

Molecular characteristics of sedimentary organic matter in controlling mercury (Hg) and elemental mercury (Hg⁰) distribution in tropical estuarine sediments

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Research Highlights

- The biogeochemical cycling of Hg in estuarine sediment was investigated
- Quantity and quality of SOM controlled dispersal of Hg_T in estuarine sediment
- High MW-SOM > at middle and upstream locations, > low MW downstream
- Hg preferentially adsorbed to SOM of high MW, Hg⁰> with low MW
- Competition between Hg^{II} reduction and complexation by SOM control Hg_T

Abstract

Sedimentary organic matter (SOM) plays an important role in hosting and reducing Hg^{II} in marine/estuarine sediment. This study provides a better understanding on the influence of nature of SOM, in regulating sedimentary mercury (Hg) and elemental mercury (Hg⁰) distribution, and speciation in the Zuari and Mandovi Estuaries that are representative of monsoon fed tropical estuaries, located in the central west coast of India. Salinity of the overlying water column controlled the physical and chemical characteristics of SOM in the estuarine systems. The high molecular weight (MW) SOM dominated at the mid and upstream (low salinity region) of the estuaries, whereas, the low MW SOM prevailed at the downstream (high salinity region). Sediment Hg showed more affinity towards the SOM of high MW. Increasing MW of SOM increased total sedimentary Hg_T in both the estuaries. SOM with low MW in the estuarine sediment displayed a negative relationship with the sediment Hg concentration. Distribution of Hg⁰ concentration in the estuarine sediment suggests that reduction of Hg^{II} in presence low MW SOM was a dominant process. It was also found that distribution and speciation of Hg⁰ in the estuarine sediment depends on the quantity, quality of the SOM, and the total sediment Hg loading. This study demonstrated that the competition between Hg-SOM complexation and Hg^{II} reduction by SOM controls Hg^{II}/Hg⁰ distribution in tropical estuarine sediment systems.

Keywords: tropical estuary; estuarine sediment; Mercury speciation; Mercury complexation; Mercury reduction

1. Introduction

Mercury (Hg) exists in the environment as chemical forms with diverse chemical reactivity with inorganic, organic and biotic ligands in marine/estuarine environments. Mercury has three different oxidation states, viz., Hg^0 , Hg^{I} and Hg^{II} . The abundance of Hg^{I} is negligible in natural and marine environments (Chan et al., 2003). Elemental mercury (Hg^0) is volatile and fairly insoluble in water. Hg^0 predominates in the atmosphere (Xu, et al., 1999; Ariya et al., 2015). However, the presence of Hg^0 in estuarine and marine sediment has also been reported in the literature (Bloom, *et al.*, 2003; Gray *et al.*, 2004; Fitzgerald, *et al.*, 2007). The low abundance of Hg^0 in marine sediment is probably due to transfer from the sediment to the overlying water column and finally, to the atmosphere. Hg predominantly remains as Hg^{II} in natural and marine environments (Mason and Fitzgerald, 1993; Morel et al 1998). Reduction of Hg^{II} to Hg^0 in marine/estuarine sediments is a very important process. The formation of Hg^0 in sediment and transfer to the atmosphere could decrease sediment Hg concentration, and reduce the possibility of methylmercury formation in sediment and bioaccumulation in the system (Ravichandran, 2004). Unfortunately, very few studies have been reported in the literature on distribution of Hg and its conversion to Hg^0 , and Hg mobility in tropical marine/ estuarine sediment systems (Gu, B. *et al.*, 2011; Zheng, W *et al.*, 2012; Zheng et. al., 2013). The knowledge of Hg distribution in sediment and its conversion to Hg^0 in different estuarine systems in India (the second highest emitters of atmospheric Hg) would provide information that would be useful to those controlling and attempting to reduce Hg pollution in marine/estuarine environment.

It has been reported that sediment organic matter (SOM) plays an important role in hosting and reducing Hg^{II} in marine sediment (Ravichandran, 2004; Gu et. al., 2011; Schartup et al., 2012; Chakraborty et al., 2015; Zheng, et al., 2012; Ravichandran, 2004; Barkay et al.2003; Siciliano et al. 2002). The nature of SOM has been reported to control Hg transport, transformation, and its bioavailability in natural and marine environments (Gabriel and Williamson 2004; Ravichandran, 2004; Hsu-Kim et al., 2013; Jiskra et al., 2014; Chakraborty et al., 2015; Murphy and Zachara, 1995; Chakraborty 2015; Schartup, et. al., 2015; Hammerschmidt, et al., 2004; Stoichev et al. 2004).

Estuarine systems receive organic matter with completely different chemical and physical properties from multiple sources (Boschker et al., 1999; Goñi and Thomas 2000; Tamet al., 2001; Goñi et al., 2003; Benstead2006). SOM in estuaries is primarily a mixture of terrestrial and marine derived material. In addition to different sources of SOM, estuarine SOM further undergoes diverse transformation by microbial activity (Decho and Herndl 1995; Moran, et al., 2000). Thus, the chemical heterogeneity of SOM changes drastically from upstream to downstream because of the chemistry of the system.

Terrestrial organic matter interacts differently with Hg than marine derived materials (Stuermer and Payne 1976; Francois, 1990; Repeta et. al., 2002; Schartup, et. al., 2015; Chakraborty et al, 2015). However, the exact reason for these differences in reactivity is not known. It is believed that changes in chemical heterogeneity (i.e., differences in polyfunctionality, polyelectrolyte property and polydispersity) of SOM along the estuaries are probably responsible for different Hg-SOM interactions. Hg associates with SOM of higher molecular weight (MW) (Ravichandran, 2004; Lee et al., 2011; Chakraborty et al, 2015, 2014a, b, c). Increasing dissolved organic matter (DOM) concentrations in water column has also been reported to increase complexation/reduction processes of Hg^{II} in water column and decreases Hg sequestration by sediments (Chakraborty et al, 2014c; Drexel et al., 2002; Haitzer et al., 2002; Skyllberg et al., 2000; Ravichandran, 2004). The process of Hg-SOM interaction (i.e. complexation and reduction reactions) in estuarine systems is very complex and convoluted.

Previous studies have reported that Hg-SOM interaction depends on Hg/SOM ratio (Tipping, et. al., 2010; Leterme, et. al., 2014; Yin, et. al., 2016). Strong association of Hg with SOM takes place at low Hg/SOM ratio (Zhong and Wang 2009; Schartup, et. al., 2012). Haitzer et al (2002) have reported that Hg prefers to form Hg–thiol bonds at low Hg/SOM ratio. Lability of Hg-SOM complexes has been reported to increase with increasing Hg/SOM ratio in sediments (Drexel et al., 2002; Haitzer et al., 2002; Skyllberg et al., 2000; Ravichandran, 2004). Several studies have also shown that nature of SOM influences Hg⁰ formation, distribution in marine and estuarine sediment (Ullrich, et al., 2001; Boufford and Amyot, 2009). However, the impact of Hg-SOM interaction on Hg, Hg⁰ distribution, and Hg chemistry in tropical estuarine sediment is poorly known. The objective of this study was to test the hypothesis that molecular characteristics of SOM control distribution and binding of Hg and Hg⁰ in tropical estuarine systems.

