

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

Parthasarathi Chakraborty^{1*}, Robert P. Mason², Saranya Jayachandran¹, Krushna Vudamala¹, Kazip Armoury¹, Arindam Sarkar¹, Sucharita Chakraborty, Pratirupa Bardhan¹, Richita Naik¹

¹National Institute of Oceanography (CSIR), India, Dona Paula, Goa, 403004, India.

² Department of Marine Sciences, University of Connecticut, Groton, Connecticut 06269, United States

Corresponding Author: Phone-91-832-2450495/688; Fax: 91-832-2450602;
E-mail: pchak@nio.org

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.

Keywords: Mercury speciation; Oxygen minimum zone; Methylmercury in sediment; Arabian Sea.

CAPSULE ABSTRACT: Distribution and speciation of sedimentary Hg across the OMZ in the Arabian Sea

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 and Magos, 2003). The net global emission of Hg has been reported to increase in the last few decades (Streets et al. 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 matters 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 sulphide 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 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, 1976; 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 sulphur 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 ($O_2 < 10 \mu M$) 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 (Wyrki, 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 toward the north of the western continental margin (off Gujarat) of India (Muraleedharan and Kumar 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; 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 (**Figure. 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 ($O_2 < 10 \mu M$) 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 sediments 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 30cm ×15cm ×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 -° 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). Ramaswamy 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 analyser 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 reported values of $\delta^{13}C_{org}$ and $\delta^{15}N$ in ϵ -Amino-n-Caprioic acid are -25.3 ‰ and 4.6 ‰ respectively.

Carbon and nitrogen isotopic ratios in sediments are expressed as δ values ($\delta^{13}C_{org}$ and $\delta^{15}N$) with reference to Vienna Pee Dee Belemnite (V-PDB) and atmospheric N_2 , respectively.

$$\delta^{13}C_{org} \text{ and } \delta^{15}N = [(R_{sample} - R_{standard}) / R_{standard}] \times 1000 \quad (1)$$

where $R = {}^{13}C/{}^{12}C$ and ${}^{15}N/{}^{14}N$.

The analytical precision of replicate analyses of selected samples (n=3) was <2% for C_{org} and TN and <0.2‰ for $\delta^{13}C_{org}$ and $\delta^{15}N$.

2.4. Determination of Hg in sediments by Direct Mercury Analyzer

A Direct Mercury Analyzer (Tri cell DMA-80) from Milestone, Italy was used for Hg analysis. The basic principle of DMA-80 is based upon thermal decomposition, catalytic conversion of interfering substances, preconcentration of Hg by gold amalgamation, and atomic absorption spectrophotometry. A pre-weighed sample is taken in a quartz tube and introduced into the machine. Controlled heating stages are applied to dry and then thermally decompose the sample. The decomposition products are then carried through a catalyst bed with a continuous flow of oxygen (99.9% pure). The interfering decomposed products are then removed by the catalyst bed. All Hg species are selectively trapped by gold (forming a Hg-gold amalgamation). The amalgamator is subsequently heated (at 850 °C) to release the Hg vapour into the single beam, fixed wavelength atomic absorption spectrophotometer. The absorbance measured at 253.7 nm is proportional to the Hg content in the sample.

Certified reference material (CRM) was used to calibrate the instruments, validate the analytical methods and check the quality of the measurements. Marine sediment reference materials, MESS-3 and PACS-2 (from National Research Council Canada), were used as the CRM. The certified reference concentration of Hg in MESS-3 and PACS-2 were 0.091 ± 0.009 mg/kg and 3.04 ± 0.20 mg/kg respectively. The analysis of certified Hg from MESS-3 and PACS-2 found concentrations of 0.090 ± 0.004 and 3.02 ± 0.10 mg/kg, respectively. The analytical precision was expressed as the average \pm standard deviation (n=3) for Hg. The DMA-80 achieves a detection limit as low as 0.0.02 ng of Hg.

2.5. Determination of total chromium reducible sulfur in sediment samples

Chromium-reducible sulfur (CRS) in sediment was quantified by the following method. An amount of ~0.2 g of sediment sample was placed into a 3-neck round-bottom flask. A volume of 10 mL of dimethylformamide (DMF) was added into the flask. The mixture was thoroughly stirred with a magnetic stir bar to secure an efficient mechanical breakup of the sample. DMF enhances the reactivity of reduced sulfur species in the sediment samples. It also allows oxidation to take place at an enhanced rate. As soon as the sample was mixed with DMF, the reaction flask was connected to the gas line and flushed with N₂ for 10 min. Subsequently, 8 mL of 5M HCl was injected through the chemical port followed by the addition of 16 mL of 1M CrCl₂ solution. The sample is bubbled at a rate of 2 to 5 bubbles per second with N₂ for 2 h and the system was stirred continuously. Zinc acetate solution was used as the sulfide trap. The liberated sulfide was trapped as zinc sulfide in 20 mL of 5% (w/v) ZnAc-solution. The resulting zinc sulfide precipitate was redissolved by adding 2ml of 50% HCl and the liberated sulfide was measured on a spectrophotometer at 670nm by Cline

method (Cline, 1969). Given the method of determination, this fraction is equivalent to chromium reducible sulfur (CRS).

2.6. Methylmercury (MeHg) extraction

The procedure is based on the method of Maggi et al. (2009), and other similar methods in the literature. Approximately 1.0–2.0 g of dry sediment (freeze dried) was placed in 100 mL screw-capped polypropylene tube. The sediment sample was then hydrolyzed with 6M HCl (10 mL). The sample with 6M HCl was vertically stirred for 5 min using a mechanical shaker. The sample was further, centrifuged at 2400 rpm for 10 min and the supernatant liquid phase was discarded (no significant MeHg concentration was detected). A definite volume (20 mL) of toluene was added to the sediment residue and was vigorously mixed for 20 min. The sediment and toluene mixture was centrifuged (2400 rpm for 20 min). The supernatant, containing organomercury species was collected in falcon tubes. The whole procedure was repeated. The combined organic extracts were further back extracted with 6mL of 1% (v/w) L-cysteine aqueous solution to strip MeHg from toluene. Then, an aliquot of the L-cysteine extract was immediately analysed with the Hg analyser (DMA-80). Overall, the method relies on the fact that while the MeHg is extracted into the toluene and then back extracted with the L-cysteine, the same does not occur for inorganic Hg, primarily because of the differences in speciation in strong HCL solution (inorganic Hg complexes are charged, MeHg is mostly present as CH_3HgCl). Therefore, these extraction steps enable separation of MeHg from inorganic Hg. Certified reference material of MeHg in sediment (SQC1238-50G) (from Sigma Aldrich) was used to validate this analytical measurement method. The certified reference concentration of MeHg in SQC1238 was $10.0 \pm 0.3 \mu\text{g/kg}$. The determined MeHg concentration in the CRM was $9.5 \pm 0.3 \mu\text{g/kg}$. The Acceptance Limits for the CRM have been reported to be 5.1 - 14.9 $\mu\text{g/kg}$. The analytical precision was expressed as average \pm standard deviation ($n=5$) for MeHg.

