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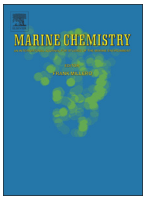

Effects of bottom water oxygen concentrations on mercury distribution and speciation in sediments below the oxygen minimum zone of the Arabian Sea

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ABSTRACT

This study investigated the influences of varying dissolved oxygen (DO) levels in overlying bottom water, sediment grain size, total sedimentary organic carbon (C_{org}), and total sedimentary sulfide concentrations on the distribution and speciation of mercury (Hg) and methylmercury (MeHg) in coastal sediments from a transect across the oxygen minimum zone (OMZ), in the Arabian Sea, off the west coast of India. The C_{org} concentration increased with the increasing finer particulate in the sediments and decreasing DO level of the overlying bottom water. Increasing concentrations of C_{org} (under suboxic overlying water) increased accumulation of Hg in the sediments. However, depleted DO level of the overlying bottom water did not enhance the concentration of MeHg in the underlying sediments. The concentration of sedimentary MeHg decreased with the increasing C_{org} and total Hg concentrations in the sediments. The nature of the C_{org} played a key role in controlling the distribution and speciation of Hg in the sediments. This study suggests that increased concentrations of inert C_{org} (with $C/N > 11$) increased Hg-C_{org} complexation and decreased the net methylation rate of Hg in the sediments from the study area. Overall, the nature of C_{org} controlled Hg-methylation in the surface sediments of the OMZ in the Arabian Sea.

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1. Introduction

Mercury (Hg) is an important contaminant of the environment due to its toxic nature, rapid trans-boundary movement and high rate of bioaccumulation of its most toxic form, methylmercury (MeHg) into aquatic organisms (Peralta-Videa et al. 2009; Zhang and Wong 2007; Ullrich, Tanton, and Abdrashitova 2001; Fitzgerald et al., 2007; Mason et al., 2012). Consumption of fish and seafood with elevated levels of MeHg is an important human and environmental health concern (Sunderland and Mason 2007; Clarkson et al., 2003). The net global emission of Hg has been reported to increase in the last few decades (Streets and Zifeng, 2011; Driscoll et al. 2013; Amos et al. 2014; Amos et al. 2015; Gustin et al. 2015). Much of the Hg originating from both anthropogenic and natural sources is, eventually, transported to the marine environment via rivers and atmospheric deposition. In coastal and estuarine systems, Hg is quickly scavenged by particulate matter from water column and deposited to bottom sediments (Merritt and Amirbahman 2007; Hung and Chmura 2006; Sunderland and Mason, 2007) and this is an important sink for the global Hg cycle (Amos et al., 2014). Methylation of Hg occurs in coastal and estuarine sediments but the importance of MeHg production in coastal sediments as a source to coastal and open ocean fish is still debated (Chen et al., 2014; Mason et al., 2012; Driscoll et al., 2013). The distribution and speciation of Hg in marine sediment depends on several factors, such as: (i) texture of sediments; (ii) distribution of different mineral phases; (iii) quality and quantity of organic matter; and (iv) the redox condition. Total organic carbon (C_{org}) (a good representative of sedimentary organic matter) has been reported as one of the important factors controlling Hg distribution and speciation in marine sediment (Chakraborty et al. 2015a, 2014a, 2014b; Hammerschmidt and Fitzgerald, 2004; Hollweg et al., 2009). Additionally, the fate of Hg and MeHg in marine sediments depends on chemical complexation that is impacted by the reduction/oxidation status of sediments, adsorption and desorption processes and the nature of sedimentary organic carbon (C_{org}) and the concentration of sulfide and organic thiols (Ravichandran 2004; Fitzgerald, et al., 2007; Hammerschmidt and Fitzgerald 2004; Chakraborty et al. 2014a; Chakraborty et al. 2014b; Chakraborty et al., 2015a; Chakraborty et al., 2015b; Chakraborty et al., 2015c; Chakraborty et al., 2015d; Hollweg et al., 2009, 2010; Schartup et al., 2014; Merritt and Amirbahman, 2008; Vudamala and Chakraborty, 2016).

