Estuarine, Coastal and Shelf Science 159 (2015) 50–59

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: www.elsevier.com/locate/ecss

Controls on methylmercury accumulation in northern Gulf of Mexico sediments

Bian Liu [a], Laurel A. Schaider [a], Robert P. Mason [b], James P. Shine [a], Nancy N. Rabalais [c], David B. Senn [a, *]

[a] Department of Environmental Health, Harvard T.H. Chan School of Public Health, 401 Park Dr., Boston, MA 02215, USA
[b] Department of Marine Sciences, University of Connecticut, 1080 Shennecossett Rd., Groton, CT 06340, USA
[c] Louisiana Universities Marine Consortium, 8124 Highway 56, Chauvin, LA 70344, USA

ARTICLE INFO

Article history:
Received 9 January 2015
Accepted 24 March 2015
Available online 1 April 2015

Keywords:
mercury
methylation
demethylation
sediment
organic carbon
coastal ecosystem

ABSTRACT

We examined Hg biogeochemistry in northern Gulf of Mexico (nGOM) sediments along a ~400 km east–west transect off the Louisiana coast in order to characterize primary controls on net methylmercury (MeHg) production and accumulation in sediments and evaluate the potential influence of water column hypoxia. Total Hg (THg) and MeHg concentrations ranged from 52 to 340 pmol g^{-1} and 0.08 to 1.4 pmol g^{-1}, respectively, and exhibited no clear east–west spatial trends, or trends related to water column hypoxia. Potential methylation and demethylation rate constants (k_m and k_{dm}), from enriched isotope spikes (^{201}Hg(II) and Me^{199}Hg) to intact sediment cores, were substantially higher (0.02–0.19 d^{-1} and 39–63 d^{-1}, respectively) than in other coastal sediment systems. The percentage of Hg present as MeHg in sediment cores (%MeHg = 0.04–1.1%) was comparable to other systems. Both %MeHg and k_m decreased with sediment depth and were significantly correlated, but neither was correlated with organic carbon (OC). Together, OC and k_m explained 56% of the variation in [MeHg]. These results suggest that OC primarily acts as a MeHg-binding ligand in nGOM sediments, unlike some other coastal systems where OC has been shown to directly influence Hg methylation.

1. Introduction

It is crucial to understand the factors that influence the production and bioaccumulation of methylmercury (MeHg) in coastal environments given that the majority of fish consumed by humans in the United States (US), and most of the world, comes from coastal and marine waters (US EPA, 2002a; Sunderland, 2007; Driscoll et al., 2013) and consumption of fish is the major route of MeHg exposure (US EPA, 1997b). In many locations, such as the Gulf of Mexico, coastal fish represent a substantial fraction of the commercial and recreational catch (Lincoln et al., 2011; Harris et al., 2012), and in such locations, understanding the biogeochemical cycling of Hg in sediments is important, as recent studies have suggested that *in situ* production of MeHg in coastal sediments is a major source of MeHg to the overlying water column and biota (Mason et al., 1999; Balcom et al., 2004; Sunderland et al., 2006; Hammerschmidt et al., 2008; Hollweg et al., 2009, 2010), though this may not always be the case (Balcom et al., 2010; Sunderland et al., 2010; Chen et al., 2014).

Mercury dynamics in coastal sediments are controlled by a complex set of interrelated biotic and abiotic factors (Ullrich et al., 2001; Fitzgerald et al., 2007; Merritt and Amirbahman, 2009; Driscoll et al., 2012; Chen et al., 2014). Methylation of ionic inorganic mercury (Hg(II)) to MeHg is thought to primarily occur as a by-product of anaerobic microbial activity, in particular by sulfate-reducing bacteria (SRB; Compeau and Bartha, 1985; Choi and Bartha, 1994), iron-reducing bacteria (Fleming et al., 2006; Kerin et al., 2006), and potentially other microorganisms as suggested by the recent discovery of methylating genes in a variety of anaerobic organisms (Gilmour et al., 2013; Parks et al., 2013). For coastal sediments, SRB are likely the dominant methylators, as demonstrated in the Chesapeake Bay (Hollweg et al., 2009), since they are the main organisms responsible for organic matter degradation in coastal ecosystems (Capone and Kiene, 1988). The net production of MeHg and the quasi-steady state MeHg concentration in sediments are dictated by both the activities of methylating microbes (Compeau and Bartha, 1985; Choi and

