E3S Web of Conferences **1**, 33004 (2013)
DOI: 10.1051/e3sconf/20130133004

An examination of the factors controlling net methylation in estuarine sediments: Results from measurements and models

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Abstract. An examination of the distribution of mercury and methylmercury across estuarine ecosystems in the northeast USA was completed under a number of projects. Sites ranged from Maine to the Chesapeake Bay and included both pristine and contaminated sites. In addition to measurements of bulk sediment and porewater, methylation and demethylation rates were also measured. Results showed that the relationships between sediment-porewater partitioning and methylation potential with sediment organic content are complex and that sediment organic content alone is not always a good predictor of the potential for a system to produce methylmercury. Modeling and correlations between variables suggest that the sulfur content of the system needs to be considered and for high organic content sediments, both sulfur and organic content.

Key words: Mercury, methylmercury, coastal, methylation, demethylation, bioaccumulation

Introduction

Monomethylmercury (CH_3Hg) is a neurotoxin that can cause long-term developmental delays in children, effects on fetal growth, and has been linked to impaired cardiovascular health in adults (Karagas et al., 2012; Fitzgerald and Clarkson, 1991). For most fish eating populations, marine fish are the major source of human exposure to CH_3Hg. Most of the inputs of Hg to the ocean are from the atmosphere but it appears that most of the CH_3Hg is produced within the coastal and open ocean environment (Mason et al., 2012). Therefore, we need to improve our understanding of how changes in emissions of mercury (Hg) on a global scale, and inputs of Hg to coastal systems, affect concentrations in coastal and open ocean fish. Better constraints on estimated lifetimes of different Hg forms in marine ecosystems and of the biogeochemical factors driving interspecies conversions are needed to understand factors controlling accumulation in marine food webs.

A recent literature review concluded that coastal systems and methylation in coastal sediments are not important in terms of bioaccumulation of CH_3Hg into open ocean fish (Mason et al., 2012). However, the majority of the global fish/shellfish harvest for human consumption is from the coastal fisheries (FAO 2008) and it is apparent from numerous studies that methylation within estuarine and coastal waters is important for exposure of estuarine, coastal and migratory fish. For this reason, we have focused on coastal systems across the eastern USA in a number of studies to evaluatethe factors controlling the net methylation of Hg in these ecosystems, as well as its bioaccumulation. This paper will focus on the biogeochemical aspects and will attempt to synthesize the recent advances made in understanding Hg fate and transport, and methylation, and CH_3Hg demethylation in coastal environments.

Materials and Methods

We examined the concentrations of Hg, CH_3Hg and ancillary parameters such as natural organic matter (NOM) and reduced sulfide species in sediments and porewaters across a geographic range of estuarine locations. The locations chosen differed substantially in total mercury (HgT) and organic carbon loading and included sites from a number of studies (Hollweg et al., 2009; Schartup et al., 2012). The main goal was to examine the underlying mechanisms controlling differences between ecosystems, and to develop models of sedimentary Hg and CH_3Hg cycling, and to examine

the main sources of CH_3Hg in these systems. The estuarine sites that were selected for their biogeochemical characteristics, Hg content, and location and are in the Northeastern US: Wells, ME; Portsmouth, NH; Long Island Sound (CT, NY); Hackensack, NJ; Delaware River, DE and Chesapeake Bay, (MD, VA)(Fig. 1). There were several sampling sites within each location which varied in water depths, salinity and other physical factors. Sites were also examined in terms of their potential for net *in situ* Hg methylation by estimating both Hg methylation and CH_3Hg degradation rates using stable isotope spike enrichment incubation experiments (Hollweg et al., 2009; Hintelmann and Evans, 1997).

Fig. 1. Locations of the sampling sites along the northeastern USA.

Samples were analyzed using standard techniques for Hg and MeHg, developed during our studies in the Chesapeake Bay (Hollweg et al., 2009; 2010) and further refined in our recent studies (Schartup et al., 2012). When possible, sediment Hg content was quantified using a DMA 80 solid phase Hg analyzer. Otherwise, Hg was determined after digestion and oxidation with bromine monochloride (BrCl) by tin chloride ($SnCl_2$) reduction. The elemental Hg formed was sparged and trapped on gold columns prior to quantification. In most studies CH_3Hg was determined after distillation of the sample prior to ethylation derivitization, sparging and trapping on Tenax. Depending on the sample, cold vapor atomic fluorescence (CVAFS) or ICP-MS were used to quantify the amount of Hg or CH_3Hg trapped on the columns (gold or Tenax) (Hollweg et al., 2009).