The changing redox condition at the sediment-water interface is expected to play an important role in determining the speciation, mobility and bioavailability of sedimentary Hg. Methylation of sedimentary Hg

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and diffusion and advection of MeHg into the overlying water has also been reported to depend on redox condition at the sediment-water interface (Mason et al., 2006; Hammerschmidt and Fitzgerald, 2004). Some fraction of sedimentary Hg is also transported from sediment to the overlying water column due to sediment resuspension. The exchange of MeHg across the sediment-water interface can exacerbate the exposure of pelagic living organisms, although the importance of sediment as a source is not consistent across coastal ecosystems (Balcom et al., 2008; Sunderland et al., 2010; Chen et al., 2012; Gosnell et al., 2015). Methylation of Hg in sediment has been reported to be more favourable in anoxic regions of estuarine and freshwater environments, especially near the redox interface (Campeau & Bartha, 1984; Olson & Cooper, 1974; Benoit et al., 2003; Hall et al., 2008; Mehrotra and Sedlak, 2005). Methylation is primarily biologically-mediated, and the methylating genes (hgcA and hgcB) have so far only been found in anaerobic microbes (Parks et al., 2013; Gilmour et al., 2013). However, in anoxic environments there is also increased Hg interaction with reduced sulfur in marine sediments. High concentrations of sulfide and organic thiols in marine sediments have been reported to limit MeHg production, primarily by influencing the bioavailability of Hg to methylating bacteria (Hollweg et al., 2009; Schartup et al., 2015). Sulphate reducing bacteria (SRB) play a key role in terms of MeHg production in anaerobic coastal marine sediments as they are the primary microbes responsible for carbon remineralization in these sediments. Overall, MeHg production under anaerobic conditions in marine sediment has been reported to depend on both the quantity and quality of C_{org} and sulfide concentrations, which influence both bioavailability of Hg to methylating organisms and microbial activity.

It is well known that the bottom waters of the western continental slope of India is affected by oxygen deficiency ($O_2 < 10$ μM) near the water-sediment interface, which is driven both by inputs of organic matter from the productive surface waters and lack of water column mixing due to high stratification in the region (Naqvi et al., 2006; Naqvi et al., 2000). The suboxic/hypoxic overlying water column (oxygen minimum zone (OMZ)) of the western continental slope of India could therefore be expected to enhance MeHg formation in sediments, as found in estuaries such as Long Island Sound and the Chesapeake Bay, and potentially increase the dissolved benthic flux of MeHg to the overlying water (Hollweg et al., 2010; Balcom et al., 2008). On the contrary, however, a study in the Gulf of Mexico did not find that MeHg in bottom waters correlated with the extent of hypoxia (Liu et al., 2015). The importance of hypoxia in influencing MeHg formation in underlying sediments was one focus of this study.

To date, there is no baseline data available on the distribution and speciation of Hg and MeHg across the OMZ of the west coast of India (Naqvi et al., 2009; Naqvi et al., 2010; Kondo and Moffett, 2013). As a large percentage of the marine fish production is supported by coastal ecosystems (Botsford et al., 1997; Pauly et al., 2002), it is necessary to understand the importance of the nearshore OMZ region in enhancing MeHg concentrations as global marine OMZs may become “hot spots” for MeHg in terms of human exposure (Sunderland et al., 2009; Mason et al., 2012), and are likely to increase in extent in a changing climate (Doney et al., 2012).