2. Materials and methods

2.1 Study area and Sample collection

Figure 1 shows sediment sampling locations in the Zuari and Mandovi Estuaries of Goa, central west coast of India. Both the rivers originate in the Western Ghats of India and flow into the Arabian Sea. The Zuari and Mandovi Rivers are 92 km and 77 km long, respectively. The shapes of these estuaries are channel type at the upstream and funnel-shaped at the downstream. The lengths and widths of both the estuaries vary with tidal and seasonal flooding. The rivers are influenced by the saline water inflow up to a considerable distance during dry season (February to May), but receive large volume of freshwater during the wet season (June to September).

Sediment sampling in the Zuari and Mandovi Estuaries was done during September 2017 (wet season) and February 2018 (dry season), respectively, to understand the influence of different types of SOM on Hg and Hg⁰ distribution, and their binding chemistry with natural ligands along the estuaries. Data from the different seasons were not compared, but employed to emphasize the significance of different types of SOM and their molecular characterization on Hg and Hg⁰ distribution and speciation. Sediment samples were collected using Van Veen grab sampler (Gage, 1975). The top 0-5 cm of the sediment was carefully removed and stored in zip-lock bags at low temperature.

Sediment samples were brought immediately (within 4-6 hours) to the laboratory and freeze-dried. It has been reported that there is negligible Hg loss from sediment samples during freeze-drying (Parker and Bloom, 2005). There may be volatilization of Hg⁰ during drying; however, one study showed a loss rate of about 1% per day for pure liquid Hg⁰ (1-mm droplet) at 65°C, suggesting that losses of Hg⁰ from sediments would be small during freeze-drying (Parker and Bloom, 2005). The temperature, salinity, dissolved oxygen; turbidity of the overlying water column was also measured during the sediment sampling using a Sea-Bird Electronics CTD. CTD stands for conductivity, temperature, and depth, and refers to a set of electronic instruments that measure these properties in seawater. Water depth in both the estuaries varied between 2 and 7 m.

2.2 Sediment texture

Grain size distribution of the estuarine sediments was determined by Malvern laser particle size analyzer (Mastersizer 2000). Frozen sediment samples were oven dried at 50°C, followed by separation of the sand fraction using a wet sieve of <62 µm. The silt and clay fraction were analyzed in the laser particle size analyzer (Ramaswamy and Rao, 2006; Chakraborty et al., 2015). Duke's latex and glass sphere standards were used in a range of 0.2-62 µm for calibration of the instrument as described in the literature (Ramaswamy and Rao, 2006). Each sample was analyzed three times and the average value was considered.

2.3 Elemental analysis

Bulk sediment samples were freeze dried and ground with an agate mortar. Total inorganic carbon (TIC) in the studied sediments was analyzed by using Coulometer (UIC coulometer). Anhydrous calcium carbonate was used as certified reference material (99.5% pure, Merck, Germany). Total carbon (TC) and total nitrogen (TN) in the sediments were determined by using Flash 2000 CHN elemental analyzer (Thermo Fisher Scientific Inc). NC Soil Standard (National Institute of Standards and Technology (NIST), Maryland, USA) was used as a certified reference material (Chakraborty

et.al.2015). The precision of the analysis was within $\pm 5\%$. Total sedimentary organic carbon (SOM) was calculated by subtracting TIC from TC.

2.4 Spectrophotometric measurements

UV-Visible Spectrophotometer (Merck, Spectroquant Pharo 300) was used for the molecular characterization of SOM. The SOM was extracted by a slightly modified protocol described in He, et.al. (2016). 20 mL of 0.05 N sodium hydroxide (NaOH) solution was added to 0.5g of powdered sediment samples and the pH of the slurry was adjusted to 10. The slurry was vertically shaken for 12 hr at 50 rpm to extract SOM from the sediment. The slurry was centrifuged at ~ 3000 rpm for 10 mins. The alkali extract (containing SOM) was separated by slow decantation and used for SOM characterization by UV-Vis spectrophotometer (Pharo-300 Spectroquant, Merck Millipore). Absorbance of the extracted SOM was determined at wavelengths ranging from 200 nm to 700 nm. Spectral absorbances at 250, 364, 465 and 665 nm were used to calculate the E_2/E_3 , E_4/E_6 ratios as described in the literature (Chen et al, 1977 and Helms et al, 2008). Accuracy of the spectrophotometer was repeatedly checked by using the NIST-grey glass filters SRM 1930 and Holmium oxide Solution Merck reference material for Spectroquant® PhotoCheck (Travis, et al., 2005).

2.5 FTIR spectroscopy

Fourier Transform Infrared (FT-IR) Spectrometer (Shimadzu's FTIR spectrometer) was used for qualitative analysis of different functional groups present in the SOM. Pellets were made from 1:100 mixture of bulk finely ground sediment and KBr. Finely powdered moisture free KBr was used as a blank. Detail description of the procedure is presented in the literature (Singh, et. al., 2011). IR spectrophotometer was calibrated by using polystyrene as a calibration standard to get the correct response of the instrument. IR spectra were stacked to analyze the change in nature of the SOM by using software IR solutions.

2.6 Determination of Total mercury (Hg_T) in the sediment

Total mercury concentration in the sediment was determined by Direct Mercury Analyzer (Tri-cell DMA-80, from Milestone, Italy). Working procedure of the DMA-80 involves the techniques of thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry. MESS-3, a certified reference material (CRM) obtained from National Research Council of Canada), was used as an instrument calibration standard. The concentration of Hg in the CRM was 0.090 ± 0.001 mg.kg⁻¹. After a satisfactory recovery ($>98\%$), the calibration curve was used for Hg analysis in different matrices. Precision of the measurement was within $\pm 1\%$. Laboratory made

aqueous Hg standard was used to check the calibration. Detailed working principle of DMA-80 has been presented in the literature by *Chakraborty et al 2014a, 2019*.

2.7 Determination of Hg⁰ in the sediment

Concentration of Hg⁰ in sediment was determined using a method described by *Bouffard and Amyot (2008)*. The dried sediment samples were divided in two aliquots (each aliquot of ~0.25 mg). Total Hg (Hg_T) concentration was measured in the first aliquot by a Direct Mercury Analyzer (DMA-80). The second aliquot was heated at 150° C for 2 hours to remove Hg⁰ present. After 2 hours, the Hg_T of the heated sediment samples (residual Hg) was also determined. A blank sample boat was executed after each sample. The differences between the Hg_T and the residual Hg provided the Hg⁰ concentration in the sediments. The methodology used in this study for the determination of sediment Hg⁰ has been reported to be a robust methodology (*Bouffard and Amyot, 2008*). The choice of temperature was based on Hg⁰ thermodesorption temperatures as described in *Bouffard and Amyot (2008)*. It should be noted that the measurement method provided operationally defined Hg⁰ concentrations. Several interferences due to desorption of other Hg species could arise. However, 150⁰C is below thermodesorption temperature ranges for other Hg species that could be found in sediments. Simultaneous desorption of species other than Hg⁰ is thus, unlikely. Therefore, this simple and fast technique was used for the determination Hg⁰ in estuarine sediment in this study.

3. Results and Discussions

Sediment collected at the downstream regions of both the estuaries were dominated by coarser particle(>63µm). The finer particles (silt and clay, <63µm) dominated at the mid-stream of the Zuari Estuary (Table 1). However, the textural pattern in the Mandovi estuarine sediment did not show a general trend. The finer and coarser particles were equally distributed in the major part of the Mandovi Estuary.