3. Results and discussions

3.1. Basic hydrographic and sedimentological conditions of the study area

The sediment samples were collected in such a way to ensure that there were distinct variations in the dissolved oxygen (DO) concentration of the overlying bottom waters across the OMZ. Variation of dissolved oxygen (DO), salinity and temperature of the overlying bottom water (above the sediments) at the five sampling sites across the OMZ in the west coast of India are presented in **Table 1**. The DO levels in the overlying bottom water were found to vary from oxic ($80.4 \mu\text{M}$) to hypoxic ($49.1 \mu\text{M}$) and then close to suboxic ($4.5 \mu\text{M}$) across the OMZ (from the continental shelf towards the continental slope). In this study, the overlying bottom water was collected ~1-2 m above

the sea bed, and the actual DO level at the sediment-water interface was potentially lower than the DO values reported here. The salinity of the bottom water in the study area varied slightly from 35.1 to 36.6 ppt. However, the temperature of the overlying bottom water decreased with the increasing depth.

The particle size distributions of sediments in the study area are presented in **Table 1**. It was found that coarser sediment (ranging from ~75 – 90% sand) dominated in the continental shelf areas but finer particles (silt+clay) dominated (ranging from ~75 - 95%) along the continental slope.

3.2 Distribution and sources of sedimentary organic matter

Sedimentary organic carbon (C_{org}) and total nitrogen (TN) are presented in weight percentage. Figures 2a and 2b show that C_{org} and TN in sediments decreased with increasing DO of the overlying bottom water ($R^2 = 0.81$; $p < 0.05$ for C_{org} ; $R^2 = 0.78$; $p < 0.05$ for TN). The highest concentration (4.4%) of C_{org} was found in the sediment where the overlying bottom water had the lowest DO concentration (4.5 μM). This finding suggests that a low-oxygen environment helps to preserve C_{org} in the sediments by decreasing the rate of degradation of organic matter (Berger et al., 1988, 1989; Anderson et al., 2001; Sarmiento et al., 1998; Canfield 1994). The concentrations of C_{org} , TN were also found to increase (from 1.06 - 4.38% and 0.06-0.46% respectively) with an increasingly higher fraction of finer particles in the sediment (down the continental slope across the OMZ) (**Table 2**). Significant positive correlations were found between the C_{org} ($R^2 = 0.80$; $p < 0.05$) (**Figure 3**) and TN ($R^2 = 0.84$; $p < 0.05$) and the finer particle (silt + clay) content in the bulk sediments. This indicates a higher sorption and affinity of Hg to the C_{org} and TN on the finer particles in the studied sediments, as found in other studies (Hedges and Keil., 1995; Paropkari et al.1987), likely because of the higher surface area available. Overall, the combination of low DO concentration of the overlying bottom water and high finer particles content (silt and clay) increased the C_{org} content in the underneath sediment from the continental slope areas.

As it has been reported that C_{org} in sediments derived from different origin (from marine or terrestrial) have different Hg complexing capacity (Schartup et al, 2015; Hollweg et al., 2010; Chakraborty et al., 2015a), the type of OC also can control Hg speciation in marine sediment. Thus, measurement of stable isotopes and C: N ratios were made to understand the nature of C_{org} in the studied sediment across the OMZ.

The C:N_{molar} ratio and $\delta^{13}\text{C}_{org}$ have been widely used (Peters et al., 1978; Meyers and Ishiwatari, 1993; Meyers, 1997; Zhang et al., 2009) to understand the sources of C_{org} in sediments. Freshly deposited marine produced organic matter has a C:N_{molar} ratio of 6-9 (Bordovskiy, 1965; Prahl et al.,

1994, 1980; Perdue et al, 2007) and $\delta^{13}\text{C}_{\text{org}}$ of -20.5‰ (Gearing, 1988; Jia and Peng, 2003) while vascular terrestrial C3 plant produced organic matter has a C:N_{molar} ratio of 12-14 or more (Hedges et al., 1986; Prahl et al., 1994, 1980) and $\delta^{13}\text{C}_{\text{org}}$ of -30 to -23 ‰ (Smith and Epstein, 1971; Pancost and Boot, 2004). However the terrestrial C4 plant produced organic matter is richer in $\delta^{13}\text{C}_{\text{org}}$ (~ -17 to -9 ‰, (Smith and Epstein, 1971 Pancost and Boot, 2004;). Intermediate values could indicate a mixture of both marine and terrestrial derived organic matter.

Table 2 shows the changes of C:N_{molar} ratio , $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}_{\text{TN}}$ in the studied sediment across the study area. The decrease in C:N_{molar} ratio down the continental slope across the OMZ suggests that C_{org} in the sediments collected from the continental slope was mainly influenced by marine derived organic matter (from in-situ biological production). Furthermore, the stable isotopic ratio of C_{org} ($\delta^{13}\text{C}_{\text{org}}$) in the sediments confirms the likely increasing influence of marine organic matter towards the continental slope across the OMZ. The variation of $\delta^{13}\text{C}_{\text{org}}$ from -20.33‰ near the continental shelf to -19.99‰ on the continental slope supports the notion of the increasing marine influence towards the slope, but also suggests that the contribution from terrestrial organic matter is small. The $\delta^{15}\text{N}$ data support this inference. The differences in the nature of organic matter could influence Hg distribution and speciation in this area. For example, Schartup et al. (2015) demonstrated the contrasting effects of marine and terrestrially derived dissolved organic matter on Hg speciation and bioavailability in seawater and suggested that dissolved organic matter composition is a critical driver of Hg reactivity and bioavailability in offshore marine waters. The Hg and MeHg bound to marine OC were more bioavailable than when bound to terrestrial OC. However, as the overall effect of marine and terrestrially derived organic matter on Hg distribution and MeHg production is not known across the OMZ, further analysis was performed to understand the distribution and speciation of Hg in the studied sediments, and the controlling factors.

3.3. Distribution of Hg in sediment across the OMZ

Total Hg concentrations in the sediments (expressed on a dry weight basis) were low, ranging from 8.8 - 70.2 $\mu\text{g.kg}^{-1}$ (**Table 2**). The concentrations were similar or lower to the Hg concentrations reported in pristine coastal sediments from the different parts of the world. The concentration of total Hg ([Hg]_T) was found to increase with the depth of the continental slope and a strong significant positive correlation coefficient was also found with the finer particle content ($R^2 = 0.87$; $p < 0.05$) (**Figure 4**).

The total Hg content in the sediment was high in the continental slope area (sediments dominated with finer particles) compared to the shelf area (coarser particle dominated sediments). The total concentrations of Hg in the sediments gradually increased with the increasing C_{org} but the

relationship was not significant ($R^2 = 0.54$; $p > 0.05$). As noted above, the fine-grained sediment content and C_{org} were strongly correlated. It has been suggested that C_{org} is effective in binding Hg, and is an important factor in controlling Hg concentration in sediment (Hollweg et al., 2010; Hammerschmidt and Fitzgerald 2004; Liu et al., 2015). Hollweg et al. (2010) also found higher concentrations of total Hg in deeper sediments (600-900 m depth) on the slope of the mid-Atlantic Bight, and found a relatively constant ratio of Hg: C_{org} with distance offshore. Overall, the C_{org} -normalized Hg concentrations found here (8-20 $\mu\text{g kg}^{-1} \%C_{org}^{-1}$ or 16-40 $\text{pmol g}^{-1} \%LOI^{-1}$) are in the same range as those found off the coast of North America (Hollweg et al., 2010; Hammerschmidt and Fitzgerald, 2006) even though at these locations bottom water DO was always $>100 \mu\text{M}$.

