danube), Wettin (Saale), Dessau (Mulde) and Cumlosen (Elbe). All samples were frozen with liquid nitrogen in the field and freeze-dried before cryo-archiving. THg was quantified by AAS after combustion and amalgamation on a gold trap, while MeHg was analyzed by GC-AFS after alkaline extraction and ethylation. The investigations provide first insights into seasonal variations of MeHg concentrations in the SPM samples of the above-mentioned rivers. While the Elbe catchment is strongly affected by legacy inputs of anthropogenic mercury (e.g., chemical industry in former East-Germany), the Danube River exhibits much lower levels of historical Hg contamination. The results revealed clear differences between the respective rivers in absolute concentrations of THg, MeHg and MeHg/THg ratios. Concentration maxima of THg in winter and MeHg in summer are a feature among all study sites. 2021 MeHg concentrations in SPM showed distinct seasonal increases at Cumlosen (4.4 to 19.6 ng/g) and Dessau (3.6 to 15.4 ng/g), while rather small increases occurred at Wettin (5.3 to 9.4 ng/g). Much lower concentrations of MeHg were found at Jochenstein (0.4 to 2.6 ng/g), yet with the most pronounced seasonal increase (~6-fold) of all study sites, indicating favorable conditions for Hg methylation in summer 2021 likely related to the damming of the Danube River at this location. Statistical analyses including hydrological and hydrochemical parameters (discharge, temperature, dissolved oxygen, dissolved organic carbon, etc.) during the collection period as well as the concentrations of THg and MeHg showed strong positive correlations ($p<0.001$) between the concentration of MeHg in SPM and prevailing water temperature. This can be explained by increased microbial MeHg production in summer, although it remains unclear how much of this response is from the incubation of SPM in the sedimentation box during the sampling period. Our long-term trend from 2016 to 2024 suggests rising water temperatures, may they be local (as from power plants) or broad-scale (as induced by global climate change), may counteract anticipated declines in MeHg concentrations in response to national and international measures to reduce Hg (and MeHg therein) in water bodies.

1.8 Application of multi-box models in mercury contaminated sites: Idrijca and Soča/Isonzo rivers and the Gulf of Trieste

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Keywords: mercury, modelling, box model, river, coastal sea

From the vicinity of the former Hg mine in Idrija, Slovenia, and along the contaminated catchments of rivers Idrijca and Soča/Isonzo, Hg-rich suspended sediments are transported downstream and into the Gulf of Trieste. Hg methylation takes place both in the river and in the marine sediment, from where it is remobilised into the water column and the food chain. Hydrological modelling based on historical data considering climate change scenarios has shown that riverine transport is likely to increase by more than 50 % and Gulf outflow to decrease slightly. More Hg will therefore be mobilised and available for transformations.

Due to their robustness, ease of development and improvement, transparency and low input data requirements, multi-box models are a suitable tool for assessing different possible scenarios of water and sediment flows, fluxes and transformations in the river-marine system under consideration. A relatively simple multi-box model was developed in MS Excel, consisting of six compartments representing the river system and a seventh for the marine part. Machine learning tools were used to determine the ratio of water discharges between the compartments and the lateral inflow. Relationships between discharge and suspended sediment and Hg concentrations were determined from measurements. Hg speciation considered dissolved and particulate total and methyl mercury (THgD, THgP, MHgD, MHgP) and dissolved gaseous mercury (DGM), with both methyl species and DGM accounted for by partition coefficients. Volatilisation and evasion in the marine environment were calculated as additional output. Mass balances of all variables are calculated for each compartment. Hg transformations between species are governed by first order kinetics.

The Hg transport and transformation model has been verified with previously available data. Calibration and validation of the model require a deeper understanding of the transformation processes, which we aim to achieve by using machine learning tools on the extensive dataset obtained in an ongoing research project. The main advantage of multi-box models is that, as either new data or improved knowledge on transformations becomes available, the model can be extended to include additional compartments in any physical direction, and more Hg species and transformations can be introduced.

The research was financially supported by the Slovenian Research Agency (programme P2-0180, project J1-3033).