The concentration of TIC in sediment varied from 0.07 to 0.32 (%) and 0.06 to 1.39 (%) in the Mandovi and Zuari Estuaries, respectively (Table 1). The concentration of sedimentary TIC was low in the upstream regions, but gradually increased towards the downstream regions of both the estuaries.

The SOM content in the Zuari and Mandovi Estuaries varied from 0.13 to 3.94 % and 1.08 to 3.06 %, respectively (Table 1). High concentrations (ranging from 3.94 to 1.68 %,) of SOM were observed in the mid-estuarine region of the Zuari Estuary followed by the upstream region and lowest concentration (ranging from 0.13 to 0.65 %) of SOM was found in the downstream region. However, the highest concentration of SOM was found in the upstream of the Mandovi Estuary (2.49 %). The

concentration of TN in the sediment ranged from 0.03 to 0.3 % in the Zuari Estuary whereas, 0.08 to 0.21 % in the Mandovi Estuary.

3.1 Variation in concentration of sedimentary organic matter (SOM) along the estuaries

The variation of SOM in both the estuaries with changing salinity of the overlying water showed an inverted parabolic structure (**Figure 2a**). This indicates that relatively high concentration of SOM was present in the mid of the estuary (where salinity ranged from ~15 to 25 PSU). The SOM concentration in the upstream (salinity < 10PSU) was relatively less than the SOM concentrations found at the middle of the estuary, but higher than the downstream region (salinity > 25PSU). This high concentration of SOM in the mid of the estuary was probably due to the coagulation/flocculation processes of SPM from the overlying water column in the mid of the estuary. The detailed chemical characterization of SOM was carried out to understand the nature and distribution of SOM in the tropical estuarine systems.

3.1.1 C/N molar ratios of SOM

C/N ratios are often used to distinguish between marine and terrestrial origins of sediment organic matter (Ishiwatari and Uzaki, 1987; Jasper and Gagosian, 1990). Marine derived organic matter typically have C/N ratios between 4 and 10, whereas terrestrial plants have C/N ratios of >20. This difference arises from the nonexistence of cellulose in SOM from marine sources and its abundance in terrestrial plants. In this study, C/N ratio were determined and used to identify their sources along the estuary. However, carbon isotopic ratios are nowadays widely used to distinguish between marine and continental plant sources of SOM and to identify organic matter from different types of land plants.

The C/N molar ratio in the SOM varied from 5.8 to 10.4 (during February 2018, dry season) and 10.9 to 55.5 (September 2017, wet season) in the Mandovi and Zuari estuarine systems, respectively. The C/N ratio did not vary significantly from the upstream to the midstream in the Mandovi Estuary. The average value of C/N in the estuarine sediment of Mandovi River was 8.9 ± 1.5 . This low C/N molar ratio of SOM carried the signature of marine derived/ freshly deposited labile organic matter in the Mandovi estuarine sediment. However, the C/N ratio varied in the Zuari Estuary. The ratio increased towards the downstream part of the Zuari Estuary. The mean C/N molar ratio in the Zuari Estuary was 22. The higher value of C/N molar ratio indicated that SOM in the Zuari Estuary was inert in nature and probably derived from the adjacent terrestrial region. This is because of the large terrestrial influx during the monsoon season. Shynu et al (2015) also reported that the major sources of SOM in the Zuari Estuary are terrestrial plants during the wet season.

3.1.2 Chemical characterization of SOM

The E_2/E_3 ratio of SOM was used to understand the dispersal pattern of SOM (with respect to their MW) in the estuaries. The E_2/E_3 ratio is inversely related with the MW of SOM (De Haan and De Boer, 1987; Peuravouri and Pihlaja 1997). Table 1 represents the variation of E_2/E_3 ratio of the SOM along the estuaries and suggests that SOM with high MW predominated at the upstream region of both the estuaries. The midstream region contained SOM with moderate MW. The downstream sampling location had the highest E_2/E_3 values indicating the presence of SOM with low MW.

Figure 2b shows that salinity of the overlying water column probably controlled the physical and chemical characteristics of the SOM in the estuaries. The E_2/E_3 values decreased with increasing salinity of the overlying water column (at the upstream to downstream region). It has been reported that microbial metabolism, photo-degradation (Nebbioso 2013; Helms 2008) or adsorption on suspended particles (Stedmon CA, et al 2007) predominates at high salinity region of an estuary. It has also been reported in the literature that bacterial counts are high in the downstream region of the Zuari Estuary and decreased towards upstream (Gardade and Khandeparker, 2017; Qasim and Sengupta, 1981). Therefore, it is suggested that high bacterial activity in the high salinity region (downstream) probably played an important role in degrading SOM (i.e. formation of low MW SOM). The E_4/E_6 ratio represents the absorbance by SOM at 465 and 665 nm, and was used as a proxy for the characterization of the SOM. E_4/E_6 ratio inversely relates with aromaticity of the SOM. Low E_4/E_6 ratio also reflects well-decomposed SOM which has a relatively lower polarity (Kang and Xing, 2008; Helms et al; Summers et al. 1987). The E_4/E_6 ratio of the studied SOM decreased from 1 to 6 from the upstream to downstream region. Thus, the aromaticity of the SOM probably increased from the upstream to the downstream of both the estuaries.

Based upon the above findings, it is suggested that the SOM of smaller size were more aromatic in nature and predominated at the downstream locations. A very similar observation has been reported by Christl, et al., (2000), stating that SOM of smaller size fractions mostly having more percentage of aromatic carbon than the larger size. The SOM in the downstream region of the estuaries was found to be more polarized in nature.

3.3 Chemical heterogeneity of SOM using FT-IR spectroscopic studies

Fourier-transform infrared spectroscopy (FTIR) has been extensively applied for the structural characterization of SOM in nature. FTIR is very useful for the identification of different functional groups in SOM (Esteves et al., 1998; Rodriguez et al., 2016). SOM is a supramolecular association of small organic molecules and heterogeneous in nature; therefore, different functional groups are present

depending on the chemical environments. Although, the IR-spectra consist of few broad bands, however, it still provides basic information about the complexity of SOM in natural environment. Therefore, FTIR was used for further chemical characterization of the studied SOM. **Figure SM1** shows the variation in the IR spectra of the SOM from (a) low salinity region (<10 PSU) and (b) high salinity (<30 PSU) region. The SOM exhibited a typical absorption band in the regions of 3622 cm^{-1} that was due to H-bonds in -OH groups and the overlapping band of primary amine >N-H stretching at 3250 cm^{-1} . Rodriguez et al., (2016) have also shown that a broad and intense band centered at about 3400 cm^{-1} is due to the associated OH stretching vibrations (alcohols, phenols and carboxylic acids) in humic substances. The bands at 1863 cm^{-1} and 1789 cm^{-1} were observed due to the presence of >C=O stretching of aromatic ester and -COOH groups. It has been reported that the band at 1720 cm^{-1} highlights the acidic character of the aquatic humic substances (Lumsdon and Fraser, 2005; Pernet-Coudrier et al., 2011). However, it was not possible to differentiate the acidic character of SOM in the studied sediments along the estuaries. Absorption band at 1620 cm^{-1} was observed because of the aromatic >C=C< and H-bonding >C=O. The broad peak around $1000\text{ to }1050\text{ cm}^{-1}$ is attributed to >C-O stretching of polysaccharide or similar substances (Stevenson, 1994). However, SOM from the high salinity region (downstream region) showed different absorption band at the finger print region (from about $1500\text{ to }500\text{ cm}^{-1}$). An intense peak at 1493 cm^{-1} was observed and represents the aromatic stretching of >C=C<. The low salinity pool sediment show an insignificant band at around 1493 cm^{-1} . Thus, FTIR spectra qualitatively supports the presence of more aromatic SOM at the upstream of the estuaries.

