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Preface

JES Special issue in Mercury Biogeochemistry and Fate

Tom Sizmur, Nelson O'Driscoll, Yong Cai

The global and regional redistribution of mercury within the environment is of primary importance to both natural ecosystems and human health. The ratification of the Minamata Convention on Mercury by 91 parties represents a key step in protecting ecosystems and future societies from increasing mercury accumulation. However, key to the continued quantification and mitigation of mercury pollution is the fundamental science controlling its speciation, movement, bioaccumulation, and impacts on ecosystems. This special issue brings together a diverse collection of papers detailing advances in the science of mercury pollution. The papers provide new insights into fundamental processes, environmental (bio)monitoring, analytical techniques, and remediation technology.

Mercury is extraordinary as an inorganic environmental pollutant because it has several species with very different solubilities, vapour pressures, and capacity for bioaccumulation and toxicity, thus making it a very mobile element. Its impacts are equally important both at highly contaminated sites affected by point source discharges (e.g. chlor-alkali plants and gold mining), and in remote ecosystems, far from emissions sources as a globally distributed pollutant (most notably in the Polar Regions). One industry which receives attention due to the potential to cause mercury toxicity directly to some of the poorest communities in the world is the mining and production of gold that uses mercury as an amalgam to extract the gold from the ore. Gold mining using mercury has been identified by the United Nations as being the largest emitter of mercury in the global budget, and is therefore a research area of intense interest. Gutiérrez-Mosquera et al. (2018) investigated Hg in blood, hair, and urine from inhabitants of the San Juan Mning District in Western Colombia. The authors found higher levels of mercury in males than females living in the mining district, largely due to occupational exposure, and a higher fish consumption. It was also postulated that females are better able to metabolise methylmercury (MeHg), which is more toxic and bioaccumulative than divalent mercury (Hg(II)) or elemental mercury (Hg(0)). Females are more likely to unintentionally remove the volatile Hg(0) adsorbed directly on hair during gold panning activities, due to frequent cosmetic hair treatments. Mercury contaminant originated from mercury mining is one of the major sources of mercury pollution in Central China. Understanding the transformation pathway and formation of toxic methylmercury is important for local residents who potentially expose to mercury at elevated levels via different sources. Jia et al. (2018) investigated Hg contamination and identify the main soil Hg methylator in the study area. They measured the concentrations of total mercury and MeHg in vegetables and the corresponding rhizosphere soil, and estimated the health risk posed by total mercury and MeHg present in vegetables. Their results suggest that vegetable may pose health risk to local residents.

Rice ingestion is also known to be an important source of mercury to human populations, particularly those living in close proximity to mercury mining operations such as the Wanshan Mercury Mining district in Guizhou, China, one of the world's largest mercury mining regions. Rice is a particularly susceptible crop for accumulating mercury because it can grow in wet, often flooded, anoxic conditions which is conducive to the methylation of Hg(II) to the more toxic and more bioaccumulative MeHg. To advance our understanding of human exposure to mercury from rice ingestion, Z. Wu et al. (2018), Q.R. Wu et al. (2018) compared four different *in vitro* methods to assess the bioaccessibility of mercury in rice to humans. Each method uses contrasting ingredients and extraction durations to simulate the passing of the rice through the gastro-intestinal system. The Physiologically Based Extraction Test was found to provide the most consistent results. Rice samples collected form 13 different Provinces in China were compared to rice from the Wanshan Mercury Mining district. Less than 50% of total Hg in rice was found to be bioaccessable (less than the bioaccessable portion often found in fish), and the estimated daily intake was below WHO reference values. However, there was a considerably higher concentration of Hg in rice from the Wanshan Mercury Mining district, compared to other locations. Soils and rice samples from paddies surrounding both abandoned mining sites and an active smelter in the Wanshan Mercury Mining district were taken by Yin et al. (2018). The authors found