However, not all studies have found a strong correlation between Hg and C_{org} . For example, Mason and Lawrence (1999) found a non-linear relationship in Baltimore Harbour sediments, and Schartup et al. (2014) suggested that total sediment sulfur was a better proxy for Hg binding capacity in sediments. As Hg binds strongly to both inorganic and organic reduced sulfur ligands, it is expected that the binding strength and the degree of complexation of Hg would increase in the presence of higher, slowly oxidizing C_{org} under low oxygen conditions, especially as these would promote sulphate reduction and the formation of reduced sulphide in the sediment. Overall, the total Hg content in the sediments did gradually increase with the decreasing DO concentrations of the overlying water column and increasing finer particles and C_{org} content of the sediments. However, there did not appear to be any relationship between CRS, overlying DO and sediment C_{org} . Indeed, some of the sites with the highest CRS had low C_{org} and high overlying water DO (**Table 2**). These differences likely reflect the degree to which water column mixing is replenishing DO, which would occur more frequently for the shallower sites. To further examine the influence of environmental conditions, we examined the MeHg concentration in the sediments under varying DO concentration of the overlying bottom water.

3.4. Distribution of MeHg in sediment across the OMZ

The concentrations of MeHg found in the studied sediments across the OMZ are shown in **Table 2**. The concentration of MeHg was found to be high with respect to the total Hg concentration in the sediments (ranging from ~0.9 to 9% of the total Hg content in the sediment). The relative percentage of MeHg in the sediments was high compared to those measured by others in estuarine and other coastal waters (mostly $<2\%$) (see summary in Liu et al., 2015). While this could be considered as a potential artefact in the analytical method, the high recovery and accuracy of the measurement of the MeHg in the sediment SRM suggests that this is not the case. The sites with the higher %MeHg had very low total Hg concentrations (8.8 and 10.9 $\mu\text{g kg}^{-1}$) and were sites with low C_{org} . The

measurements presented here represent the surface sediments and it is probable that deeper sediments had lower MeHg and %MeHg, as found for some sites within the Chesapeake Bay (Hollweg et al., 2009).

Overall, while the MeHg concentration was relatively consistent across sites (overall variability about a factor of 2), it did not correlate with the total Hg concentration in the sediments and the %MeHg was highly variable. Methylation of Hg in estuarine sediment has been reported to be more favourable under anaerobic conditions (Compeau & Bartha, 1984; Olson and Cooper, 1974), which provides a favourable environment for the methylating bacteria (anaerobes) (Gilmour et al., 2013). Continuous input of fresh labile carbon under suboxic condition stimulates SRB activity, which would enhance methylation of Hg in marine sediments; otherwise microbial activity may be limited even though conditions suitable for methylation persist. Alternatively, higher levels of organic matter could limit availability of Hg for methylation. In this study, MeHg concentration was inversely correlated with C_{org} , as found by other investigators (Hammerschmidt and Fitzgerald, 2004). There was no correlation of MeHg with CRS, in contrast to the results of Schartup et al. (2014), but similar to the results of Liu et al. (2015). Here, as with the Gulf of Mexico sediments, the reduced sulfur content was low and this likely resulted in the lack of correlation, as the correlation found by Schartup et al. (2014) was for sediments with relatively high reduced sulfur content.

We predicted that the MeHg content in the sediment should negatively correlate with the concentration of DO of the overlying bottom water if anoxia in the water column enhanced methylation in sediments. However, a strong positive correlation was observed between the MeHg concentration in the sediments and DO level (**Figure. 5a**). The concentration of MeHg in the sediments gradually decreased with the decreasing DO level of the overlying bottom water. Our results appear to support those of Liu et al. (2015) who did not find a correlation between sediment methylation and overlying water DO in the Gulf of Mexico.

3.5. Factors affecting the distribution, speciation of Hg in the sediments across the OMZ

In many studies, the quality of C_{org} has been reported to influence Hg- methylation rate in coastal sediments (e.g. Hollweg et al, 2010; Schartup et al., 2015). Organic matter derived from marine produced organic matter has been reported to have less Hg complexing capacity than terrestrial organic matter in marine sediment, and this likely reflects the lower C_{org} to organic sulphur (OS) ratio in such sediments (Hollweg et al, 2010). A very similar observation has been reported by others (Schartup et al, 2015; Lamborg et al., 2004). These authors have reported that C_{org} can limit Hg-methylation in an estuarine ecosystem and as a result C_{org} is often described as the primary control over MeHg production. Input of autochthonous carbon has been reported to influence the

concentration of MeHg in coastal sediments (Lambertsson and Nilsson, 2006). It was discussed in the previous section that C_{org} in the sediments collected from the continental slope was mainly influenced by marine organic matter, whereas the C_{org} from the shelf area had more terrestrial influence, and this likely results in the observed differences found in this study. Overall, the number of sites is too small to completely tease out the contrasting influence of C_{org} source on bioavailability compared to the influence C_{org} and reduced sulphur content on partitioning and bioavailability. We therefore further examined the influences of varying DO levels (of the overlying bottom water) and nature of C_{org} on Hg distribution and its speciation in the sediments across the OMZ.

The increasing Hg and C_{org} concentrations in the sediment with decreasing DO concentration of the overlying bottom water was probably due to strong complexation of Hg with different binding sites of C_{org} in the sediments. This complexation reaction may inhibit MeHg production in the sediments. One usually should expect a strong positive correlation of MeHg content with C_{org} in the sediments (Covelli et al, 2000; Hollweg et al, 2010). However, a negative correlation was found between the MeHg concentration and the C_{org} content in the studied sediment, which was consistent with the results of Hammerschmidt and Fitzgerald (2004). As discussed in Schartup et al. (2014) differing trends in the relationship between Hg and C_{org} have been found across ecosystems and this likely reflects the differences in OS: C_{org} ratio for the different locations. For example, the shelf and slope stations in Hollweg et al. (2009) had a ratio that was 5-10 times lower than that of the Chesapeake Bay. The results in this study may be attributed to strong complexation reaction of Hg with C_{org} under suboxic conditions which probably prevented MeHg production.

Lability of sedimentary organic matter is known to affect methylation of Hg in sediments (Kim et al., 2011). 'Labile' is the term used to describe organic matter with low C: N ratios ($C/N=4-10$), whereas 'non-labile' describes organic matter with high C: N ratios ($C:N >11$). Kim et al (2011) suggested that surface sediments, which contained a large fractions of fresh algal organic material ($C:N =5.8-7.8$), showed higher Hg(II) methylation rates than deeper sediments ($C:N >10$). They also suggested that the C:N ratio can be used as a proxy for the lability of organic matter that influences Hg(II) methylation rate in marine sediments. The C:N ratios in the studied sediments were in the range between ~11 and 21 throughout the study period (**Table 2**) and therefore were less labile in nature. Thus, the concentration of total Hg in the sediment along the continental slope area was found to be higher but with less MeHg. Furthermore, a sequential extraction study (the protocol has been described in detail by Chakraborty et al., 2014c; Chakraborty and Babu 2015b, Chakraborty et al., 2016) was performed on the sediment samples and it was found that a major fraction of the total Hg was strongly associated with the organic/reduced sulphide phases in the sediments. Sulphide

concentration in sediment has also been recognized as important factor to control bioavailability of Hg to methylating bacteria (Lambertsson and Nilsson, 2006; Hammerschmidt and Fitzgerald, 2004& 2006; Hollweg et al., 2009; Schartup et al., 2014). There was no significant relationship found between the concentrations of MeHg in the studied sediment with the CRS concentrations in the sediments. The CRS concentration in the sediment was in the low range ($\sim 1.5\text{-}15\mu\text{g.kg}^{-1}$) (Table 2) of what can be found in coastal sediments (Liu et al., 2015; Hollweg et al., 2009; Schartup et al., 2014). The sequential extraction analysis results also showed that more complexation of Hg with C_{org} with higher C/N ratio in the sediments decreased MeHg formation in the study area.