3.4 Distribution of total sediment mercury (Hg_T) in the estuarine systems

The total Hg concentrations in sediment from the Mandovi Estuary ranged from $35.3\text{ to }60.8\text{ }\mu\text{g.kg}^{-1}$ (with an average $48.9\pm 10.5\text{ }\mu\text{g.kg}^{-1}$) (Table 1). In the Mandovi Estuary, higher Hg_T was found in the downstream region. A very similar observation has been reported by Chakraborty et al (2019). However, the variation of Hg_T was not large along this estuary.

Hg_T in the Zuari Estuary varied from $5.2\text{ to }149.0\text{ }\mu\text{g.kg}^{-1}$ (with an average of $50.6\pm 39.3\text{ }\mu\text{g.kg}^{-1}$) (Table 1). Higher concentration of sediment Hg was found in the middle of the Zuari Estuary (ranging from $45.6\text{ to }148.9\text{ }\mu\text{g.kg}^{-1}$). Lowest Hg_T was observed in the downstream region of the Zuari Estuary (ranging from $\sim 5.2\text{ to }28.9\text{ }\mu\text{g.kg}^{-1}$).

Figure 3a shows that the concentrations of sedimentary Hg_T in both the estuaries increased with increasing salinity of the overlying water column in the upstream and mid-stream region of the Zuari and Mandovi Estuaries. One of the probable reasons for the increasing Hg_T from the upstream to the

middle of the Zuari Estuary was increasing coagulation/flocculation of Hg-bound particles with increasing salinity of the overlying water column. Hg_T in the downstream region of the Mandovi Estuary was found to be relatively higher than the mid or upstream region. This difference was probably because of the change in the sampling time during the dry season. Our recent study has shown that seawater brings Hg bound SPM in the Mandovi Estuary during dry season (Chakraborty et al., 2019).

It is important to note that there was a drop in the total sediment Hg concentration in the downstream region of the Zuari Estuary as showed in **Figure.3a** (marked in red circle). It was plausibly due to decrease in SOM concentrations (a major hosting phase for sedimentary Hg) in the downstream region of the estuary (as reported by Chakraborty and Babu 2015). **Table 2** indicates that a strong positive correlation ($r=0.89$, $p<0.05$) existed between the concentrations of SOM and the sedimentary Hg concentrations. Figure SM 2 suggests that the Hg_T gradually decreased with decreasing SOM concentrations in the studied sediments at the downstream region. This finding suggests that SOM was probably one of the major hosts for Hg in the sediments. It has been reported that decrease in reduced organic sulphur, -thiol and other sulfur containing moieties decreases Hg concentration in sediments (Skylberg et al, 2000; Hesterberg et al., 2001).

In addition, mixing of Hg-rich sediments from the mid of the estuary with the Hg-poor marine sediments (as determined in the coastal sediment) would decrease the Hg_T in the downstream sediment of the Zuari Estuary. Concentration of Hg_T was correlated with E_2/E_3 ratio of the SOM (representing the varying MW of the SOM). **Figure 3b** shows that the Hg_T gradually decreased with increasing E_2/E_3 ratio, i.e. with decreasing MW of the SOM at the downstream region. A major fraction of Hg_T was found to associate with the higher MW of the SOM in the sediments at the upstream and mid of the estuaries. Data shown in Figure 3c indicates that increasing E_4/E_6 ratio of the SOM was associated with increased sediment Hg concentration. The increasing E_4/E_6 ratio indicated increasing polarity of the SOM that enhanced Hg-SOM complexation and hence, increased Hg_T in the sediment.

It is well documented that the nature of reactions (complexation or reduction) of Hg^{II} with SOM depends on the quality and quantity of SOM. Therefore, the variation in distribution pattern of Hg^0 in the estuarine sediments with respect to the nature of SOM was examined.

3.5 Distribution of Hg^0 in the estuarine sediments

The fraction of Hg^0 in the studied sediments varied from 0.4 to 52 % of total mercury (Hg_T) (5.2 to 149 $\mu g.kg^{-1}$) in the Zuari Estuary (Table 1).

The highest fraction of Hg^0 was found in the sediment collected at the downstream sampling locations ranging from ~ 11 to 30% (5.9 to 8.1 $\mu\text{g.kg}^{-1}$) of the Hg_T followed by the upstream part of the estuary, ranging from ~ 20 to 52% (2 to 15.2 $\mu\text{g.kg}^{-1}$). The middle part of the estuarine region showed lowest concentration of Hg^0 , ranging from ~ 0.4 to 11 % of the Hg_T (0.4 to 10 $\mu\text{g.kg}^{-1}$). The upstream location showed minimum variation in the absolute concentration of the Hg^0 (6 to 8 $\mu\text{g.kg}^{-1}$). Subsequently, in the Mandovi Estuary, the Hg^0 concentration varied from 1.6 to 25.2 % (0.96 to 13.4 $\mu\text{g.kg}^{-1}$) of the Hg_T in the sediment. At a few stations, Hg^0 concentration was below the detection limit of the DMA-80.

Variation in sediment Hg^0 concentration was correlated with the other physicochemical parameters, such as grain size, SOM, salinity, E_2/E_3 (representing MW), E_4/E_6 (representing polarity of the SOM), etc. Figure 4a shows that the fraction of Hg^0 in the sediment decreased with the increasing salinity of the overlying water column (in the upstream region, the first part of the graph). However, the fraction of Hg^0 increased with the increasing salinity in the downstream region (where the salinity was higher than 20 PSU). **Figure 4b** shows that the sediment Hg^0 concentration was negatively correlated ($r^2=0.5$, $p<0.05$) with the increasing finer grain size ($<4 \mu\text{m}$) content of the sediment.

Figure 5a shows that the percentage of Hg^0 decreased ($r^2=0.64$, $p<0.05$) with the increasing SOM concentration in the sediment. Increased concentration of SOM (at < 20 PSU) resulted in increased Hg-SOM complexation and retention of Hg in the sediment and decreased Hg^0 formation. These observations suggest that Hg-SOM complexation probably predominated at the finer grain size sediments, and therefore, the % Hg^0 decreased with decreasing grain size and increasing SOM.

Figure 5b shows that the percentage of Hg^0 in the sediment increased with increasing E_2/E_3 ratio (i.e. with the decreasing MW of the SOM). This indicates association of Hg with higher MW of SOM predominated at the upstream and Hg^0 formation decreased (Chakraborty et al., 2014b, 2014c, 2015b). However, the relative fraction of Hg^0 increased with decreasing MW of SOM at the downstream region of the estuaries. It has been reported that the bacterial abundance at the mouth of the Zuari Estuary was high during post-monsoon (Khandeparker et al., 2017; Qasim and Sengupta, 1981). The high bacterial abundance would consume the high MW SOM and produced low MW SOM downstream and the Hg^{II} reduction reaction predominated over complexation. As a result, degradation of SOM (forming low MW SOM) at the downstream sampling locations (salinity >20 PSU) decreased Hg complexation and acted as a substrate to increase Hg^{II} reduction (formation of Hg^0). **Figure 5c** shows the impact of varying E_4/E_6 ratio (represent changing polarity) on sediment Hg^0 concentrations. The fraction of Hg^0 (with respect to Hg_T) in the sediment linearly increased with the increasing E_4/E_6 ratio. This study demonstrated that relatively low MW SOM predominated in the downstream region and acted as a

substrate responsible for Hg^{II} reduction. **Figure 5d** shows that the relative fraction of Hg^0 gradually decreased with increasing Hg loading in the sediment. This observation indicates that complexation of Hg^{II} with SOM increased sediment Hg concentration and decreased relative % of Hg^0 in the sediment. It is proposed that the competition between Hg^{II} reduction and complexation by SOM was the key factor in controlling sediment Hg distribution in the tropical estuarine systems.