* Corresponding author. Current address: San Francisco Estuary Institute, 4911 Central Avenue, Richmond, CA 94804, USA.
E-mail address: davids@sfei.org (D.B. Senn).

http://dx.doi.org/10.1016/j.ecss.2015.03.030
0272-7714/

Bartha, 1994) and the bioavailability of inorganic Hg species for methylation (Benoit et al., 1999, 2003; Hammerschmidt and Fitzgerald, 2004; Hsu-Kim et al., 2013; Jonsson et al., 2014), as well at the extent of demethylation. While methylation is primarily confined to anaerobic environments, demethylation occurs in both oxic and anoxic environments, and therefore can strongly influence net MeHg production and accumulation in sediments (Hintelmann, 2000; Whalin et al., 2007; Drott et al., 2008b; Hollweg et al., 2009). In addition, the flux of MeHg from sediments to the water column, which depends on sediment biogeochemistry and physical and biologically-mediated advection (Boudreau, 2000; Tseng et al., 2001; Sunderland et al., 2004; Liu et al., 2009), also influences the transfer of MeHg from sediments to aquatic food webs (Fitzgerald et al., 2007; Merritt and Amirbahman, 2009; Driscoll et al., 2012; Chen et al., 2014).

Although there is consensus on the abiotic and biotic factors that influence MeHg dynamics in sediments (Fitzgerald et al., 2007; Merritt and Amirbahman, 2009; Hsu-Kim et al., 2013), it remains difficult to predict net MeHg production and MeHg concentrations across systems and the exchange between sediments and overlying water. The complexity is well-illustrated by the linkages among sediment MeHg and cycling of organic carbon (OC) and sulfur (S) (Schartup et al., 2013, 2014). Moderate amounts of OC and mildly reducing conditions are optimal for Hg(II) methylation by providing sufficient substrate to support SRB activity and enhancing the amount of bioavailable Hg, such as dissolved neutrally charged Hg species (HgS^0, HOHgSH, $Hg(SH)_2$) and nanoparticulate HgS (Benoit et al., 1999; Graham et al., 2012; Hsu-Kim et al., 2013). Positive correlations have been observed between dissolved OC (DOC) and MeHg production, as reflected by dissolved MeHg (Hall et al., 2008) or by methylation potentials (Mitchell and Gilmour, 2008). However, higher levels of labile OC, which promote greater SRB activity and higher levels of sulfide, do not necessarily translate into higher methylation rates. The increased dissolved S(-II) leads to a shift in dissolved Hg speciation towards less bioavailable negatively charged Hg–S complexes, including Hg bound to sulfide in sediments, thus limiting the amount of Hg(II) that is bioavailable to SRB (Gilmour et al., 1998; Benoit et al., 1999; Jonsson et al., 2014). In addition, because OC strongly binds Hg(II) (Ravichandran, 2004; Skyllberg, 2008), high levels of OC in the sediments can also decrease dissolved Hg(II) in porewater and hinder methylation (Hammerschmidt and Fitzgerald, 2004; Hammerschmidt et al., 2008; Hollweg et al., 2009). In some ecosystems, sediment OC was found to be negatively correlated with methylation potentials while positively correlated with the sediment-water partitioning coefficient of total Hg and MeHg (Hammerschmidt and Fitzgerald, 2004; Hammerschmidt et al., 2008; Hollweg et al., 2009). On the other hand, the presence of DOC can enhance methylation by limiting the growth of nanoparticles (β-HgS(s)) that have low bioavailability (Graham et al., 2012). Moreover, recent studies across a large number of estuarine environments suggests that OC is not the primary factor controlling partitioning and bioavailability of Hg for methylation in coastal sediments, and that total sediment S provides a better measure of these factors (Schartup et al., 2013, 2014). More information is needed to examine these apparently conflicting observations and to better understand the processes that influence MeHg production in coastal marine sediments.