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considerable contamination of the rice with Hg and MeHg due to both mining and smelting activities. They found that mercury more readily methylates in soils surrounding the smelter, where deposition is more recent. MeHg concentrations in soil and rice grains show clear relationships with soil properties, such as sulphur or organic matter content, since both S and SOM reduce the bioavailability of Hg to mercury-methylating bacteria. A clear mercury-selenium (Hg-Se) antagonism was observed in rice, which results in lower uptake of Hg by the root cells of rice plants where Se concentrations are elevated. Hg-Se antagonsim was further investigated by Liu et al. (2018) in the protozoa *Tetrahymena malaccensis*. The protozoa was exposed to individual or combined doses of mercury (as Hg(II) and MeHg) and selenium (as Se(IV), Se(VI) and selenomethionine) to elucidate the mechanisms by which Hg-Se is known to reduce Hg toxicity. Selenomethionine was found to reduce Hg toxicity at lower doses than Se(IV) or Se(VI). This finding may be due to its Se^{2-} oxidation state, which more readily conjugates with Hg than Se^{4+} or Se^{6+} does. The results indicate, however, that the detoxifying effect of Se may be due to a reduction of Hg uptake by organisms exposed to Se. Interestingly, it was also found that Hg(II) and MeHg enhanced the detoxification of Se at very high toxic concentrations, indicating mutual detoxification.

Another major global hotspot of mercury pollution is the Marano and Grado coastal Lagoons in Northeast Italy, which are contaminated with Hg from an upstream chlor-alkali plant and the Idrija cinnabar mine in western Slovenia, both of which have now ceased to directly discharge. Turritto et al. (2018) monitored the suspended particulate matter and the associated particulate mercury in the narrow channel that serves as a tidal inlet between the Grado lagoon and the Gulf of Trieste. The monitoring indicated that particulate Hg was greatest on the ebb tide, indicating that the erosion of tidal flats and salt marshes in the lagoon provides a net export of particulate sediment to the Gulf of Trieste. This net export of sediment results in a net export of mercury, even when high concentrations of particulate Hg entering the lagoon associated with high rainfall in the catchment upstream, is taken into account. Petranich et al. (2018) investigated mercury cycling at the sediment-water interface in the Marano and Grado Lagoons. MeHg concentrations were greatest in sediments 2-3 cm below the sediment-water interface, where methylation is favoured by anoxic conditions and a greater activity of sulphate reducing bacteria. Dissolved MeHg concentrations were seasonally dynamic, and seemed to be controlled primarily by temperature, with the greatest concentrations observed in summer. Methylation was elevated in the sediments of a fish farm where water circulation is artificially slowed by the construction of shallow channels and ponds, and organic matter emanating from the fish farm accumulates and creates hypoxic environments conducive to Hg methylation.

Due to the environmental damage caused by mercury contaminated discharges by industries such as mines or chlor-alkali plants, a considerable effort has been invested in the design of technologies to remediate wastewater emanating from mercury contaminated sources. Y.J. Li et al. (2018), D. Li et al. (2018) describe the synthesis of a novel adsorptive material containing alkynyl functional groups and a high surface area. The material has a high capacity for removing mercury from wastewater due to strong chemical interactions between alkynyl groups and mercury ions. Even if these chemical sorption sites become saturated, mercury undergoes continued physisorption to create multilayers of Hg(II) on the surface of the carbonaceous material. The material can be regenerated and reused while retaining >90% of the adsorption capacity.

While point source emissions of mercury to the environment can cause impacts on ecosystems locally, these local hotspots of mercury pollution can undergo volatilisation and contribute to the global atmospheric pool of mercury. Deposition can occur far away from emission sources and pollute remote ecosystems. The Minamata Convention requires governments to compile emission inventories for all major mercury emissions sources, including industrial gold production. Much attention in the past has focused on artisinal and small scale gold production and the assumption currently applied is that mercury emissions from large scale gold production plants are similar to artisanal and small scale gold production. Z. Wu et al. (2018), Q.R. Wu et al. (2018) provide a comprehensive investigation of the Hg emissions from all stages of the gold production process at two large gold smelters in China, and reveal that emissions inventories (based on measurements made from artisanal and small scale gold mining) currently overestimate the Hg emissions at these large gold production facilities. However, the authors highlight considerable uncertainty in the emission factor estimates because a primary variable influencing emission is the concentration of Hg in gold concentrates entering the plants, and this can differ by up to six orders of magnitude.