Conclusions

This study indicated that salinity of the overlying water column played an important role in controlling physical and chemical characteristics of the SOM in the estuaries. SOM with high MW dominated in the middle and upstream sampling locations, whereas, the SOM of low MW predominated downstream. Increasing MW of SOM increased sedimentary Hg_T in both the estuaries and Hg showed more affinity towards SOM of high MW. SOM with low MW showed a negative relationship with sediment Hg concentration and acted as a substrate that was responsible for sediment Hg^{II} reduction in the tropical estuarine system. Thus, the distribution of Hg and its binding chemistry in the estuarine sediment depend on the quantity and quality of the SOM. Additionally, competition between Hg-SOM complexation and Hg^{II} reduction by SOM controls Hg distribution in sediments along the tropical estuarine systems.

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Captions and Legends

Figure 1: The sampling locations from the Mandovi and Zuari estuaries, central west coast of India.

Figure 2: a) Variation of the SOM concentration as a function of salinity of the overlying water column; b) Variation of E_2/E_3 ratio of SOM as a function of salinity of the overlying water column from the Mandovi(◆) and Zuari(●) estuaries.

Figure 3: a) Variation of Hg_T as a function of salinity of the overlying water column; b) Variation of Hg_T as a function of E_2/E_3 ratio of SOM; and c) Variation of Hg_T as a function of E_4/E_6 ratio in the SOM from the Mandovi(◆) and Zuari(●) estuaries.

Figure 4: Variation of Hg^0 as a function of a) salinity of the overlying water column and b) varying clay content in the sediment from the Mandovi(◆) and Zuari(●) estuaries.

Figure 5: Variation of Hg^0 (%) as a function of a) varying SOM concentration b) changing E_2/E_3 c) E_4/E_6 ratio in the SOM, (d) varying Hg loading in the sediments from the Mandovi(◆) and Zuari(●) estuaries.

Table Legends

Table 1: Salinity of overlying water column, sediment texture, total organic carbon (SOM)(in dry weight %), total nitrogen (TN)(in dry weight %), Carbon/Nitrogen molar ratio (C/N), E_2/E_3 , E_4/E_6 , Hg_T ($\mu g.kg^{-1}$) and Hg^0 in the estuarine sediments from the Zuari and Mandovi estuarine regions.

Table 2: The Pearson correlation between the salinity of overlying water column, sediment texture, total organic carbon (SOM) (in dry weight %), total nitrogen (TN) (in dry weight %), Carbon/Nitrogen molar ratio (C/N), E_2/E_3 , E_4/E_6 , Hg_T ($\mu g.kg^{-1}$) and Hg^0 ($\mu g.kg^{-1}$) in the estuarine sediments from the Zuari and Mandovi estuarine regions.

