

## MERCURY CONTAMINATION AND CYCLING IN THE COASTAL ZONE

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### **Background and Objectives**

Consumption of marine fish and seafood products is the principal pathway by which humans are exposed to the very toxic organo-mercurial, monomethylmercury (MMHg). Consequently, there is an urgent need for increased knowledge and understanding of the marine biogeochemical cycling of mercury (Hg) and the impact of anthropogenically related Hg inputs. Biologically productive, nutrient-rich near-shore regions, which support major commercial and recreational fisheries, are of special interest. Accordingly, our EPA-STAR Hg research is focused on Long Island Sound (LIS), its watershed, and river-seawater mixing zones. This major natural resource can provide a valuable analog for other near shore/urban marine ecosystems. Our process-reaction focused investigations are designed to allow the results to be applied in other marine regions. Such an approach is essential given the complexity and variability of fertile estuaries and adjacent coastal waters, which are major repositories for natural and pollutant riverborne/watershed derived substances such as Hg. Our specific objectives are concerned with several major features of the aquatic biogeochemistry of Hg, particularly elemental mercury ( $\text{Hg}^0$ ) cycling and emissions, MMHg production, interactions between terrestrial watersheds, rivers and near shore marine waters, and the role of organic matter in governing the availability of Hg for competing methylation/reduction reactions.

Rather than trying to include all of our research on Hg cycling in the coastal zone, this discussion is focused on the mechanisms of MMHg formation. The cycling of MMHg in marine environments, especially biologically productive coastal regimes, is understudied. Despite the paucity of information concerning the sources, *in situ* production, biogeochemistry, and bioaccumulation of MMHg in near shore marine sediments appear as potentially significant sources of MMHg to food webs in the coastal zone, and possibly the open ocean via hydrological or biological transport. Such sediments often

are a major repository of pollution-derived Hg that has accumulated over the past 150 years ("legacy Hg"). Additionally, they host active communities of sulfate-reducing bacteria (SRB)—the principal group of organisms mediating transformation of inorganic Hg to MMHg. The activity of SRB in coastal marine sediments is extraordinarily large; they mineralize most of the organic carbon. Given the combination of potential reactants (SRB, large burdens of "legacy Hg" and modern Hg inputs), we posited considerable production of MMHg in near shore sediments.

Our three-part working hypothesis consists of the following postulates; (1) sedimentary Hg methylation by SRB is an important source of MMHg in the coastal zone, (2) bioturbation enhances Hg methylation in marine sediments, and (3) reworking of sediments by benthic infauna makes a portion of potentially immobile "legacy Hg" (e.g., Hg sequestered in solid sulfide phases) available for microbial MMHg production. These hypotheses are being tested in our local coastal waters of LIS, a large (3200 km<sup>2</sup>) coastal embayment in the northeastern United States that supports a highly productive commercial and recreational fishery. LIS is the subject of numerous biogeochemical investigations and a long-term monitoring program of its water quality. Current and historic pollution, including sewage, has perturbed LIS significantly. As a consequence, it has longitudinal gradients in pollutant Hg, sediment geochemistry and benthic infaunal and microbial activities. Such gradients in LIS are expected to encompass the range of sediment characteristics found in most other coastal regimes. Thus, information on the biogeochemistry of MMHg in LIS is directly applicable to comparable coastal marine sediments and systems.

## Methods

We examined the biogeochemistry of MMHg in sediments of LIS in March, June, and August. Box cores were collected from the *R/V John Dempsey* (CT DEP) and the *R/V Connecticut* (University of Connecticut). A gradient in sediment type exists longitudinally in LIS, ranging from fine-grain, organic-rich substrate in the western Sound (WLIS) to large grain size (sandy), low organic material in the east (ELIS). We collected surface sediment (top 8 cm) from three representative locations along the sediment-type continuum, examined concentrations of total Hg and MMHg, and evaluated the influence of microbial activity and selected sediment characteristics on Hg levels. Rates of Hg methylation were assayed by injecting a <sup>200</sup>Hg-enriched standard (stable isotope) into sediment cores and incubating at ambient conditions. Methylmercury produced from the isotope (CH<sub>3</sub><sup>+</sup><sup>200</sup>Hg<sup>+</sup>) was determined by inductively coupled plasma mass spectrometry (ICPMS).