1.9 Tracing mercury contamination down the European coast through speciation and isotopic analysis

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Keywords: Mercury, isotope ratio, marine organisms, speciation, 10^{13} Ω amplifiers

Mercury (Hg) is a toxic heavy metal, emitted into the environment due to natural processes and anthropogenic human activities. As a result of its complex biogeochemical cycle, Hg undergoes different chemical transformations which play a key role in its bioavailability, mobility, and toxicity. Methylmercury (MeHg), the most toxic form of Hg tends to bioaccumulate and biomagnify along the marine food chain. Therefore, fish consumption is considered the main exposure source of humans to MeHg. This latter is a potent neurotoxin capable of crossing the blood-brain barrier, posing health risks to individuals at all stages of life, from infants to adults, thereby signaling the importance of reducing human exposure to MeHg. However, determination of the concentrations of total Hg (THg) and MeHg does not provide sufficient information on the source of Hg contamination. In this work, we examined the Hg speciation and isotopic composition in various tissue types—muscle, liver, and hepatopancreas—from predatory fish and shellfish (cod and crab) collected along the coasts of Europe (Norway, Great Britain, France and Portugal). Hg isotopic analysis is often compromised by low Hg concentration levels. Therefore, to address this problem, multi-collector inductively coupled mass spectrometry (MC-ICP-MS) unit equipped with highly sensitive 10^{13} Ohm amplifiers is used to measure Hg isotope ratios in samples containing sub μg L^{-1} Hg levels with high precision (≈0.1 ‰ at 0.1 ppb THg). By combining the Hg isotopic composition with the information on the fractions of inorganic Hg and MeHg in the tissues studied, we aim at revealing deeper insights into the MeHg bioaccumulation, biomagnification, and the biogeochemical Hg cycle along the European coast.

1.10 Enhanced insight into the biogeochemical cycle of Hg in the Antarctic marine environment of Terra Nova Bay via isotopic analysis

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Keywords: Mercury, isotope ratio, marine organism, Antarctica, biogeochemical cycle

Mercury (Hg) is a globally significant pollutant, which is particularly concerning due to its ability to undergo long-range atmospheric transport and to be bioaccumulated and biomagnified in aquatic ecosystems, even in remote regions like Antarctica. This study explores the biogeochemical cycling of Hg in the marine coastal environment of Terra Nova Bay (Antarctica) by determining the total content of mercury (THg) and its isotopic composition in fish (*Trematomus bernacchii*), bivalve molluscs *(Adamussium colbecki*) and sediment samples, collected in 1996-98 and 2021. The results indicate a significant decrease in the THg concentration in organisms from the 1990s to 2021, with a concurrent shift toward higher δ^{202}Hg (governed by mass-dependent isotope fractionation MDF) and lower Δ^{199}Hg and Δ^{201}Hg values (governed by mass-independent isotope fractionation MIF) in fish organs. These changes suggest changes in the exposure to Hg and the photochemical processes that the element and its species undergo, likely influenced by differences in the environmental conditions during the sampling periods, such as light exposure and ice cover. Sex-specific analysis of fish samples further suggests differences in Hg accumulation and both MDF and MIF isotopic patterns between male and female specimens, emphasising a potential effect of sex on Hg exposure and dynamics. Finally, the linear increase of Δ^{199}Hg as a function of Δ^{201}Hg during trophic transfer suggests MeHg bioaccumulation along the food chain. These findings provide valuable insights into the biogeochemical cycling of Hg in the Antarctic coastal marine environment and underscore the need for ongoing monitoring of Hg in this fragile ecosystem.

1.11 Distribution of colloidal, truly dissolved, and DGT-labile fractions of mercury in the fresh waters

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Keywords: Mercury, DGTs, colloids, bioaccumulation

Mercury (Hg) is regarded as one of the most toxic elements impacting on human and ecosystem health. It is a naturally occurring element, however, since the industrial revolution anthropogenic Hg inputs exceed natural inputs by at least a factor of five. Humans are exposed to Hg mainly through their diet, especially through the consumption of fish and other products from the aquatic environment.