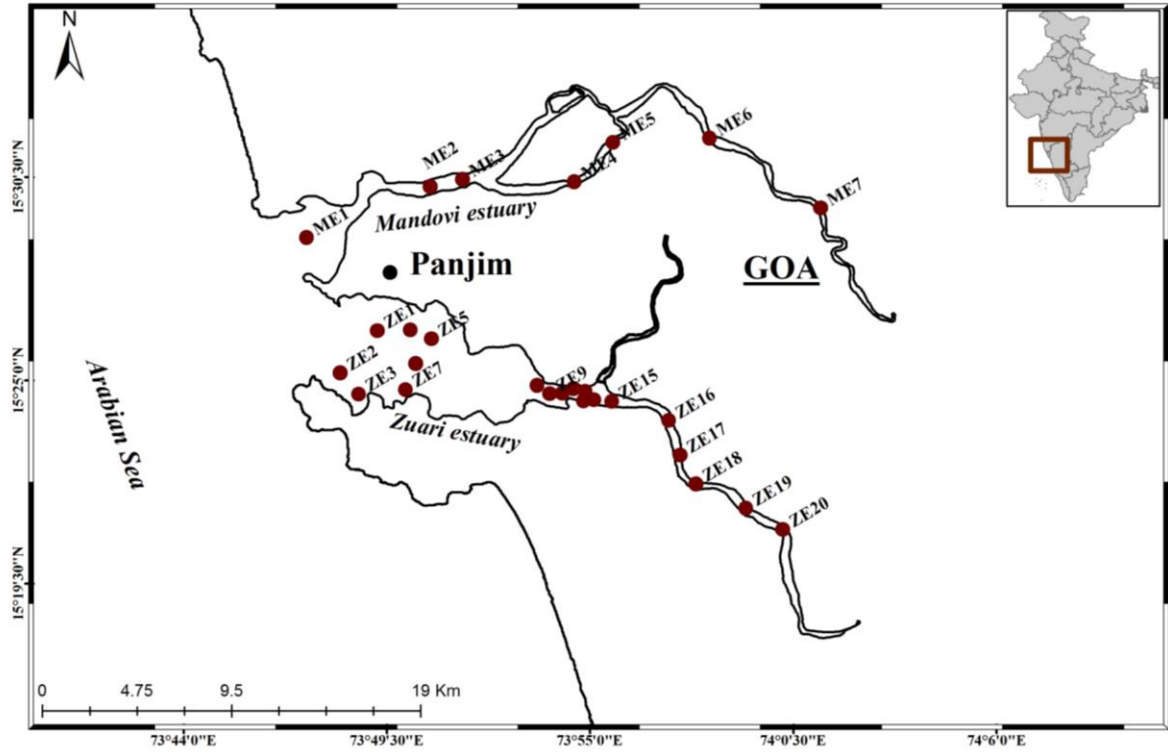


Figure 1

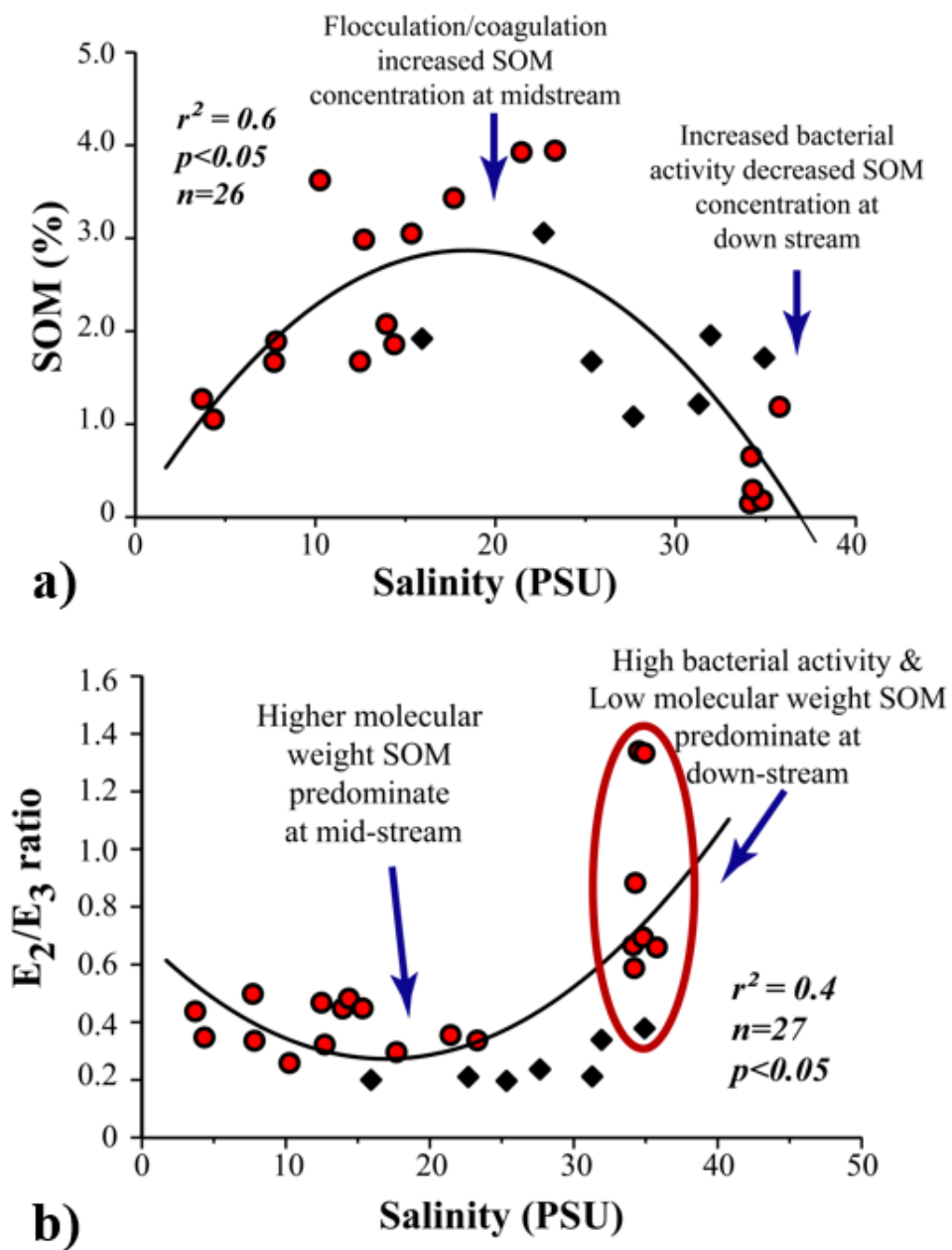


Figure 2

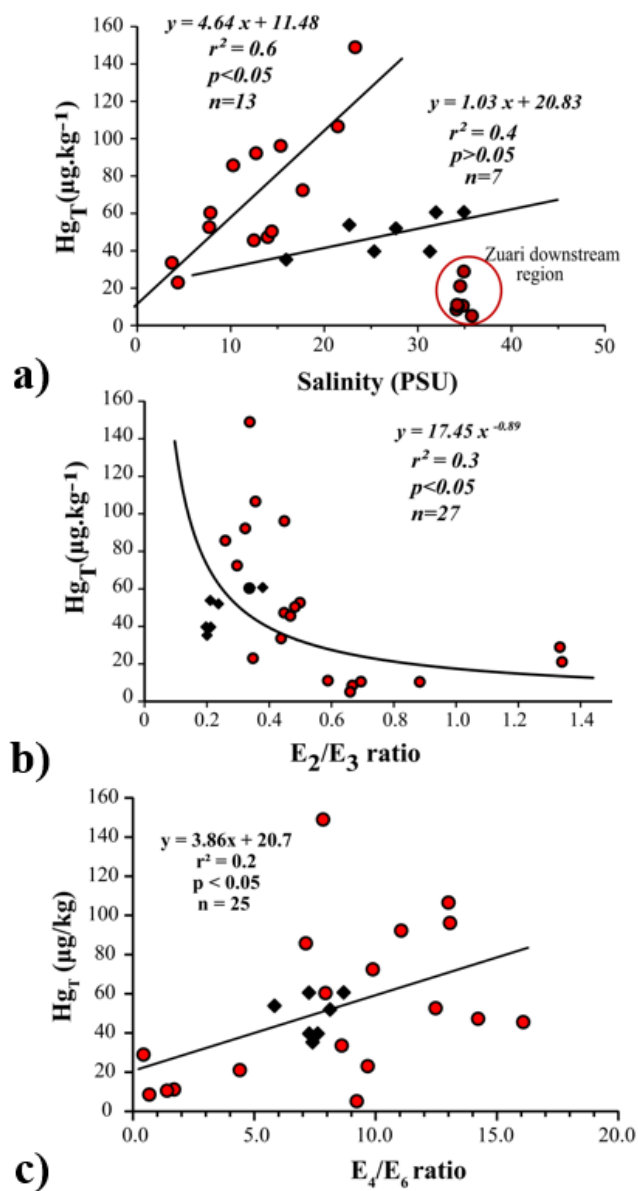


Figure 3

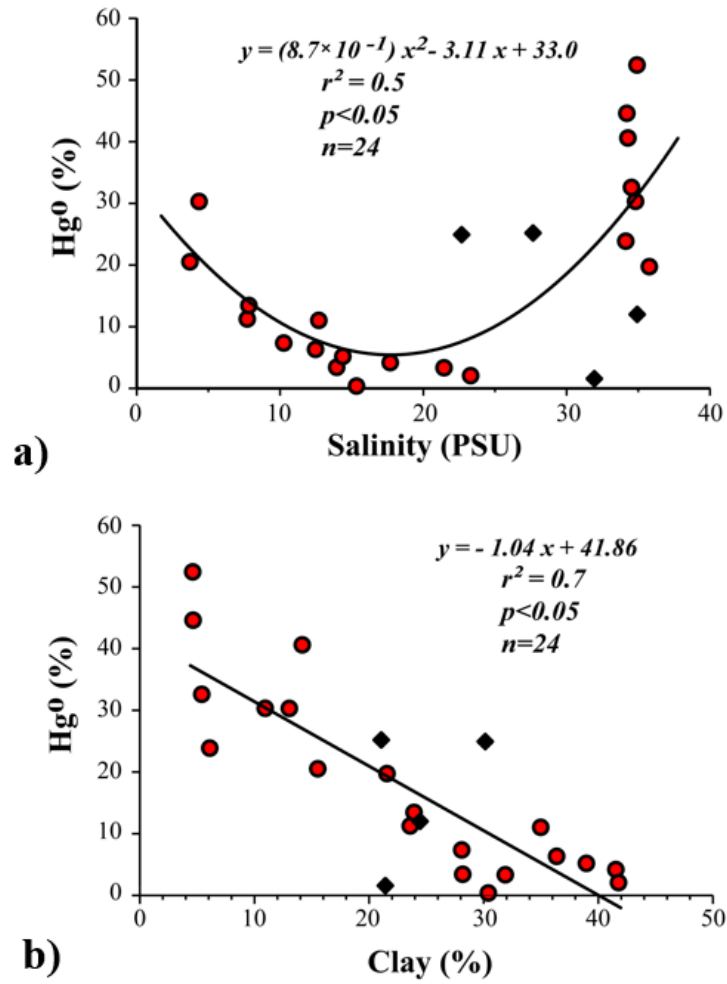


Figure 4

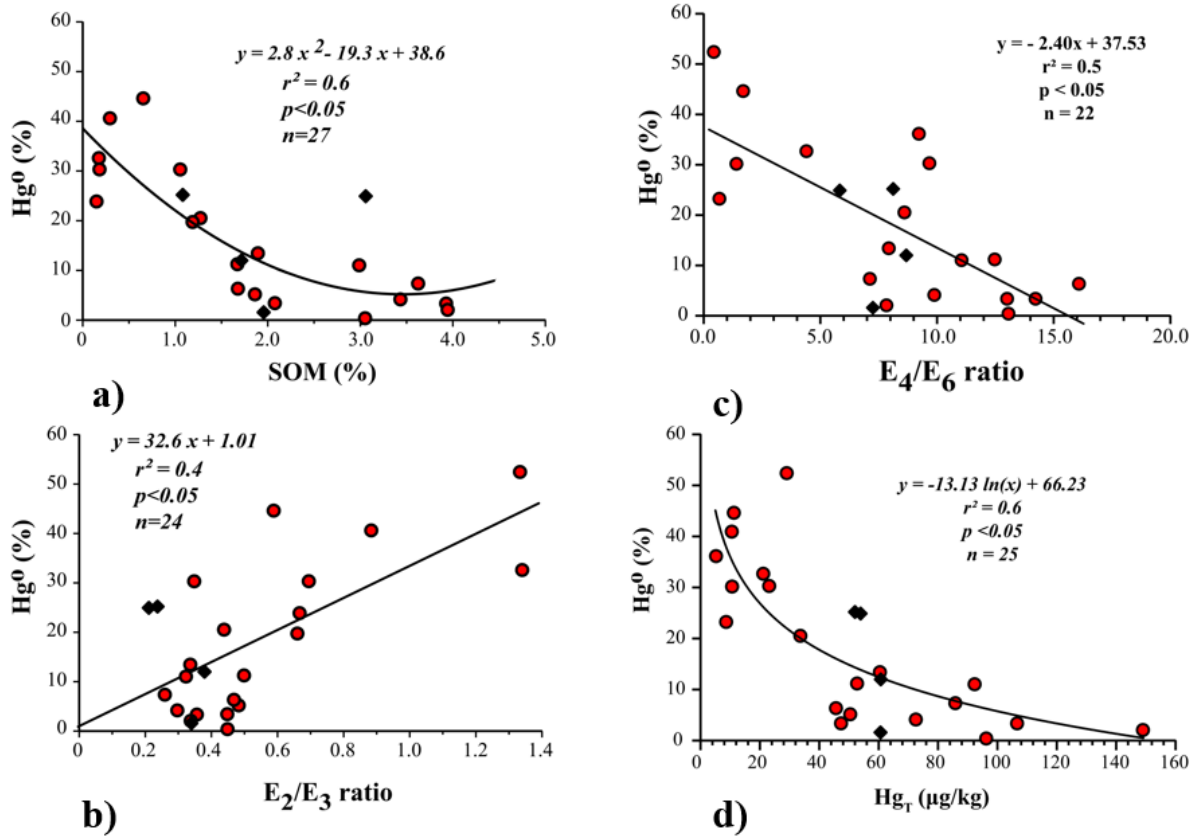


Figure 5

Table 1: Salinity of the overlying water column, sediment texture, total organic carbon (SOM) (in dry weight %), total nitrogen (TN) (in dry weight %), Carbon/Nitrogen molar ratio (C/N), E₂/E₃, E₄/E₆, Hg_T and Hg⁰ in the estuarine sediments from the Zuari and Mandovi estuarine regions.

SAMPLE ID	Lat (°N)	Lon (°E)	Salinity (PSU)	Clay (%)	Silt (%)	Sand (%)	TC (%)	TN (%)	TIC (%)	C/N molar ratio	SOM (%)	E ₂ /E ₃	E ₄ /E ₆	Hg _T (µg.kg ⁻¹)	Abso. Hg ⁰ (µg.kg ⁻¹) Avg±std dev	Hg ⁰ (%)
ZE1	15.44	73.82	34.2	4.6	30	65.3	2.04	0.04	1.39	55.5	0.65	0.59	1.69	11.2 ±0.4	5.0 ±0.2	44.6 ±1.3
ZE2	15.42	73.80	34.3	14.2	25	60.9	0.62	0.03	0.33	24.4	0.29	0.88	14.00	10.5 ±0.3	4.3 ±0.1	40.6 ±1.2
ZE3	15.41	73.81	35.8	21.6	48	30.4	2.27	0.09	1.09	30.8	1.19	0.66	9.22	9.5 ±0.2	1.9 ±0.2	19.8 ±0.4
ZE4	15.44	73.84	34.8	10.9	31	57.9	0.59	0.03	0.41	22.7	0.18	0.69	1.40	10.6 ±0.3	3.2 ±0.1	30.3 ±0.9
ZE5	15.44	73.85	34.9	4.6	40	55.6	0.36	0.03	0.23	13.7	0.13	1.33	0.43	29.0 ±0.9	15.2 ±0.5	52.5 ±1.6
ZE6	15.42	73.84	34.1	6.1	18	76.1	0.30	0.03	0.15	11.0	0.15	0.67	0.67	8.6 ±0.3	2.0 ±0.1	23.9 ±0.7
ZE7	15.41	73.83	34.5	5.4	13	81.4	0.90	n.d.	0.72	n.d.	0.17	1.34	4.40	21.1 ±0.6	6.9 ±0.1	32.6 ±0.7
ZE8	15.43	73.90	23.3	41.8	47	11.0	4.13	0.3	0.18	15.8	3.94	0.34	7.83	149 ±1.5	3.1 ±0.1	2.1 ±0.1
ZE9	15.41	73.90	21.4	31.9	43	24.9	4.12	0.26	0.19	18.8	3.93	0.36	13.00	106.6 ±1.1	3.6 ±0.1	3.4 ±0.1
ZE10	15.41	73.90	12.7	35.0	46	19.4	3.53	0.22	0.54	19.0	2.99	0.32	11.05	92.3 ±0.9	10.2 ±0.1	11 ±0.1