Information of the impact of OMZ on MeHg formation in underlying sediments and its flux to the water column is limited and contradictory. Liu et al. (2015) concluded that there was no indication of enhanced MeHg concentration and formation in the sediments of the so-called “dead zone” in the Gulf of Mexico. Others (Mason et al., 2006; Emili et al., 2011) have shown that total Hg and MeHg fluxes from sediments are enhanced by low oxygen concentrations in the overlying waters. The aim of this study was therefore to examine the influence of dissolved oxygen (DO) concentrations in bottom water, sediment grain size, C_{org} and total sedimentary sulfide concentrations on the distribution and speciation of Hg in coastal sediments from the Arabian Sea to further examine these factors. The study involved transects across the oxygen minimum zone, off the west coast of India.

2. Materials and methods

2.1. Description of study sites

Sediment samples were collected from the western continental margin of India. The typical characteristics of the western continental margin of India are associated with the semi-annual reversal in wind stress associated with the monsoon, water mass intrusions from marginal seas and the other oceans, and limited mixing due to no opening to the north with no subtropical convergence or deep water formation. This gives the upper waters of the Arabian Sea a unique thermohaline structure and circulation (Wyrtki, 1971; Morrison and Olson, 1992; Morrison et al., 1999). It has been reported that upwelling-favourable conditions exist along the southern shelf, which is less conspicuous towards the north of the western continental margin (off Gujarat) of India (Muraleedharan and Prasannakumar, 1996). There is always a permanent pycnocline in this region. However, the top of the pycnocline undergoes a change in depth due to seasonal forcing and giving rise to the seasonal pycnocline formation in this area (de Boyer et al., 2004; Prasanna Kumar et al., 2004; Shetye et al. 1994).

Samples were collected from the continental margin (off Gujarat state) along transects roughly perpendicular to the coasts of the study area (Fig. 1). The sediment samples were collected on board *ORV Sindhu Sankalp* (*SSK71*) during 8th-21st November 2014. This study area (western continental shelf of India) is affected by natural oxygen deficiency ($O_2 < 10$ μM) in the water-column. The sediment samples were collected in such a way to ensure there were distinct variations in the dissolved oxygen (DO) concentration of the overlying bottom waters. The sediment samples were collected from the outer shelf (SPC # 15, 16), the upper slope (SPC # 17), the middle slope (SPC # 20) and the deeper region of the slope (SPC # 21).

Dissolved oxygen concentration in the overlying bottom seawater was determined by the Winkler method. The detailed description of the method has been given in the literature (Broenkow and Cline, 1969; Bryan et al., 1976). The pH of the water samples was determined with a pH meter (LabIndia, Mumbai, India). A CTD rosette (Sea-Bird, USA) was used to determine the salinity of the overlying bottom water. The overlying bottom water was collected ~1–2 m above the sea bed. Thus, the actual DO level at the sediment-water interface was probably lower than the DO values reported here.

The sedim-4ents were collected from continental shelf to slope areas. Table 1 presents the details of the sampling location. The surface sediment samples were collected by using spade corer of 30 cm × 15 cm × 50 cm, and were stored at −4 °C and brought back to the laboratory. The sediments were then sub sectioned, freeze dried and were stored (packed in air tight zip lock bag) at -4 °C until analysis.

2.2. Sediment texture

Texture of the sediment (<63 μm fraction) was analysed using a Particle Size Analyzer (LPSA from Malvern Mastersizer 2000). Ramaswami and Rao (2006) have described the procedure in detail. The sand data is presented in weight percentage (wt%) and the silt and clay in vol(%) in this study.

2.3. Elemental and isotopic analysis

Total organic C (C_{org}) and total N (TN) contents along with the stable C and N isotopic compositions were measured using a Eurovector EURO3000 elemental analyzer connected to a Thermo DELTA V PLUS isotope-ratio mass spectrometer operated in a continuous-flow mode (Owens and Rees, 1989). The details of the procedure has been described in the literature (Bardhan et al. 2015). ε-Amino-n-Caprioic acid, ($C_6H_{15}NO_2$; ACA) was used a laboratory standard reference material for calibration of elemental data as well as $\delta^{13}C_{org}$ and $\delta^{15}N$. The

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