In waters, Hg is commonly found to be complexed with ligands: dissolved organic matter (OM) and inorganic nanoparticles. The functional groups and size of the complexes may drive Hg bioavailability. The knowledge of size-distribution and lability of Hg in aquatic systems is important for estimation of the ecological effects. One of the approaches that can be used to better investigate Hg speciation is size fractionation of inorganic and organic colloids. In parallel, mercury-specific diffusive gradients in thin films (DGTs) have been widely used as a biomonitoring tool to assess the lability of Hg compounds in different natural media.

This study aims to assess the relationship between size fractionation, chemical lability and bioavailability of Hg on contrasting study sites: rivers Seine and Deûle, France. Two chosen rivers are characterized by different origins of Hg contamination (urban vs industrial). Our goal is to determine Hg species distribution, as well as to characterize the abundances of truly dissolved, colloidal and DGT-labile fractions for every study site. To this end we used a centrifugal-ultrafiltration technique (CUF) combined to asymmetrical-flow fractionation (AF4) link to multi-detectors for the determination of Hg-bound to colloidal pool. Complementarily, we used Hg specific DGTs contained resin gel, made of 3-mercaptopropyl functionalised silica, imbedded into polyacrylamide gel, a 1.5 % agarose diffusive layer of various thicknesses, and protected by PES (Polyethersulphone) membrane for in situ sampling.

Preliminary results obtained by AF4 and fluorescence excitation-emission matrix spectroscopy indicate the difference in term of origine, nature and composition of OM and colloids in between both rivers, the question is how it will affect DGT-labile Hg species and can it be related to size-fraction obtained by CUF. The data collected during this project could serve to refine existing models to predict the fate of Hg and other trace metals in aquatic food webs.

1.12 Favorable conditions for the microbial community in young riverine sediments lead to increased mercury methylation

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Keywords: SPM, mercury, methylation, microbial community, bioavailability

Elevated mercury (Hg) levels in biota, exceeding the environmental quality standard for Hg, are a main reason for German rivers not reaching a “good” chemical status according to regulations of the EU Water Framework Directive. Old river sediments containing legacy Hg from past industrial input are thought to be mainly responsible whereas new Hg input has been vastly reduced. Freshly mobilized suspended particulate matter (SPM) from floodings or river management excavations can be prone for transformation of inorganic Hg species into organic methylmercury (MeHg) by anaerobic microbes when SPM is resettling as young sediments. MeHg bioaccumulates in the aquatic food chain and can affect humans. Therefore, it is crucial to understand the conditions and mechanisms leading towards a higher bioavailability of Hg for finding mitigation strategies. The German river Elbe and its tributaries Saale and Mulde are strongly Hg contaminated, so that they were chosen for collecting field samples during different seasons of the year. During several field campaigns, water phase SPM was collected via flow-through centrifugation whereas SPM-derived “freshly” deposited sediment was collected from sedimentation boxes. Also, cores of old sediments from groyne fields were taken. All samples were analyzed for total Hg (THg) and MeHg. The composition of the microbial community was analyzed with long-read 16S sequencing (PacBio). We found significantly higher MeHg/Hg ratios, TOC and redox potential in freshly deposited sediments in sedimentation boxes in comparison to water phase SPM or old sediments. Depending on the elevated TOC contents and redox potential, the taxonomic composition of the microbial communities was also changed depending on the bacteria’s metabolic capabilities in Hg resistance or Hg methylation. These results correspond to higher abundances in Hg-methylating bacteria in freshly deposited sediments in contrast to older sediments and water phase SPM. Due to the risk of Hg methylation by microbial communities, redistributed and resettling SPM containing Hg poses a threat to riverine biota and humans. The higher frequency of flooding events and higher water temperatures might promote conditions for enhanced microbial Hg methylation, so that river management strategies need to take these effects into account for reducing the threat of higher Hg bioavailability as MeHg.