Overall, it is concluded that the concentrations of MeHg decreased with the increasing concentration of non-labile C_{org} (in the sediments) in this study area. Decreasing DO concentrations in the overlying water column increased the concentrations of non-labile C_{org} which probably helped Hg to undergo stronger complexation reactions and remained preserved in C_{org} . This strong complexation of Hg with C_{org} probably inhibited MeHg production in the sediments (**Figure 5b**).

4. Conclusions

This is the first study that has dealt with the impact of varying oxygen levels in the overlying bottom water on Hg distribution and speciation in the underlying sediment across the oxygen minimum zone of the Arabian Sea. It was found that C_{org} concentration increased with the increasing finer particulates 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. It was found that the nature (labile/inert) of C_{org} played a more important role than water column DO in controlling the distribution and speciation of Hg in these areas.

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References

- Amos, H. M., Jacob, D. J., Kocman, D., Horowitz, H. M., Zhang, Y., Dutkiewicz, S., Sunderland, E. M., 2014. Global biogeochemical implications of mercury discharges from rivers and sediment burial. *Environ. Sci. Technol.* 48(16), 9514-9522.
- Amos, H. M., Sonke, J. E., Obrist, D., Robins, N., Hagan, N., Horowitz, H. M., and Sunderland, E. M., 2015. Observational and modeling constraints on global anthropogenic enrichment of mercury. *Environ. Sci. Technol.* , 49(7), 4036-4047.
- Anderson, L.D., Delaney, M.L., and Faul, K.L., 2001. Carbon to phosphorus ratios in sediments: Implications for nutrient cycling. *Global Biogeochem. Cycle.* 15: 67-79.
- Balcom, P. H., Hammerschmidt, C. R., Fitzgerald, W. F., Lamborg, C. H., O'Connor, J. S., 2008. Seasonal distributions and cycling of mercury and methylmercury in the waters of New York/New Jersey Harbor Estuary. *Mar. Chem.* 109(1), 1-17.
- Pratirupa Bardhan, Karapurkar, S.G., Shenoy, D.M., Kurian, S., Sarkar, A., Maya, M.V., Naik, H., Varik, S., Naqvi, S.W.A., 2015. Carbon and nitrogen isotopic composition of suspended particulate organic matter in Zuari Estuary, west coast of India . *J. Mar. Syst.* .141, 90–97.
- Berger, W.H., Fischer, K., Lai, C., Wu, G., 1988. Ocean carbon flux: Global maps of primary production and export production, in Agegian, C.R., ed., *Biogeochemical cycling and fluxes between the deep euphotic zone and other ocean realms*: NOAA. National Undersea Research Program. Research report. 88-1, 131- 176.
- Berger, W.H., Smetacek, V.S., Wefer, G., 1989. *Productivity of the ocean present and past*. New York, John Wiley& sons. 471.
- Benoit, J. M., Gilmour, C. C., Heyes, A., Mason, R. P., Miller, C. L., 2003. Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems. In ACS symposium series (Vol. 835, pp. 262-297). Washington, DC; Am. Chem. S.; 1999.
- Bordovsky, O.K., 1965. Accumulation of organic matter in bottom sediments. *Mar. Geol.* 3, 33–82.
- Botsford, L. W., Castilla, J. C., Peterson, C. H., 1997. The management of fisheries and marine ecosystems. *Science*, 277 (5325), 509-515.
- Broenkow, W.W. and Cline, J.D., 1969. Colorimetric determination of dissolved oxygen at low concentrations. *Limnol. Oceanogr.* 14(3), 450-454.
- Bryan, J.R., Riley, J.P. Williams, P.L., 1976. A Winkler procedure for making precise measurements of oxygen concentration for productivity and related studies. *J.Exp.Mar. Biol. Ecol.*, 21(3), 191-197.
- Campeau, G., Bartha, R., 1984. Methylation and demethylation of Mercury under controlled redox, pH and salinity condition. *Appl. Environ. Microbiol.* 48, 1203- 1207
- Canfield, D.E., 1994. Factors influencing organic carbon preservation in marine sediments. *Chem. Geol.* 114, 315-329.
- Chakraborty, P., Sharma, B., Raghunath Babu, P. V., Yao, K.M., Jaychandran, S., 2014a. Impact of total organic carbon (in sediments) and dissolved organic carbon (in overlying water column) on Hg sequestration by coastal sediments from the central east coast of India. *Mar. Pollut. Bull.* 79, 342-347.

Chakraborty, P., Yao, K.M., Chennuri, K., Vudamala, K. Babu, P.R., 2014b. Interactions of mercury with different molecular weight fractions of humic substances in aquatic systems. *Environ. Earth Sci.* 72(3), 931-939.

Chakraborty, P., Raghunath Babu, P. R., Vudamala, K., Ramteke, D., Chennuri, K., 2014c. Mercury speciation in coastal sediments from the central east coast of India by modified BCR method. *Mar. Pollut. Bull.* 81(1), 282-288.

Chakraborty, P., Sarkar, A., Vudamala, K., Naik, R., Nath, B.N., 2015a. Organic matter- A key factor in controlling mercury distribution in estuarine sediment. *Mar. Chem.* 173, 302-309.

Chakraborty, P., Raghunath Babu, P.V., 2015b. Environmental controls on the speciation and distribution of mercury in surface sediments of a tropical estuary, India. *Mar. Pollut. Bull.* 95, 350-357.

Chakraborty, P., Vudamala, K., Chennuri, k., Armoury, K., Linsy, P., Ramteke, D., Sebastian, T., Jayachandran, S., Naik, C., Naik, R., Nath, B.N., 2015d. Mercury profiles in sediment from the marginal high of Arabian Sea: an indicator of increasing anthropogenic Hg input in sea. *Environ.Sci.Pollut.R.* DOI 10.1007/s11356-015-5925-1

Chakraborty, P., Vudamala, K., Coulibali, M., Ramteke, D., Chennuri, K., Lean, D., 2015c. Reduction of mercury (II) by humic substances- influence of pH, salinity of aquatic system. *Environ.Sci.Pollut.R.* 22(14), 10529-10538.

Chakraborty, P., Chakraborty, S., Jayachandran, S., Madan, R., Sarkar, A., Linsy, P. Nath, B.N., 2016. Effects of bottom water dissolved oxygen variability on copper and lead fractionation in the sediments across the oxygen minimum zone, western continental margin of India. *Sci. Total Environ.*, doi:10.1016/j.scitotenv.2016.05.125

Chen, J., Hintelmann, H., Feng, X., Dimock, B., 2012. Unusual fractionation of both odd and even mercury isotopes in precipitation from Peterborough, ON, Canada. *Geochim. Cosmochim. Ac.*, 90, 33-46.

Chen, C.Y., Borsuk, M.E., Bugge, D.M., Hollweg, T., Balcom, P.H., Ward, D.M., Williams, J. Mason, R.P., 2014. Benthic and pelagic pathways of methylmercury bioaccumulation in estuarine food webs of the northeast United States. *PloS one*, 9(2), e89305.