## Results and Discussion

The highest rates of Hg methylation in sediment are associated with the zone of transition from oxic to anoxic, sulfidic pore waters (i.e., redox transition zone). Both MMHg and total Hg (organically-bound Hg, inorganic Hg and MMHg) were related positively with organic matter in surface sediment; however, rates of Hg methylation were inversely

related to organic matter. In other words, although comparatively more MMHg was present in organic-rich western LIS sediments, the rate of Hg methylation was greater in the eastern Sound. We hypothesize that organic matter affects Hg methylation by influencing partitioning of inorganic Hg between dissolved and particulate phases, thereby regulating the availability of dissolved Hg to methylating bacteria. More dissolved Hg is available to methylating bacteria in ELIS where sediment organic matter levels are lower.

Higher methylation rates in ELIS can also be attributed to the effect that sulfide has on Hg speciation, and, subsequently, bioavailability of dissolved Hg complexes to methylating bacteria. We suggest that elevated sulfide levels inhibit the bioavailability of Hg for methylation in WLIS as compared to ELIS sediments. Sulfide affects the chemistry of inorganic Hg in sediments by forming dissolved Hg-sulfide complexes, including  $\text{HgS}^0$ ,  $\text{HgS}_2^{2-}$ , and  $\text{HgHS}_2^-$ . The uncharged species ( $\text{HgS}^0$ ) is a major dissolved Hg-sulfide complex when sulfide concentration is low, and charged complexes, mainly  $\text{HgHS}_2^-$ , are dominant at higher sulfide levels. The mechanism for uptake of inorganic Hg by methylating bacteria is thought to be due to diffusion of neutrally charged  $\text{HgS}^0$  through the cell membrane. Consequently, maximum rates of Hg methylation in sediment occur where sulfide levels are low. Sediments in ELIS have lower concentrations of sulfide, and this favors speciation of dissolved inorganic Hg as  $\text{HgS}^0$  and its subsequent methylation to MMHg.

Marine sediments are mixed and irrigated by benthic infauna (i.e., bioturbation) and such disturbance may enhance Hg methylation. Over long time scales (years to decades), the feeding habits and subsurface migration of benthic infauna redistribute sedimentary particles to depths of greater than one meter in sediment. On much shorter time scales (hours to days), bioturbation also can transport particles to depths of at least 10 cm and affect the chemistry of pore water in surface sediments. Unlike WLIS, the sediment profile of  $^{200}\text{Hg}$  methylation in the eastern Sound varies dramatically with depth. Such excursions of the  $^{200}\text{Hg}$  methylation rate corresponded to peaks in a bioturbation index (change in organic carbon normalized to change in depth in sediment), suggesting a link between physical sediment disturbance and enhanced Hg methylation in coastal marine sediments. Bioturbation seems to introduce fresh organic matter to depths where active sulfate reduction occurs, or it may promote chemical conditions that favor dissolution of inorganic Hg substrate, both of which may result in increased methylation in sediment.

## Conclusions

The estimated sediment-water flux of dissolved MMHg ( $\sim 11 \text{ kg y}^{-1}$ ) points to sedimentary production and mobilization of MMHg as the principal source to LIS. Additionally, bioaccumulation estimates suggest that most of the MMHg in LIS plankton is attributable to sedimentary synthesis and mobilization. Assuming that all of the sediment-derived MMHg is accumulated by phytoplankton in LIS, which has  $200\text{-}400 \text{ g C m}^{-2} \text{ y}^{-1}$  primary production, we predict that they would have  $0.7\text{-}1.4 \text{ ng MMHg g}^{-1}$  wet weight. Our average measured level of MMHg in suspended particulate matter of LIS,

most of which is autochthonous, is  $0.9 \text{ ng g}^{-1}$ . Therefore, it is likely that most of the MMHg in higher trophic levels of LIS, which ultimately derive organic matter and MMHg from primary producers, also can be attributed to Hg methylation in the sediments.