N.H. Sea Grant Research Project Completion Report

Today's date: July 13, 2011

Project number: R/CE-139

Project title: Mercury dynamics in estuarine sediments: biogeochemical controls on bioavailability and bioaccumulation along a chemical gradient

Project initiation date: 6/1/08

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Technicians, industry partners, collaborators, etc. (specify which) and affiliations:
Deenie Bugge (Technician), Vivien Taylor (Post-doctoral Associate)

Brief project overview/Abstract:
We are interested in mechanistically assessing the role of estuarine sediments as long-term sinks or sources of Hg and MeHg, and investigating the link between MeHg production and mobilization in sediments to its bioavailability and bioaccumulation by resident benthic communities. We performed a) pore-water and sediment Hg, MeHg and ancillary chemistry analyses, b) analysis of abundance and diversity of targeted microbial communities and mer genes using molecular techniques, and c) analysis of the Hg and MeHg in benthic primary consumers and benthic omnivores.

Objectives:
a) To understand the biogeochemical controls on Hg and MeHg transformation in and mobilization from the sediment pore waters with respect to changes in organic matter concentration and the benthic infaunal density.

b) To link MeHg production and mobilization in sediments to the bioavailability and bioaccumulation of Hg and MeHg by resident intertidal benthic communities.

Research findings/accomplishments/progress to date:
2008 Field Research
We conducted a complete field sampling campaign in August 2008 at four sites in Great Bay estuary. These sites included Portsmouth mudflats, Squamscott mudflats, Chapman Spartina salt marsh and a salt panne in the same salt marsh. At each site, we performed the following measurements: pore-water concentrations of inorganic Hg, MeHg, hydrogen sulfide, iron, DOC, alkalinity and pH; sediment concentrations of inorganic Hg, MeHg, acid-volatile sulfide, organic carbon content, and porosity; sediment microbial analysis, including concentrations of sulfate reducers, iron reducers (geobacter), methanogens, and the mer-A gene; inorganic Hg and MeHg concentrations in fish (Fundulus), green crab and polychaetes.
Results show the same level of total Hg contamination at both mudflats, but considerably lower concentrations of pore-water inorganic Hg in Portsmouth mudflat than in Squamscott mudflat. This, together with significantly lower AVS, methanogen and mer-A concentrations in Portsmouth mudflat than in Squamscott mudflat has prompted us to consider the potential role of bioturbation at the former site. Squamscott mudflat had significantly higher sediment MeHg concentrations than Portsmouth mudflat. Pore-water MeHg was also higher in the former site close to the sediment-water interface. As we had previously hypothesized, the MeHg concentration was highest at the sediment-water interface in the salt panne possibly due to the presence of ponded water.

The MeHg biota:sediment concentration factor (BSCF) in Fundulus was higher in Portsmouth mudflat (118) compared to that in Squamscott mudflat (37). The same trend was also observed for the crab and the polychaete at both sites. This is largely due to lower sediment MeHg concentrations at Portsmouth mudflat. Recent studies have shown a greater MeHg flux, but not necessarily higher MeHg production, at sites that are more subject to bioturbation.

2009 Field Research
We conducted field sampling in May 2009 and September 2009 at three sites, and July 2009 at one site in Great Bay estuary. Our results from August 2008 allowed us to hypothesize that bioturbation may have an important role in MeHg dynamics and bioaccumulation by higher organisms. We tested this hypothesis by collecting chemical, microbial and biological samples in May, July and September of 2009. In May and September, full chemical and microbial analysis of the mudflats and the salt panne was performed. In July, samples from the salt panne were only collected and analyzed. September samples included benthic invertebrates samples for density and taxonomy to quantify differences in the bioirrigation potential of the Portsmouth and Squamscott mudflats.

Our geochemical analyses show that sediments at both mudflats are physically mixed (inferred from the 7Be data), albeit via different mechanisms. Sediment mixing at Portsmouth was due to the presence of polychaetes, whereas at Squamscott, it was due to flow and sediment transport. At both sites, 7Be data showed mixing down to a depth of 10 cm. At Portsmouth, bioirrigation by the benthic infauna resulted in introduction of oxygen into the sediment and flushing of sediment porewater. High concentrations of protein-like labile DOC were found at down to a depth of 10 cm at Portsmouth, whereas porewater DOC at Squamscott was largely consisted of humic and fulvic acids. The labile DOC is known to promote microbial growth and Hg methylation. Introduction of oxygen into Portsmouth sediment resulted in relatively high concentrations of Fe(III) hydroxide that in turn resulted in removal of inorganic Hg from the porewater. This may cause less inorganic Hg available for methylation. We did not directly measure sediment fluxes of species, but it is well known that sites that are subject to bioirrigation exchange chemical species with the overlying waters continuously. This can result in high frequency release of MeHg into the overlying water.

2010 Field Research
We conducted field sampling and full chemical analysis in June 2010 and September 2010 at three mudflat sites, Portsmouth, Squamscott and Adam’s Point, in Great Bay estuary. In contrast to our previous observations, the infaunal benthic activity at Portsmouth was lower, particularly in September 2010. This caused a considerably lower solid-phase Fe(III) hydroxide concentration at this site, which in turn resulted in a higher porewater total Hg and sediment MeHg concentrations. In June 2010, during the time between the deployment and the withdrawal of the peepers, there was evidence for 5 cm of freshly deposited sediment at the Squamscott mudflat. Perhaps due to the presence of this fresh sediment, high sediment MeHg
concentrations were relatively broader at this site, spanning from 1 to 7 cm. In contrast, in September 2010, there was evidence of 5 cm of sediment erosion at Squamscott mudflat. Sediment erosion exposed sulfidic sediments that produce little MeHg, and as a result, there was relatively lower MeHg in Squamscott sediment in September 2010. The Adam’s Point mudflat at the times of sampling was subject to physical mixing by horseshoe crabs. The AVS at this site, however, was higher, and sediment MeHg concentration was lower at Adam’s Point than the other two sites.

**Impacts to date:**

The long term impacts of our research to date will be in clarifying the relationship of sediment biogeochemistry with bioavailability of MeHg in aquatic organisms. Our findings suggest that MeHg concentrations in sediments alone do not determine bioavailability to intertidal organisms and that ecologically mediated processes such as bioturbation and bioirrigation may enhance the flux of MeHg to the water column and increase bioavailability while geochemical factors such as carbon may reduce bioavailability of MeHg.

**Problems encountered:**

We have not encountered any major problems. However, due to the highly dynamic nature of the *Spartina* salt marsh and its possible influence on Hg cycling, we decided not to pursue sampling at the upland sites. Porewater samples from 2010 were analyzed at the Dartmouth Trace Element Analysis core facility and blanks for inorganic Hg were high resulting in unuseable data.

**Publications (please attach PDF or send a hardcopy if available)**

**Peer reviewed publications:**

**Pending publications:**

Voytek M.A., A. Amirbahman, J. Kirshtein, C.Y. Chen, Understanding Mercury dynamics in estuarine systems through microbial community analysis. (in prep.)

**Presentations to date, with published abstract citation if applicable:**


**Students Supported**

**Student name:** Lauren E. Brown

Institution/Department: University of Maine

Duration of support: 2 years

Type of support (stipend, travel, supplies, etc.): stipend, travel, supplies

Type of degree (undergrad, masters, PhD): M.S.

Year degree awarded: 2010

Title of thesis (if supported by N.H. Sea Grant): Sedimentary mercury dynamics at two estuarine mudflats in Great Bay, N.H.