1.13 Vertical and Temporal Variability of Mercury Mobility and Methylmercury Formation in Freshly Collected River Sediment Using a Meso-Profiling System

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Keywords: Methylmercury; Sediment; Pore Water; Depth Profile; Temporal Variability

A meso-profiling system was employed in an incubation experiment to investigate mercury (Hg) mobility and methylmercury (MeHg) formation in freshly collected surface sediment from the legacy-contaminated Elbe River (Germany). The system enables low-invasive, automated sampling of sediment pore water (PW, in this case down to 5 cm depth and at 0.5 cm spatial resolution) while continuously monitoring physicochemical parameters such as redox potential (Eh), dissolved oxygen, pH, and hydrogen sulfide with microsensors. After each completed profiling, mini sediment cores were collected and immediately frozen for Hg speciation and microbial community analysis in the solid phase. The experiments, conducted over 1, 2, 4, and 12 weeks, utilized various analytical methods including CV-AFS for total mercury (THg), GC-AFS after distillation/alkaline extraction and ethylation for MeHg, ICP-MS/MS for different elements, and dissolved organic carbon (DOC) by DOC analyzer.

During the incubation period, oxygen concentrations declined within the first few millimeters, leading to low Eh values that rapidly were detected below the oxic water phase within the sediment. The Eh values at the sediment-water interface (SWI) increased with the incubation period; however, MeHg concentrations in PW (filter cut-off <16 µm) remained low at the SWI. Notably, higher MeHg concentrations in PW were observed at deeper sediment depths, with the MeHg/THg ratio in the PW increasing with sediment depth and incubation time. Iron and DOC concentrations in the PW increased with depth but decreased over time, while dissolved sulfur concentrations decreased with depth (likely due to microbial sulfate reduction) but increased during the incubation. These patterns suggest that iron reduction may facilitate the release of sediment-bound mercury into the PW, although higher THg levels were not clearly observed under iron-reducing conditions. Additionally, MeHg concentrations and MeHg/THg ratios in the upper part of the sediment cores increased with longer incubation times, indicating that raised redox conditions in the top sediment layers promote MeHg enrichment in the bulk phase, likely influenced by higher amounts of Hg methylators at the SWI. Overall, these findings emphasize the complexity of sediment depth and redox dynamics in the mobilization and methylation of mercury within legacy-contaminated river sediments, highlighting the need for further investigation to fully understand these processes.

1.14 Biogeochemical Controls of Mercury Release and Exposure from Contaminated Sediments

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Keywords: Methylmercury, adsorption, desorption, resuspension

Sediment properties and mercury (Hg) speciation are well-known drivers for the release and exposure of Hg from contaminated sediments. Due to the complexity of these systems and the processes involved, risk assessment of contaminated sediments remains a challenge. In this presentation, I will share experimental data on i) the formation of refractory pools of Hg when transported on particles, ii) the release and exposure of Hg upon sediment resuspension, and how these factors (i-ii) are influenced by various biogeochemical factors, such as particle size distribution and organic matter content. Additionally, I will present data where passive samplers (commercially available DGTs) have been used to estimate the bioavailable fraction of Hg and evaluated alongside the chemical speciation of Hg in the dissolved phase.

To examine the formation of refractory pools of Hg, we conducted adsorption and desorption studies using soil/sediment and water slurries with different properties. Unlike traditional adsorption and desorption studies, we allowed the system to reach equilibrium to assess the formation of refractory Hg pools, i.e., pools of MeHg not readily available for re-desorption. Our data show that a significant fraction of MeHg absorbed enters the refractory pool. To examine how sediment resuspension affects the release of MeHg, we conducted microcosm experiments. In the first experiment, artificial sediment with different particle size distributions was tested. In the second resuspension experiment, we examined the accumulation of MeHg in Ceramium (an alga) and passive samplers. Finally, we applied passive samplers for THg and MeHg in sediment slurries from 25 contaminated sites and compared this data with Hg methylation rates and chemical speciation data.