Clarkson, T. W., Magos, L., Myers, G. J., 2003. The toxicology of mercury—current exposures and clinical manifestations. *New. Engl. J Med*, 349(18), 1731-1737.

Cline, J. D., 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnol. Oceanogr.* 14(3),454-458.

Covelli, S., Faganeli, J., Horvat, M., and Brambati, A., 2000. Mercury accumulation of coastal sediments as the result of long- term cinnabar mining activity (Gulf of Trieste, northern Adriatic sea). *Appl.Geochem.* 16, 541-558.

de Boyer Montégut, C., Madec, G., Fischer, A. S., Lazar, A., Iudicone, D., 2004. Mixed layer depth over the global ocean: An examination of profile data and a profile-based climatology. *J. Geophys. Res. Oceans*, 109(C12)

Doney, S.C., Ruckelshaus, M., Duffy, J.E., Barry, J.P., Chan, F ., English, C.A., Galindo, H.M., Grebmeier, J.M., Hollowed, A.B., Knowlton, N., Polovina, J ., Rabalais, N.N., Sydeman, W.J., Talley, L.D., 2012. Climate change impacts on marine ecosystems. *Ann. Rev. Mar. Sci.*, 4, 11-37

- Driscoll, C. T., Mason, R. P., Chan, H. M., Jacob, D. J., Pirrone, N., 2013. Mercury as a global pollutant: sources, pathways, and effects. *Environ. Sci. Technol.* 47(10), 4967-4983.
- Emili, A., Koron, N., Covelli, S., Faganeli, J., Acquavita, A., Predonzani, S., De Vittor, C., 2011. Does anoxia affect mercury cycling at the sediment–water interface in the Gulf of Trieste (northern Adriatic Sea)? Incubation experiments using benthic flux chambers. *Appl. Geochem.* 26(2), 194-204.
- Fitzgerald, W. F., Lamborg, C.H., Hammerschmidt, C.R., 2007. Marine Biogeochemical Cycling of Mercury. *Chem. Rev.* 107(2), 641–662.
- Gearing, J.N., 1988. The Use of Stable Isotope Ratios for Tracing the Nearshore-Offshore Exchange of Organic Matter, In: Jansson, B.O. (ed.) *Lecture Notes on Coastal-Offshore Ecosystem Studies, Coastal Offshore Ecosystem Interactions: 22.* 69-101, Berlin: Springer-Verlag.
- Gilmour, C. C., Podar, M., Bullock, A. L., Graham, A. M., Brown, S. D., Somenahally, A. C., Elias, D. A., 2013. Mercury methylation by novel microorganisms from new environments. *Environ. Sci. Technol.* 47(20), 11810-11820.
- Gosnell, K., Balcom, P., Ortiz, V., DiMento, B., Schartup, A., Greene, R., Mason, R., 2015 Seasonal Cycling and Transport of Mercury and Methylmercury in the Turbidity Maximum of the Delaware Estuary. *Aquat. Geochem.*, 1-24.
- Gustin, M. S., Amos, H. M., Huang, J., Miller, M. B., Heidecorn, K., 2015. Measuring and modeling mercury in the atmosphere: a critical review. *Atmos. Chem. Phys.* 15(10), 5697-5713.
- Hall, B. D., Aiken, G. R., Krabbenhoft, D. P., Marvin-DiPasquale, M., Swarzenski, C. M., 2008. Wetlands as principal zones of methylmercury production in southern Louisiana and the Gulf of Mexico region. *Environ. Pollut.* 154(1), 124-134.
- Hammerschmidt, C R., Fitzgerald, W.F., 2004. Geochemical Controls on the Production and Distribution of Methylmercury in Near-shore Marine Sediments. *Environ. Sci. Technol.* 38(5), 1487–1495.
- Hammerschmidt, C R., Fitzgerald, W F., 2006. Bioaccumulation and trophic transfer of methylmercury in Long Island Sound. *Arch. Environ. Contam. Toxicol.* 51,416–424.
- Hedges, J.I., Clark, W.A., Quay, P.D., Richey, J.E., Devol, A.H., Santos, U.D., 1986. Compositions and fluxes of particulate organic material in the Amazon River. *Limnol. Oceanogr.* 31, 717–738.
- Hedges, J.I., Keil, R.G., 1995. Sedimentary organic matter preservation: an assessment and speculative synthesis. *Mar. Chem.* 49, 81–115.
- Hollweg, T. A., Gilmour, C., Mason, R. P., 2010. Mercury and methylmercury cycling in sediments of the mid-Atlantic continental shelf and slope. *Limnol. Oceanogr.* 55(6), 2703-2722.
- Hollweg, T. A., Gilmour, C. C., Mason, R. P., 2009. Methylmercury production in sediments of Chesapeake Bay and the mid-Atlantic continental margin. *Mar. chem.* 114(3), 86-101.
- Hung, G. A., Chmura, G.L., 2006. Mercury Accumulation in Surface Sediments of Salt Marshes of the Bay of Fundy. *Environ. Pollut.* 142(3), 418–431.
- Jia, G., Peng, P., 2003. Temporal and spatial variations in signatures of sedimented organic matter in Lingding Bay (Pearl estuary), southern China. *Mar. Chem.* 82, 47 -54.

- Kim, M., Han, S., Gieskes, J., Deheyn, D.D., 2011. Importance of organic matter lability for monomethylmercury production in sulfate-rich marine sediments. *Sci. Total. Environ.* 409(4), 778-784.
- Kondo, Y., Moffett, J.W., 2013. Dissolved Fe(II) in the Arabian Sea oxygen minimum zone and western tropical Indian Ocean during the inter-monsoon period. *Deep-Sea Res. I.* 173, 73-83
- Lambertsson, L., M. Nilsson., 2006. Organic material: The primary control on mercury methylation and ambient methylmercury concentrations in estuarine sediments. *Environ. Sci. Technol.* 40(6), 1822-1829.
- Lamorg, C.H, Fitzgerald, W.F, Skoog, A., P.T Visscher., 2004. The abundance and source of mercury-binding organic ligands in Long Island Sound. *Mar. Chem.* 90, 151-163.
- Liu, B., Schaidler, L. A., Mason, R. P., Shine, J. P., Rabalais, N. N., Senn, D. B., 2015. Controls on methylmercury accumulation in northern Gulf of Mexico sediments. *Estuar. Coast. Shelf Sci.* 159, 50-59.
- Maggi, C., Berducci, M.T., Bianchi, J., Giani, M., Campanella, L., 2009. Methylmercury determination in marine sediment and organisms by Direct Mercury Analyser. *Anal. Chim. Acta.* 614, 32-36.
- Mason, R. P., Choi, A. L., Fitzgerald, W. F., Hammerschmidt, C. R., Lamborg, C. H., Soerensen, A. L., Sunderland, E. M., 2012. Mercury biogeochemical cycling in the ocean and policy implications. *Environ. Res.*, 119, 101-117.
- Mason, R. P., Kim, E. H., Cornwell, J., Heyes, D., 2006. An examination of the factors influencing the flux of mercury, methylmercury and other constituents from estuarine sediment. *Mar. Chem.* 102(1), 96-110.
- Mason, R.P., Lawrence, A.L., 1999. Concentration, distribution, and bioavailability of mercury and methylmercury in sediments of Baltimore Harbor and Chesapeake Bay, Maryland, USA. *Environ. Toxicol. Chem.* 18, 2438 – 2447
- Mehrotra, A. S., Sedlak, D. L., 2005. Decrease in net mercury methylation rates following iron amendment to anoxic wetland sediment slurries. *Environ. Sci. Technol.* 39(8),2564-2570.
- Merritt K.A., A. Amirbahman., 2008. Cycling of methylmercury in estuarine sediment pore waters (Penobscot River Estuary, Maine, USA). *Limnol. Oceanogr.* 53, 1064–1075.
- Merritt, K. A., Amirbahman, A., 2007. Mercury Dynamics in Sulfide-rich Sediments: Geochemical Influence on Contaminant Mobilization within the Penobscot River Estuary, Maine, USA. *Geochim. Cosmochim. Acta.* 71(4), 929–941.
- Meyers, P.A., 1997. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. *Org. Geochem.* 27, 213-250.
- Meyers, P.A., Ishiwatari, R., 1993. Lacustrine organic geochemistry- an overview of indicators of organic matter sources and diagenesis in lake sediments. *Org. Geochem.* 20: 867-900.
- Morrison, J.M., Codispoti, L.A., Smith, S.L., Wishner, K., Flagg, C., Gardner, W.D., Gaurin, S., Naqvi, S.W.A., Manghnani, V., Prosperie, L., Gundersen, J.S., 1999. The oxygen minimum zone in the Arabian Sea during. *Deep Sea Res., Part II: Topical Studies in Oceanography*, 46(8),1903-1931.

