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Biogeochemical Processes of Mercury in Natural and Contaminated Environments

S. C. Brooks, *Organizer*

ABSTRACTS

GEOC 47

Impact of bioirrigation on benthic methylmercury flux from coastal marine sediments

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The efflux of sediment-produced methylmercury (MMHg) represents an important source of MMHg to coastal food webs. Furthermore, benthic bioirrigation can stimulate pore-water exchange. We investigated the relationship between dissolved MMHg fluxes and infaunal burrow densities in Boston Harbor sediments. We determined total MMHg fluxes using core incubations and estimated diffusive fluxes from dissolved MMHg gradients near the sediment-water interface. Total MMHg fluxes ranged from -4 to 191 pmol/m²/d, and total MMHg fluxes were linearly correlated with sediment burrow densities. Diffusive fluxes were much lower than total fluxes at three of the stations. These results indicate that MMHg exchange may be significantly enhanced over molecular diffusion in bioturbated sediments and that burrow density provides a strong predictor of total MMHg flux. Distributions of Rn-222, a tracer of pore-water exchange, also increased with increasing burrow densities, suggesting that the presence of burrows enhances both MMHg production and bioirrigation.

GEOC 48

Characterization of soil mercury in contaminated soils and sediments: Implications for *in situ* immobilization

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Accidental liquid mercury spills from 1920 to 1950 from a former Dupont-Rayon manufacturing facility resulted in widespread soil and sediment contamination some 30 miles along the South River in Central Virginia. Our work involved efforts to characterize Hg in a contaminated floodplain soil. SEM-EDX studies showed relatively large, overlapping domains of Hg and S, and to a lesser extent, Cu. XAS studies determined soil Hg species Hg(II) >> Hg(I), and predominantly coordinated by reduced S atoms. Exchange studies showed that Hg release did not necessarily correspond with total soil Hg content. The results of this study suggest that soil Hg exists mostly as cinnabar-type minerals, with minor proportion of Hg-metal (Cu, Fe) oxides. Soil cinnabar is more likely to release Hg under the floodplain's periodic inundation cycles. Preliminary XAS data suggests that Hg-metal oxides may prove superior for *in situ* remediation compared to sulfur- or carbon-rich adsorbents.

GEOC 49

Flow reduction to reduce mercury flux from contaminated sediments to surface water

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When clean river water was added to maintain stable minimum streamflow in the upper reaches of a mercury-contaminated creek, mercury concentrations and flux increased across a 400 m reach of stream near the point where additional flow was added. Deposits of metallic mercury lying on a clay hardpan underlying 50 cm of armored soft sediments were acting to generate high concentrations of dissolved mercury ($> 50 \mu\text{g/L}$) within the interstitial streambed water. Diffusion and advection of that water into the surface flow produced an additional flux of 1.0 - 2.0 g/d of Hg, a substantial fraction of the total mercury input to the creek. When reduction in flow augmentation cut headwater flow by 50%, mercury input decreased from 1.1 to 0.5 g/d. The action holds promise of reducing mercury inputs from the streambed without losing the ecological benefits of more stable temperature, flow, and water quality in the stream headwaters.

GEOC 50

Indicators of change in mercury loading in an area impacted by former mercury mining activity

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The Idrija mine in Slovenia represents the second largest Hg mine in the world. Also in this region Hg mining/refining activity has severely enhanced the mobilization of Hg. Mercury laden material remains in the region and acts as a continuous source of Hg that is carried downstream the river Idrijca and Soča that empties in to the coastal environment of the Gulf of Trieste, Northern Adriatic Sea, where active transformation of Hg takes place, resulting in elevated Hg levels in fish. A number of studies have been carried out, addressing Hg behavior in river and marine water and sediments, bank soil and biosphere. In particular, these included the partitioning of mercury between air/soil, soil/water, and sediment/water at the catchment scale including Isonzo river estuary and the Gulf of Trieste. Modelling tools were developed in order to simulate mercury transport, mass balances and transformation. One of the major objectives of these studies was to search for the best indicators of change in mercury loading in the river and marine waters (sediments, water, bacteria, periphyton, fish, and other aquatic organisms) and in the terrestrial environment. It was shown that bio-indicators such as epiphytic lichens and plants can be successfully used to assess the average mercury concentrations in air. Availability of mercury in soil was assessed by chemical methods such as sequential extractions procedures and by using terrestrial isopodes (*Poclelio scaber*) as well as mushrooms and plants. Animals at higher terrestrial trophic levels such as roe deer and other predators including wolf and lynx were also investigated. The main conclusion of these studies was that in contaminated sites, biomonitoring

techniques (mercury measurements and speciation in biota) in aquatic and terrestrial environment are very useful and can successfully be used as an early warning system for humans living in these environments.