Methylation rates were determined based on the measured amount of Hg isotope methylated during the incubation time. Demethylation rates were based on the loss of the CH_3Hg isotope (Hintelmann and Evans, 1997; Hollweg et al., 2009).

We used the data to further develop a model for the partitioning of Hg between the sediments and porewater (Hollweg et al., 2012). This model is being used here to examine the factors controlling Hg methylation in sediments and the speciation and flux of CH_3Hg from sediments to the water column, as done for the Chesapeake Bay (Hollweg et al., 2010).

Results and Discussion

Sedimentary HgT concentrations ranged across many orders of magnitude, increasing in concentration from the pristine, sandy sediments of Wells (WME), to industrially contaminated areas like Portsmouth (PNH) and the Hackensack River (HNJ) (Table 1). Total Hg (HgT) and CH_3Hg were correlated across all the ecosystems, and overall the $\%CH_3Hg$ (fraction of HgT as CH_3Hg) was within a similar range across sites. The contaminated sites had comparable $\%CH_3Hg$ even though these sites also had high %LOI, and this appears to counter some literature that has shown a decrease in methylation rate with increasing sediment organic content (e.g. Hammerschmidt and Fitzgerald, 2004; Ogrinc et al., 2007). Elevated methylation potentials were found in the pristine (low organic matter) sites, as found by others (e.g. Hollweg et al., 2009) but high methylation potentials and rates were also measured at organic matter rich sites, which were often highly contaminated (Schartup et al., 2012). To examine these relationships further, we normalized the sediment Hg to carbon (pHg/C = -log[Hg]/[C]). Values of pHg/C ranged over orders of magnitude, from 5 to 7.5, and were highest in the more pristine environments. It appears for these higher pHg/C sites that methylation rate does decrease with decreasing pHg/C but at an intermediate value (pHg/C ~ 6.5) the methylation rates begin to increase and the methylation potential for the more contaminated (low pHg/C) sites is equivalent to that of the pristine sites. Thus, we suggest that high organic content sites are not always sites with low methylation potential. One likely explanation for the observed trends is that at the highly contaminated sites, partitioning is not controlled by organic carbon alone. We found that in these high NOM locations that reduced sulfur content was also high and we suggest that elevated inorganic sulfide phases and dissolved sulfide may be competing with NOM, and is the primary binding phase for Hg at high NOM.

The partitioning results support this idea. The relationship between sediment organic matter and binding capacity (distribution coefficient [K_d]) is linear below 6% LOI, but not above this value. The relationship between K_d and total sediment sulfur is also linear at low concentrations but at high sulfur content, the relationship appears to reach an asymptote. This suggests that there is a higher fraction of the Hg in the porewater than would be expected at these high NOM, high sulfur sites. Overall, this is sufficient to drive the higher methylation potentials. Modeling suggests that only a small fraction of the organic matter is responsible for mercury binding at these sites (Hollweg et al., 2012; Skyllberg, 2008) and that this results in the decoupling between LOI and K_d. The lack of a uniform methylation-organic matter relationship suggests that other site-specific factors need to be considered in studies of Hg methylation.

Table 1. Bulk sediment characteristics for the various sampling locations: Wells (WME), Portsmouth (PNH), Long Island Sound (LIS), Hackensack (HNJ), Chesapeake Bay (CBY) and Delaware River (DEL).

Site	HgT nmol/g	MeHg pmol/g	%MeHg	%LOI
WME	<0.05	0.03-0.7	0.2-1.3	0.7-3.1
PNH	1.3-3.8	2.8-7.1	0.2-0.3	6.4-11.2
LIS	0.2-1.3	1.4-8.7	0.2-0.7	2.8-11.4
HNJ	1.9-7.5	10-17	0.2-0.5	3.8-8.1
CBY	0.1-0.9	1-7	0.3-1	2.0-10
DEL	1.5-4	3-5	0.1-0.3	-

Acknowledgements

This research was completed with funding from the National Science Foundation, the National Institute of Environmental Health Sciences (Grant # P42 ES007373) and the Delaware River Basin Commission/Dept of Natural Resources and Environmental Control. Much of the work was completed as part of the PhD thesis of Amina Schartup. We thank current and former students and post-docs in the Mason and Chen labs for support in sample collection and analysis, and in data interpretation.

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