Morrison, J.M., Olson, D.B., 1992. Seasonal basinwide extremes in the T-S characteristics in the near surface waters of the Arabian Sea and Somali Basin. In: Desai, B.N. (Ed.), *Oceanography of the Indian Ocean*. Oxford & IBH Publishing Co, New Delhi, 605-616.

Muraleedharan, P. M., Prasannakumar, S., 1996. Arabian Sea upwelling-A comparison between coastal and open ocean regions. *Curr.Sci.* 70 (11), 842-846.

Naqvi, S. W. A., Moffett, J., W., Gauns, M. U., Narvekar, P. V., Pratihary, A. K., Naik, H. Shenoy, D. M., Jayakumar, D. A., Goepfert, T. J., Patra P. K., Al-Azri, A., Ahmed, S. I., 2010. The Arabian Sea as a high-nutrient, low-chlorophyll region during the late Southwest Monsoon. *Biogeosciences*. 7, 2091–2100

Naqvi, S.W.A., Naik, H., Jayakumar, A., Pratihary, A.K., narvenkar, G., Kurian, S., Agnihotri, R., Shailaja, M.S., Narvekar, P.V., 2009. Seasonal Anoxia over the Western Continental Shelf. Conference on Biogeochemical processes and Ecological variability. *Geophys. Monogr. Sr.* 185.

Naqvi, S. W. A., Jayakumar, D. A., Narvekar, P. V., Naik, H., Sarma, V. V. S. S., D'souza, W., George, M. D., 2000. Increased marine production of N₂O due to intensifying anoxia on the Indian continental shelf. *Nature*, 408(6810), 346-349.

Naqvi, S. W. A., Naik, H., Jayakumar, D. A., Shailaja, M. S., & Narvekar, P. V., 2006. Seasonal oxygen deficiency over the western continental shelf of India. In *Past and Present Water Column Anoxia*, Springer Netherlands, 195-224

Olson, B. H., Cooper, R. C., 1974. In situ methylation of mercury by estuarine sediment. *Nature*. 252, 682.

Owens, N. J., Rees, A. P., 1989. Determination of nitrogen-15 at sub-microgram levels of nitrogen using automated continuous-flow isotope ratio mass spectrometry. *Analyst*, 114(12), 1655-1657.

Pancost, R.D., Boot, C.S., 2004. The palaeoclimatic utility of terrestrial biomarkers in marine sediments. *Mar. Chem.* 92, 239–261.

Parks, J. M., Johs, A., Podar, M., Bridou, R., Hurt, R. A., Smith, S. D., Tomanicek, S.J., Qian, Y., Brown, S.D., Brandt, C.C. and Palumbo, A.V ... & Liang, L. 2013. The genetic basis for bacterial mercury methylation. *Science*, 339(6125), 1332-1335.

Paropkari, A.L., Rao, C.M., Murty, P.S.N., 1987. Environmental controls on the distribution of organic matter in recent sediments of the Western Continental Margin of India, in: Kumar, R.K., Dwivedi, P., Banerjee, V., Gupta, V. (Eds.), *Petroleum Geochemistry and Exploration in the AfroAsian Region*. 347–361.

Pauly, D., Christensen, V., Guénette, S., Pitcher, T. J., Sumaila, U. R., Walters, C. J., Zeller, D., 2002. Towards sustainability in world fisheries. *Nature*, 418(6898), 689-695.

Peralta-Videa, J. R., Lopez, M.L., Narayan, M., Saupe, G., Gardea-Torresdey, J., 2009. The Biochemistry of Environmental Heavy Metal Uptake by Plants: Implications for the Food Chain. *Int. J. Biochem. Cell Biol.* 41(8), 1665–1677.

Perdue, E. M., Koprivnjak, J.F., 2007. Using the C/N Ratio to Estimate Terrigenous Inputs of Organic Matter to Aquatic Environments. *Estuar. Coast. Shelf. Sci* 73(1), 65–72.

Peters, K.E., Sweeney, R.E., Kaplan, I.R., 1978. Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. *Limnol. Oceanogr.* 23: 598-604.

- Prahl, F. G., Bennett, J. T. and Carpenter, R., 1980. The early diagenesis of aliphatic hydrocarbons and organic matter in sedimentary particulates from Dabob Bay- Washington. *Geochim. Cosmochim. Acta.* 44, 1967-1976.
- Prahl, F.G., Bennett, J.T. Carpenter, R., 1980. The early diagenesis of aliphatic hydrocarbons and organic matter in sedimentary particulates from Dabob Bay, Washington. *Geochim. Cosmochim. Acta.* 44,1967-1976.
- Prahl, F.G., Ertel J.R., Gon~ i M.A., Sparrow, M.A., and Eversmeyer, B., 1994. An assessment of terrestrial organic carbon contributions to Washington coastal sediments. *Geochim. Cosmochim. Acta.* 58, 3035–3048.
- Prasanna Kumar, S., Narvekar, J., Kumar, A., Shaji, C., Anand, P., Sabu, P., Nair, K. K. C., 2004. Intrusion of the Bay of Bengal water into the Arabian Sea during winter monsoon and associated chemical and biological response. *Geophys. Res. Lett.* 31(15).
- Ramaswami, V., Rao, P. S., 2006. Grain size analysis of sediments from the northern Andaman Sea: comparison of laser diffraction and sieve-pipette techniques. *J. Coast. Res.* 22(4), 1000-1009.
- Ravichandran, M., 2004 .Interactions between Mercury and Dissolved Organic Matter-a Review. *Chemosphere.* 55(3), 319–331.
- Sarmiento, J.L., Hughes, T.M.C., Stouver, R.J., Manabe, S., 1998. Simulated response of the ocean carbon cycle to anthropogenic climate warming. *Nature.* 393, 245-249.
- Schartup, A. T., Balcom, P. H., Mason, R. P., 2014. Sediment– porewater partitioning, total sulfur, and methylmercury production in estuaries. *Environ. Sci. Technol.* 48, 954–960.
- Schartup, A., Ndu, U., Balcom, P., Mason, R., and Sunderland, E., 2015. Contrasting effects of marine and terrestrially derived dissolved organic matter on mercury speciation and bioavailability in seawater. *Environ. Sci. Technol.* 49 (10), 5965–5972.
- Shetye, S. R., Gouveia, A. D., Shenoi, S. S. C., 1994. Circulation and water masses of the Arabian Sea. *P. Indian As-Earth*, 103(2), 107-123.
- Smith, B.N., Epstein, S., 1971. Two categories of $^{13}\text{C}/^{12}\text{C}$ ratios for higher plants. *Plant Physiol.* 47, 380-384.
- Streets, D. G., Devane, M.K., Zifeng, L., 2011. All-time Releases of Mercury to the Atmosphere from Human Activities. *Environ. Sci. Technol.* 45(24), 10485–10491.
- Sunderland, E.M. Mason, R.P., 2007. Human impacts on open ocean mercury concentrations. *Glob. Biogeochem. Cycles.* 21(4).
- Sunderland, E.M., Krabbenhoft, D.P., Moreau, J.W., Strobe, S.A. Landing, W.M., 2009. Mercury sources, distribution, and bioavailability in the North Pacific Ocean: Insights from data and models. *Glob. Biogeochem. Cycles.* , 23(2) doi:10.1029/2008GB003425.
- Sunderland, E. M., Dalziel, J., Heyes, A., Branfireun, B. A., Krabbenhoft, D. P., Gobas, F. A., 2010. Response of a macrotidal estuary to changes in anthropogenic mercury loading between 1850 and 2000. *Environ. Sci. Technol.*, 44(5), 1698-1704.
- Ullrich, S.M., Tanton, T.W., Abdrashitova, S.A., 2001. Mercury in the Aquatic Environment: a Review of Factors Affecting Methylation. *Critical Reviews in Environ. Sci. Technol.* 31(3), 241–293.