Once mercury enters the atmospheric pool, its unique photochemistry combined with global distillation of the volatile form Hg(0) results in increased mercury inputs to Polar Regions where elevated concentrations of mercury have been observed in animals, and humans. Mallory and Braune (2018) measured mercury concentrations in the eggs and livers of two arctic seabirds (thick-billed murres and northern fulmars) collected, between 1976 and 2013 from the Canadian Arctic to provide insights on the use of these species as bioindicators of mercury pollution in the Arctic. They found that eggs were a more appropriate bioindicator of short-term annual fluctuations in exposure to mercury due to differences in weather or ice influencing access to prey. Liver samples provided a more reliable indication of long term trends. Fulmers contained higher concentrations of Hg in their livers, compared to murres, despite occupying a lower tropic position, which indicates a physiological difference between these birds in the way that they are exposed to, or excrete, mercury. The Arctic is expected to undergo considerable changes this century, which may influence how mercury interacts with organisms. Climate change is predicted to increase the duration and spatial coverage of open water in the Arctic, resulting in greater concentrations of chloride in Artic snow, due to greater inputs from sea salt aerosols. Mann et al. (2018) investigated the relationship between chloride ions and mercury photoreduction kinetics in melted snowpack by spiking melted snow with a range of chloride concentrations and exposing the samples to a range of UV intensities. The rate of mercury photoreduction was positively correlated, but the amount of Hg photoreduced was negatively correlated, to snow chloride concentration. This finding implies that greater chloride concentrations in Artic

snow, after melting, will result in less overall photoreduction, due to the formation of stable mercury chlorocomplexes, but the photoreduction that does take place will occur more quickly. Thus, more overall retention of mercury in snowmelt is expected in high chloride areas. Kalinchuk et al. (2018) provide compelling evidence that the Arctic may now become a source of mercury to ecosystems at lower latitudes. Hg(0) was measured during August 2013 over the bearing sea, with the highest concentrations observed in air masses emanating from the lower troposphere of the central Arctic Ocean. This surprising finding challenges the perceived wisdom that the Arctic is only a sink for anthropogenic Hg and implies that the Arctic Ocean exports Hg to lower latitudes, during the summer months. The precise source of mercury is not clear, but it is presumably due to the volatilization of Hg(0) from the surface of the Arctic Ocean that has built up in the surface layer of seawater while it has been covered with ice.

Mercury can also accumulate in ice and snow at lower latitudes in glaciers, which are also susceptible to change as the climate warms. Sun et al. (2018) sampled snow and ice from glaciers, high on the Tibetan Plateau, to investigate how mercury from glaciers is incorporated into mountain rivers. After the onset of snowmelt there was an early release of dissolved Hg, followed by later releases of particulate bound Hg, the majority of which is retained in the glacier and eventually released in meltwater. These findings imply that further mercury may be released from Tibetan glaciers, as the climate warms. The accuracy of such analysis of mercury in natural water is vital to support research that advances our understanding of mercury biogeochemistry and fate in the hydrosphere. Y.J. Li et al. (2018), D. Li et al. (2018) provide critical insights on a widely used method to analyse concentrations of Hg(II) in water samples. Most laboratories analysing Hg(II) concentrations in water do so by reducing the Hg(II) to Hg(0) using stannous chloride, prior to detection with Atomic Fluorescence Spectroscopy. However, stannous chloride also reduces MeHg in the absence of sulphate. When sulphate is present, it is reduced to sulphide, which then complexes the MeHg and prevents its reduction. Most natural waters contain sufficient sulphate to prevent the reduction of MeHg after the addition of stannous chloride, so (to our knowledge) the research presented in this issue would be unaffected by this phenomena, but researchers creating artificial aquatic systems should add sulphate to simulated water to ensure that Hg(II) is not erroneously quantified.