1.15 Legacy Hg pollution in Connecticut River (USA) cove sediment: leakage from an upstream Hg-boiling powerplant?

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The Connecticut River (655 km long, USA) crosses 5 New England states (MA, NH, VT, MA, CT) before discharging in Long Island Sound (LIS). The industrialized states of MA and CT have polluted the river sediment over time, best documented in the “quiet water” coves and oxbow lakes (the riverbed is all sand/silt). The Hg-T concentrations in New England wetland and lake sediment remote from point sources (e.g., on Block Island) range from 50-80 ppb Hg for the natural background to ~300 ppb Hg for sediment deposited in 1960-1970; modern sediment carries ~ 200 ppb Hg. Sediment cores taken from MA to LIS show that cove sediment South of Hartford (CT) has up to several ppm Hg. Dating of the cores with 210-Pb, 137-Cs, 14-C and chemostratigraphy based on known pollution peaks of Pb and V from atmospheric deposition, show that the Hg pollution events occurred between the mid-1920s and 1960. A cove directly South of Hartford shows Hg enrichments up to 3 ppm Hg, with a clear drop after 1960 to 500 ppb Hg in modern sediment. Modern fish in the CT river (1992-1995 study of the state of CT) have on average 0.2 to 0.3 ppm Hg for bass and perch, not unusually high values in New England. A potential source for this Hg pollution is an experimental powerplant that was located on the river floodplain in Hartford, and used to boil liquid Hg, with the Hg vapors driving turbines for power generation. The heat of condensation of the Hg back to liquid Hg was used to run a second steam cycle for electricity generation. The plant started in 1921, expanded in 1928 and the 1940s, but was converted back to steam-only in 1961. Records of Hg loss from the plant, obtained from Hg purchase receipts from the Smithsonian National Museum of American History, DC, indicate major losses in the early to mid 1930s. The location of the plant, the period of operation, and peak pollution in ~1930-1935 agree with our dated Hg pollution core studies. Mercury isotope data show differences in Δ^{199}Hg and δ^{202}Hg between pre-industrial Hg, modern Hg, and Hg from the power-generation pollution period. The latter is close to the Hg isotope composition of the ore body in Nevada, USA from which 200,000 pounds of Hg for the boiler was sourced (relatively “primitive, unprocessed” Hg). We have no knowledge of Hg in fish from the pre-1960 river, but some museum specimens may exist. Fish may have been rich in Hg during the 1930s depression when Hg pollution was most severe, and subsistence fishing may have occurred. Most of the powerplant-derived Hg was ultimately discharged into LIS, where sediment was also strongly polluted with Hg from the hat-making industry in Connecticut (1800-1940, 25 % of all felt hats made in the world came from Danbury, CT). In addition, modern sewage treatment plants added Hg to LIS sediment, which we have traced with correlations between bacterial cysts (sewage tracer) and Hg concentrations in LIS sediment, standardized on pure sewage sludge.

1.16 Organic matter and mercury interactions in a burned watershed, Salmon River Mountains, USA

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Keywords: placer mining, fire, dissolved organic carbon, methylmercury

United States environmental regulations require modern mining operations to remediate water flowing off-site, a process that includes ion exchange and pH adjustments at the source prior to discharging to a stream for natural attenuation. The natural attenuation step may be complicated by the presence of historical mines within the watershed. Impact from fire and prolonged drought may also compromise long-term mine water remediation. The Salmon River Mountains of Idaho include thousands of historical base metal mine sites, most of which are currently inactive and not undergoing active remediation. In 2022, the Moose Fire burned 574 km^2, including catchments with extensive placer tailings from that date back to 1866. We used a paired watershed approach to investigate whether mining has exacerbated the remobilization of mercury from placer tailings. Atmospheric deposition and geologic background may be additional sources of mercury to this watershed. Sediment, soil, and water samples were collected in June following peak snowmelt and in September during baseflow to determine mercury and organic carbon concentrations. Specific UV absorbance (SUVA) was calculated as the ratio of UV at 245 nm to dissolved organic carbon to determine relative amounts of aliphatic and aromatic organic matter in stream water. The working hypothesis was that organic matter associated with burned vegetation and surface soils would have increasing aromaticity, potentially including sulfur reactive groups that could bind to mercury, enhancing mobility. Preliminary results indicate that burned watersheds with placer mines have the greatest stream water mercury concentrations regardless of the aromaticity of the dissolved organic matter. There are somewhat greater SUVA values for stream water collected in September, possibly reflecting less direct input of organic matter from the overall watershed during baseflow. Our results identify an additional challenge for using natural attenuation to remediate mine waters from historic mining within watersheds impacted by fire.

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