GEOC 51

Mercury biogeochemistry beneath an *in situ* sediment cap

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In order to effectively evaluate *in situ* capping as a management strategy for mercury contaminated sediment, biogeochemical processes affecting mercury speciation must be thoroughly considered. Cap-induced biogeochemical changes and concomitant effects on methyl mercury production were observed in laboratory microcosms. Increases in methylation were observed beneath an *in situ* cap using sediment from Lavaca Bay, TX. A 1-dimensional, unsteady, reactive transport model was used to mathematically describe the complex, interrelated biogeochemical process known to affect mercury methylation. Anoxic conditions likely to occur beneath an *in situ* cap were also simulated in slurry experiments using sediment from three different environments. Mercury methylation, solid-phase partitioning, and aqueous speciation were evaluated in each of these environments using experimental observations and geochemical modeling. The results of this study provide a basis for evaluating the effectiveness of *in situ* sediment capping at mercury contaminated sites utilizing a fundamental understanding of the biogeochemical processes that control mercury methylation.

GEOC 52

Methylmercury production across San Francisco Bay regional habitats: Balancing benthic microbial activity and inorganic mercury availability

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The controls on toxic methylmercury (MeHg) production in sediments can largely be grouped into those that control either the activity of bacteria that methylate inorganic

divalent mercury (Hg(II)) or the availability of Hg(II) to those bacteria. The San Francisco Bay and its watershed is contaminated with mercury from both historic mining sources and contemporary anthropogenic inputs. For more than a decade, the USGS has conducted research into the factors that control benthic MeHg production in a diverse suite of habitats throughout this system, across a range of both salinity and hydrologic gradients. Consistent approaches were used throughout multiple individual regional studies to assess both rates of microbial activity and Hg(II) availability, as well as the geochemical constituents that influence each of these two major factors. This presentation will briefly summarize this body of research, the results of which are widely applicable to other diverse freshwater, estuarine, and coastal environments.

GEOC 53

Total Dissolved Methylmercury in Freshwaters: An Intercomparison of Water Vapor Distillation and Thiourea-Catalyzed SPE

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The current standard method for measuring dissolved methylmercury (MeHg) in freshwaters employs distillation to release MeHg from the sample matrix and ethylation-GC (D/E) with CV-AFS or ICP-MS to speciate and quantify the Hg. Here, we compare such measurements, made using isotope dilution/ICP-MS, to those of a new method that couples preconcentration by thiourea-catalyzed solid-phase extraction (TU-SPE) and Hg speciation analysis by Hg-thiourea complex ion chromatography with CV-AFS detection. Measurements of [MeHg] in split filtered water samples from streams, wetlands, and lakes in the Great Lakes region determined using the two methods are well correlated and are essentially identical in samples from waters in close contact with sulfidic sediments. However, in samples from well-oxygenated surface waters, D/E frequently recovers less than TU-SPE. The greater recovery of MeHg during TU-SPE appears to result from the much stronger ligand added to the sample releasing unexpectedly large amounts of MeHg that are tightly bound to the sample matrix. This fraction of MeHg does not volatilize during sample distillation and is detectable in distillation residues under analysis by TU-SPE. Within measurement error, the total MeHg in residues (measured by TU-SPE) plus distillates (measured by D/E) equals the mass of MeHg in whole samples analyzed by TU-SPE, but not D/E. These results lead us to hypothesize that natural waters contain an undistillable MeHg complex that is more stable and/or kinetically inert than previously known.

GEOC 54

Occurrence of monoethylmercury in the Florida Everglades: identification and verification

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Identification and verification of monoethylmercury ion (EtHg) in soil/sediment of the Florida Everglades were successfully accomplished via the use of various analytical techniques. Aqueous phenylation followed by purge and trap gas chromatography inductively coupled plasma mass spectrometry (ICP–MS) method was used for simultaneous identification and quantitation of monomethylmercury (MeHg) and EtHg. For the first time, spectra of EtHg derived from a real soil/sediment sample of the uncontaminated Florida Everglades were obtained, confirming the identity of EtHg. Stable isotope tracer technique, in combination with detection of ICP–MS, was used to elucidate the possibility of analytical artifact. The results suggest that EtHg originates from the soil/sediment samples of the Florida Everglades, but not artifact of the sample preparation or analytical procedures. EtHg in the soil/sediments analyzed was at ng/g level, similar to that of MeHg.

GEOC 55

Bioavailability of mercury to methylating bacteria in a northern Wisconsin wetland: Results from a year of field sampling

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The Allequash Creek wetland, near Boulder Junction, WI, USA is a groundwater-dominated, riparian system with a biogeochemically active hyporheic zone. Both inorganic mercury and methylmercury are present in the sediments and porewaters, and evidence strongly suggests that the latter is produced by *in situ* methylation. Through four field campaigns in summer, fall, winter, and spring, experiments were

carried out to measure the bioavailability of inorganic Hg(II) to methylating bacteria and the biogeochemical controls on methylation. Methylation and demethylation rate potentials were measured using stable isotopes of Hg(II) and methylmercury and ICP-mass spectrometry. Microbial activity rates and dominant metabolic pathways were determined using a radiolabeled organic carbon substrate in combination with a specific metabolic inhibitor. Complexes of mercury were separated by charge using an ion exchange resin. Through these and ancillary measurements, a picture is painted of the geochemistry underlying mercury methylation in this system.