Vudamala, K., Chakraborty, P., 2016. Kinetic speciation of mercury–humate complexes in aqueous solutions by using competing ligand exchange method. *Microchem. J.*, 126, 551-557.

Wyrski, K., 1971. *Oceanographic Atlas of the International Indian Ocean Expedition*. NSF-IDOE-1, Washington, DC, 531

Zhang, L., Wong, M.H., 2007. Environmental Mercury Contamination in China: Sources and Impacts. *Environ. Int.* 33(1), 108–121.

Zhang, Y.L., Vandijk, M.A., Liu, M.L., Zhu, G.W ., Qin, B. Q., 2009. The contribution of phytoplankton degradation to chromophoric dissolved organic matter (CDOM) in eutrophic shallow lakes: Field and experimental evidence. *Water Res.* 43, 4685–4697.

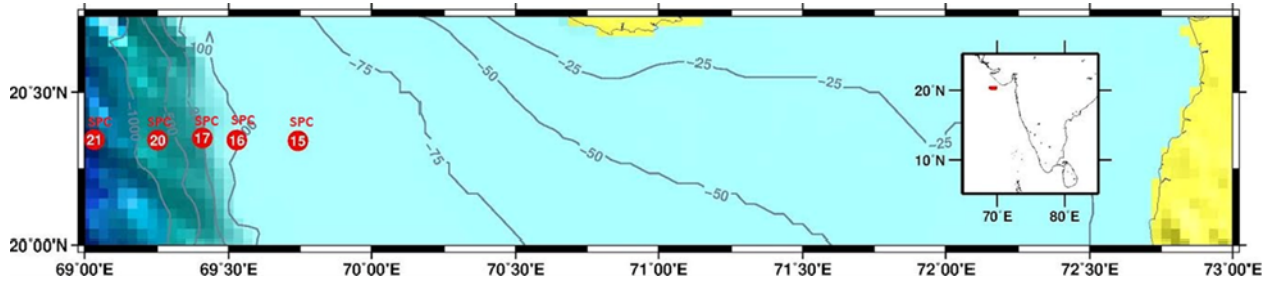


Figure 1: Study area from the continental margin (off Gujarat state) across the OMZ

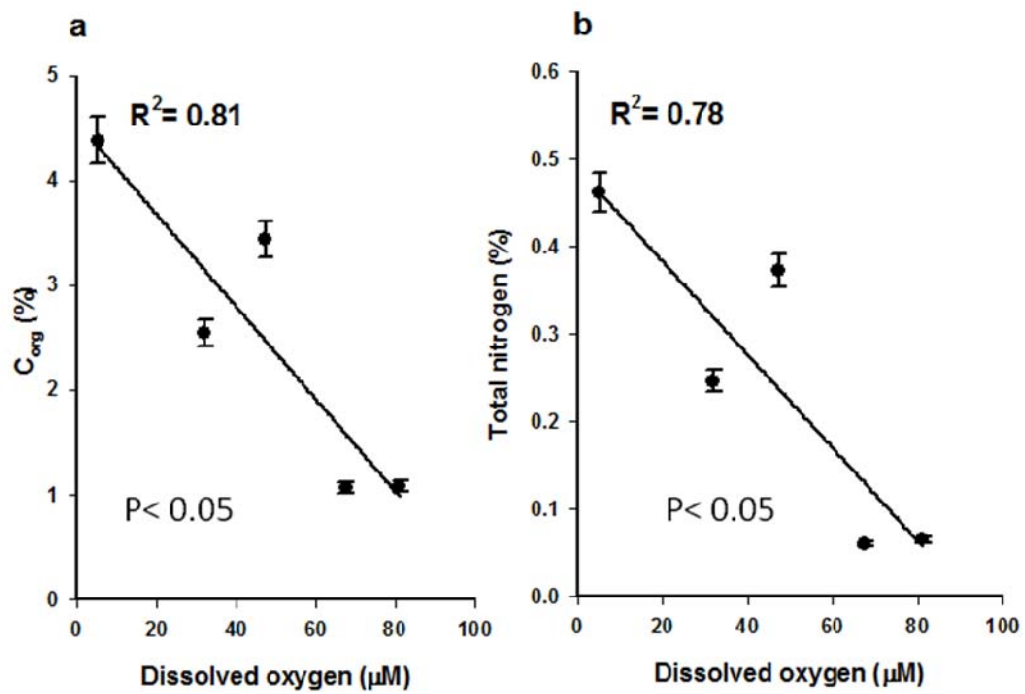


Figure 2: (a) C_{org} and (b) total nitrogen (TN) in the sediments decreased with increasing concentration of dissolved oxygen of the overlying bottom water. Error bars in the figures are standard deviation of the mean.