ZE11	15.41	73.91	17.7	41.5	56	2.3	3.55	0.25	0.12	16.4	3.43	0.3	9.88	72.5 ±0.7	3.0 ±0.1	4.2 ±0.1
ZE12	15.41	73.91	12.5	36.4	53	10.8	1.81	0.13	0.13	16.3	1.68	0.47	16.08	45.6 ±0.9	2.9 ±0.1	6.3 ±0.2
ZE13	15.41	73.91	15.3	30.4	53	16.2	3.23	0.27	0.18	14.2	3.05	0.45	13.06	96.2 ±1.0	0.4 ±0.1	0.4 ±0.1
ZE14	15.41	73.92	14.4	39.0	40	20.7	2.01	0.15	0.14	15.3	1.86	0.48	30.00	50.4 ±0.5	2.6 ±0.1	5.2 ±0.2
ZE15	15.41	73.93	13.9	28.2	38	33.5	2.19	0.15	0.11	17.0	2.08	0.45	14.22	47.3 ±1.0	1.6 ±0.1	3.4 ±0.1
ZE16	15.40	73.95	10.3	28.1	34	38.2	3.72	n.d.	0.09	n.d.	3.62	0.26	7.12	85.8 ±0.9	6.3 ±0.1	7.4 ±0.2
ZE17	15.38	73.96	7.8	23.9	35	41.5	1.95	0.17	0.06	13.2	1.89	0.34	7.93	60.4 ±0.6	8.1 ±0.2	13.5 ±0.3
ZE18	15.37	73.96	7.7	23.6	29	47.1	1.75	0.13	0.08	16.0	1.67	0.5	12.47	52.7 ±1.1	5.9 ±0.1	11.3 ±0.2
ZE19	15.36	73.99	3.7	15.5	29	56.0	1.34	0.09	0.06	17.1	1.27	0.44	8.60	33.6 ±0.7	6.9 ±0.1	20.5 ±0.4
ZE20	15.35	74.00	4.3	13.0	24	63.4	1.23	0.07	0.18	21.7	1.05	0.35	9.67	23.1 ±0.5	7.0 ±0.1	30.3 ±0.6
ME1	15.48	73.79	34.9	24.4	47	28.7	2.04	0.21	0.32	5.8	1.71	0.38	8.68	60.7 ±0.6	7.3 ±0.2	12 ±0.2
ME2	15.50	73.85	31.9	21.4	39	40.0	2.26	0.16	0.31	8.5	1.96	0.34	7.25	60.6 ±0.6	1.0 ±0.1	1.6 ±0.1
ME3	15.51	73.86	31.3	18.8	29	52.6	1.42	0.08	0.2	10.4	1.22	0.21	7.26	39.7 ±0.8	n.d.	n.d.
ME4	15.51	73.91	27.7	21.1	29	49.7	1.19	0.08	0.11	9.5	1.08	0.24	8.12	52.0 ±0.5	13.1 ±0.1	25.2 ±0.3
ME5	15.52	73.93	25.3	19.2	32	49.2	1.75	0.12	0.07	8.9	1.68	0.2	7.61	39.7 ±0.8	n.d.	n.d.
ME6	15.55	74.00	22.7	30.1	51	18.9	3.26	0.2	0.2	9.8	3.06	0.21	5.83	53.9 ±0.5	13.4 ±0.1	24.9 ±0.3
ME7	15.48	74.02	15.9	8.8	24	66.9	2.05	0.13	0.13	9.7	1.92	0.2	7.40	35.3 ±0.7	n.d.	n.d.