To help further elucidate the controls on net MeHg production and accumulation in coastal sediment, we conducted a study in the northern Gulf of Mexico (nGOM), along a ~400 km east–west transect off the coast of Louisiana, US. While there have been a number of studies focused on more northerly temperate estuarine and coastal regions in North America, and estuarine systems in the sub-tropics, there has been little study of the biogeochemical dynamics in regions such as the Gulf of Mexico, a subtropical coastal ecosystem where there is a dominant freshwater source (the Mississippi-Atchafalaya River system). Additionally, this area is an important region for both commercial and recreational fisheries and is a region potentially impacted by both terrestrial and *in situ* sources of MeHg (Rice et al., 2009; Harris et al., 2010; Senn et al., 2010; Lincoln et al., 2011; Harris et al., 2012). The coastal area of nGOM west of the Mississippi River delta supports a highly productive fishery that accounts for ~70% of the overall GOM commercial fishery landings and ~40% of the dockside value (NOAA, 2007). Further, the regional population consumes fish/seafood (in particular locally-caught) at higher rates than the general US population (Lincoln et al., 2011; Harris et al., 2012), so local sources of fish, and therefore locally-produced MeHg, are more important components of MeHg exposure in this region. However, less is known with regard to the MeHg production in the sediment of nGOM compare to other regions of the US coastline.

This work builds on our previous study (Liu et al., 2009) in this region that characterized changes in sediment Hg biogeochemistry following major large-scale physical disturbance events caused by hurricanes in nGOM. The current study explores sediment Hg biogeochemistry in nGOM under more typical conditions and the factors influencing net MeHg production. We developed multivariable regression models to assess the influence of multiple sediment parameters on MeHg accumulation, as well as potential spatial variations and water column hypoxia. The current study also presents the first estimates of potential Hg methylation and demethylation rates using isotopically-enriched Hg spikes for the region, and provides updated information on Hg dynamics in nGOM to inform future studies, such as those developing models to estimate Gulf-wide Hg budgets, and to reconcile discrepancies about the controls on net MeHg production and bioaccumulation across the coastal systems.

2. Methods

2.1. Sample collection and analysis

Box cores were collected along a ~400 km east–west transect (Fig. 1) in July 2005 (7 stations) and July 2006 (10 stations), and smaller-scale surveys focusing on the eastern stations were conducted in October 2005 (5 stations) and March 2006 (5 stations). Data collected at 7 stations between July 2005 and July 2006 were discussed in Liu et al. (2009). The current paper focuses primarily on the July 2006 sampling as it covered the broadest area of nGOM, and only makes limited use of data from other dates.

One set of cores from each station was sectioned into 1 or 2 cm increments and immediately frozen for laboratory analyses of acid volatile sulfide (AVS) and OC. AVS was measured by adding 1 M HCl to slightly thawed sediment samples at room temperature, purging with N_2 and trapping liberated H_2S in a zinc acetate buffer, and measuring ZnS formation using spectrophotometrically (US EPA, 1996). OC was measured in sediment samples that were first treated with HCl to remove carbonates (US EPA, 1997a), and subsequently analyzed by combustion, GC separation, and thermal conductivity detection (Perkin Elmer 2400, PerkinElmer, Shelton, CT). These cores were also used for subsequent analyses of major and trace elements such as S and Al using polarized energy-dispersive X-ray fluorescence (XRF) spectroscopy (Liu et al., 2009).

Another set of cores from each station was used to measure dissolved oxygen and to collect and analyze porewater. Dissolved O_2 was measured by lowering a microelectrode (Lazar, Los Angeles, CA, USA) into an intact sediment core incrementally at millimeter resolution. At a subset of stations, 2–3 cores were sectioned aboard the ship into 1 cm or 2 cm increments in a N_2 glovebox and