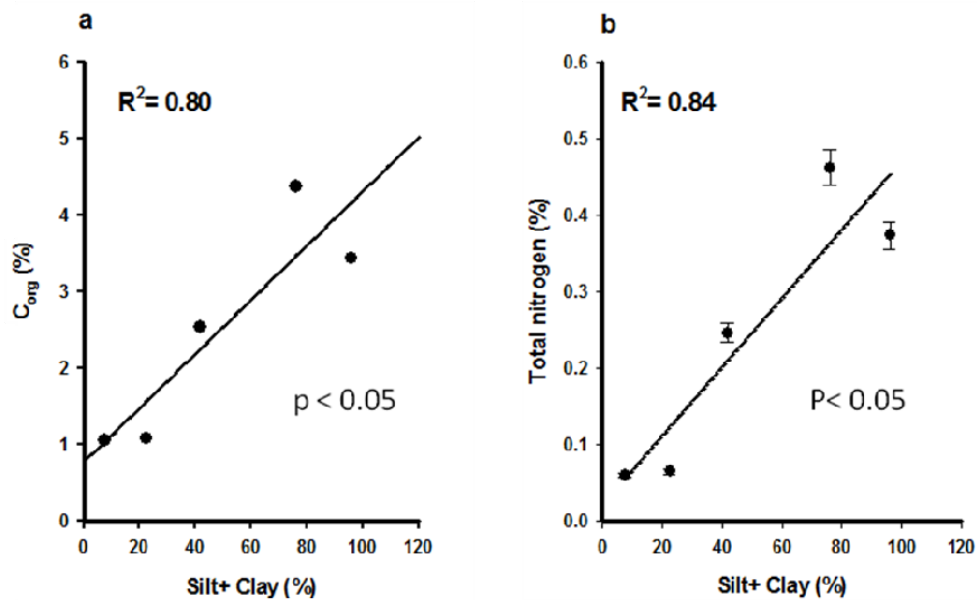


Figure 3: The concentrations of (a) C_{org} and (b) total nitrogen with increasingly higher finer particles content in the sediments

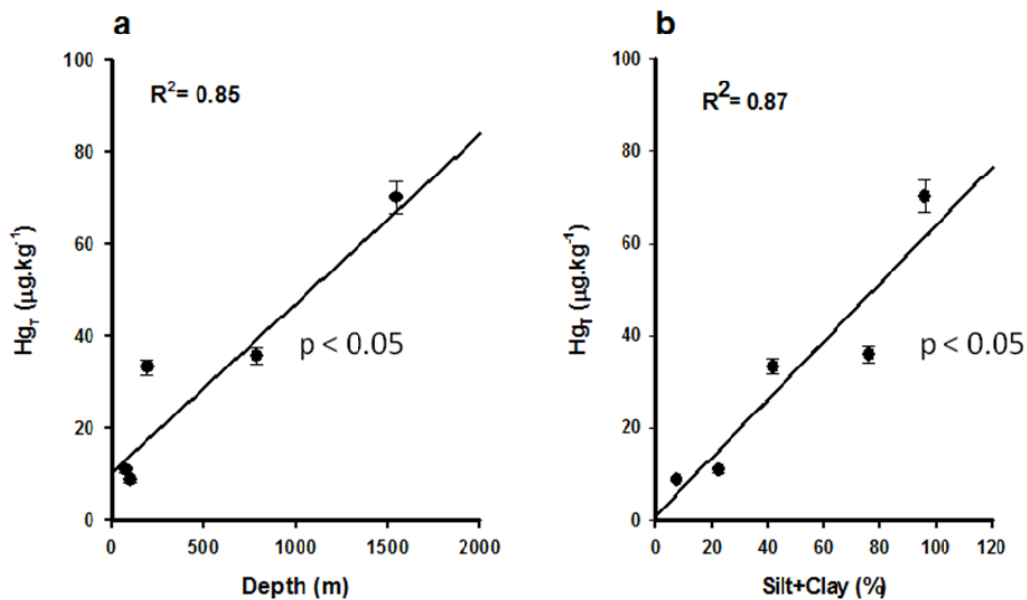


Figure 4: variation of total sedimentary Hg as a function of (a) depth and (b) finer particles

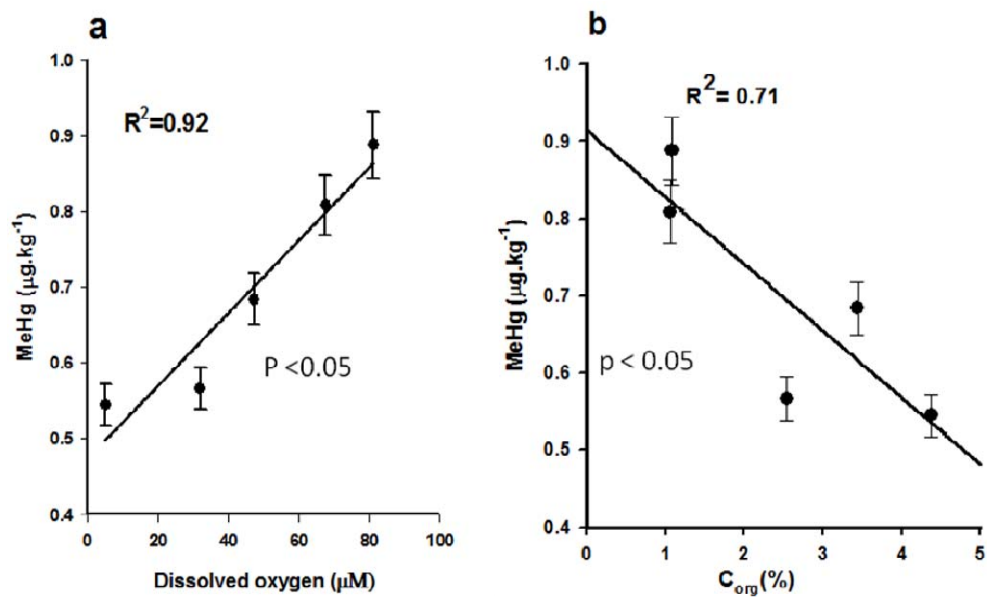


Figure 5: Variation of MeHg production as function of (a) dissolved oxygen of the overlying bottom water and (b) C_{org} in the sediments.

Table 1: Geographical locations of sampling sites, Dissolved oxygen (DO), redox state, salinity, temperature of the overlying bottom water and depth from where the sediment samples were collected

Sediment Core	LAT (°N)	LONG (°E)	Depth (m)	DO (µM)	Redox state	Salinity (ppt)	Temperature (°C)	Particle size	
								Sand (%)	Silt+ clay (%)
SPC 15	20 20.44	69 44.54	80	81.1	Oxic	36.4	23.6	77	23
SPC 16	20 20.56	69 31.71	98	67.5	Oxic	36.4	22.9	92	8
SPC 17	20 20.98	69 24.48	195	32.0	Hypoxic	35.9	19.9	58	42
SPC 20	20 20.56	69 15.06	791	5.1	Hypoxic	35.6	10.4	24	76
SPC 21	20 20.64	69 02.052	1544	47.3	Hypoxic	35.1	5.3	4	96

Table 2: The concentrations of TOC (%), TN (%), Molar C/N ratio, $d^{13}C_{org}$, $d^{15}N$ and sulphide ($\mu\text{g}\cdot\text{kg}^{-1}$) in the studied (coastal and estuarine) sediments are presented along with the total Hg, MeHg content in the studied sediments.

Station	TOC (%)	N (%)	Molar C/N	$d^{13}C_{org}$	$d^{15}N$	Sulfide ($\mu\text{g}\cdot\text{kg}^{-1}$)	Hg _T ($\mu\text{g}\cdot\text{kg}^{-1}$)	CH ₃ Hg ($\mu\text{g}\cdot\text{kg}^{-1}$)	CH ₃ Hg (% of Hg _T)
1	1.08	0.064	19.67	-20.33	7.83	15.19	10.9±0.2	0.89±0.02	8.1
2	1.06	0.060	20.77	-20.82	6.83	2.46	8.8±0.2	0.81±0.02	9.2
3	2.54	0.246	12.05	-20.86	7.99	1.46	33.3±0.7	0.57±0.01	1.7
4	4.38	0.462	11.06	-20.37	8.29	7.47	35.9±0.7	0.54±0.01	1.5
5	3.44	0.373	10.76	-19.99	8.25	4.58	70.2±1.4	0.68±0.01	0.9