Another hotspot of mercury contamination of ecosystems that makes an excellent model system is Kejimkujik National Park in Southwestern Nova Scotia, Canada. Elevated concentrations of mercury in birds and fish have been found in the past, despite the wetland park being far away from emission sources. What makes the ecosystem particularly interesting to mercury biogeochemists is that the park contains a network of lakes, which all have contrasting water chemistry. O'Driscoll et al. (2018) collected water samples taken from 10 lakes in Kejimkujik National Park with a range of DOC concentrations, and determined photooxidation and photoreduction kinetics in filtered and unfiltered samples. While DOC was not related to gross photooxidation or photooxidation rates, it was negatively associated with photoreducible Hg(II) in unfiltered, but not filtered, water. This finding is indicative of a role played by both DOC and particulate matter (perhaps due to the flocculation of DOC) in determining the availability of Hg(II) for photoreduction. Changes in the DOC concentrations of freshwater lakes (both seasonal and multiannual) thus have implications for their Hg budget and for the availability of mercury to biota. DOC can also influence the degree to which mercury is demethylated in freshwater lakes. Klapstein et al. (2018) used water from Kejimkujik lakes to investigate the role of DOM in photodemethylation. The primary method by which mercury is demethylated in freshwater lakes is by photodegradation, but high DOM concentrations (especially DOM with a low photoreactivity) can inhibit MeHg photodemethylation. DOM photoreactivity was not found to be positively correlated to DOM concentration, but, over three years, there was a positive correlation between DOM and MeHg in high carbon lakes, suggesting that, in these lakes, MeHg is largely controlled by catchment transport, rather than photochemistry.

Rivers provide a vector for transport of upstream contamination to sensitive ecosystems downstream and, ultimately to estuaries and marine environments. Mercury associated with artisanal and small scale gold mining in South America has caused contamination of the Amazon basin. Water, DOC and sediment undergoes seasonal exchanges with tropical floodplain lakes in the Amazon basin. Maia et al., 2018) investigated whether this exchange of dissolved and particulate matter between the Curuai floodplain of the central Amazon and the river provided a net source or a sink of MeHg to the floodplain. Findings indicate that MeHg was mostly associated with particulate Al and Fe oxyhydroxides and DOC. A mass balance indicated that particulate MeHg is degraded at the sediment-water interface and exported to the Amazon river during periods of low flow. However, overall, the floodplain does not seem to be a source of particulate MeHg to the Amazon. Reservoirs undergo seasonally fluctuating water levels which causes alternate periods of inundation and exposure to soils on the banks of the reservoir. Xiang et al. (2018), collected soil samples from the banks of the Three Gorges Reservoir in Hubei province, China. The authors sequenced soil microbial communities and found a greater abundance and diversity of bacteria in soils undergoing alternating flooding and drying, compared to those that are never inundated, or always inundated. This difference in the microbial community was observed alongside greater MeHg concentrations and a greater proportion of the mercury present as MeHg in the seasonally inundated soils. A higher relative abundance of bacterial families *Deltaproteobacteria* and *Methanomicrobia*, which may include organisms capable of mercury methylation, were also found in the soils subjected to alternating flooding and drying conditions. Our understanding of the dynamics of MeHg as rivers transition from a terrestrial to marine, saline, environment in estuaries and how this influences the bioaccumulation of Hg by food webs is poor. To fill this knowledge gap, Reinhart et al. (2018) investigated the benthic and pelagic food web of the St John River estuary in New Brunswick, Canada. Stable isotope analysis ($\delta^{13}C$ and $\delta^{34}S$) confirmed that energy sources shifted in the transition from freshwater to saline, but the only biota for which MeHg concentrations significantly correlated with salinity along this gradient were chironomids, which were

positively correlated with salinity. As rivers discharge in to oceans, they can become significant sources to the coastal mercury budget. For example, rivers are a major source of mercury to the Baltic Sea. Much of this Hg discharged by rivers is associated with allochthonous materials as either dissolved or particulate organic matter. Gębka et al. (2018) used stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) in an attempt to identify the provenance of dissolved and particulate organic matter associated with mercury in river outflow from four river catchments in Northern Poland, into the Baltic Sea. While a clear relationship between organic matter provenance and mercury concentrations was not apparent, an 85% greater concentration of Hg in suspended particulate matter was observed during the winter months, which coincides with more coal being burned in power plants. The authors attribute this observation to a greater level of atmospheric deposition in the catchments, which then results in more Hg being exported from the catchment through the river.

Taken together, the papers presented in this special issue on Mercury Biogeochemistry and Fate represent a diverse, but coordinated, attempt to increase our understanding of how mercury moves between environmental compartments, how its biogeochemistry has been altered by anthropogenic activities, and how it may be influenced in the future by a changing climate. While the world has committed to reduce emissions of mercury, and transition away from products containing mercury, the legacy of mercury pollution will remain far into the future and these articles provide advances in the science required to remediate and mitigate ecosystems affected by mercury.

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