Table 2: The Pearson correlation between the salinity of overlying water column, sediment texture, total organic carbon (SOM), total nitrogen (TN), Carbon/Nitrogen molar ratio (C/N), E₂/E₃, E₄/E₆, Hg_T and Hg⁰ in the estuarine sediments from the Zuari and Mandovi estuarine regions.

	Salinity	TC	TN	TIC	C/N molar ratio	SOM	E ₂ /E ₃	E ₄ /E ₆	Clay	Silt	Sand	Hg _T	Abso. Hg ⁰	Hg ⁰
Salinity	1.00													
TC	-0.35	1.00												
TN	-0.34	0.91	1.00											
TIC	0.51	-0.05	-0.25	1.00										
C/N molar ratio	0.15	0.00	-0.30	0.84	1.00									
SOM	-0.47	0.96	0.96	-0.32	-0.23	1.00								
E₂/E₃	0.47	-0.55	-0.52	0.37	0.31	-0.62	1.00							
E₄/E₆	-0.46	0.26	0.34	-0.28	-0.11	0.32	-0.24	1.00						
Clay	-0.44	0.77	0.83	-0.34	-0.25	0.82	-0.53	0.64	1.00					
Silt	-0.13	0.67	0.72	-0.05	-0.08	0.65	-0.31	0.33	0.77	1.00				
Sand	0.30	-0.76	-0.83	0.21	0.18	-0.78	0.44	-0.51	-0.94	-0.94	1.00			
Hg_T	-0.36	0.83	0.91	-0.36	-0.31	0.89	-0.45	0.26	0.76	0.56	-0.70	1.00		
Abso. Hg⁰	0.10	-0.16	-0.23	0.11	-0.08	-0.18	0.16	-0.33	-0.24	-0.03	0.14	-0.16	1.00	
Hg⁰	0.48	-0.69	-0.79	0.43	0.44	-0.76	0.66	-0.54	-0.83	-0.53	0.73	-0.70	0.52	1.00

Supporting Material

Molecular characteristics of sedimentary organic matter in controlling *mercury (Hg)* and *elemental mercury (Hg⁰)* distribution in tropical estuarine sediments

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Functional groups(qualitative information) in SOM from Zuari estuary by using FT-IR spectroscopic studies

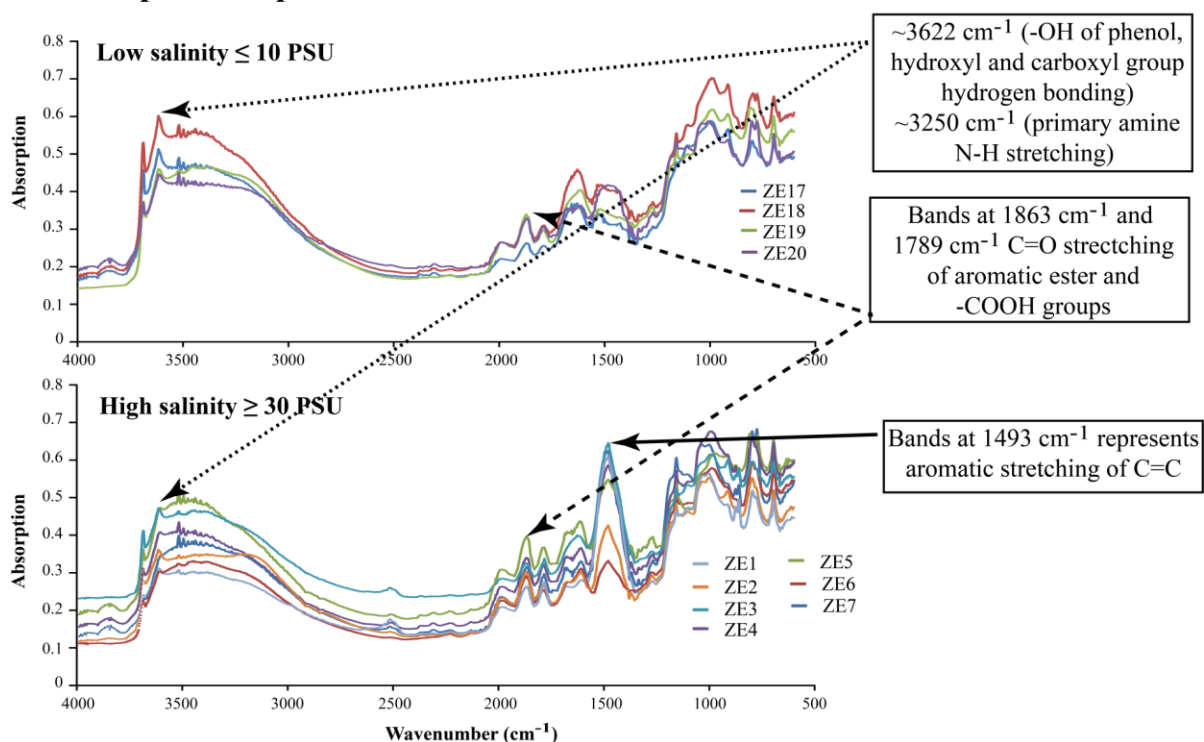


Figure SM1 FT-IR spectrum of SOM from a tropical estuarine system (Zuari estuary, Goa, India)

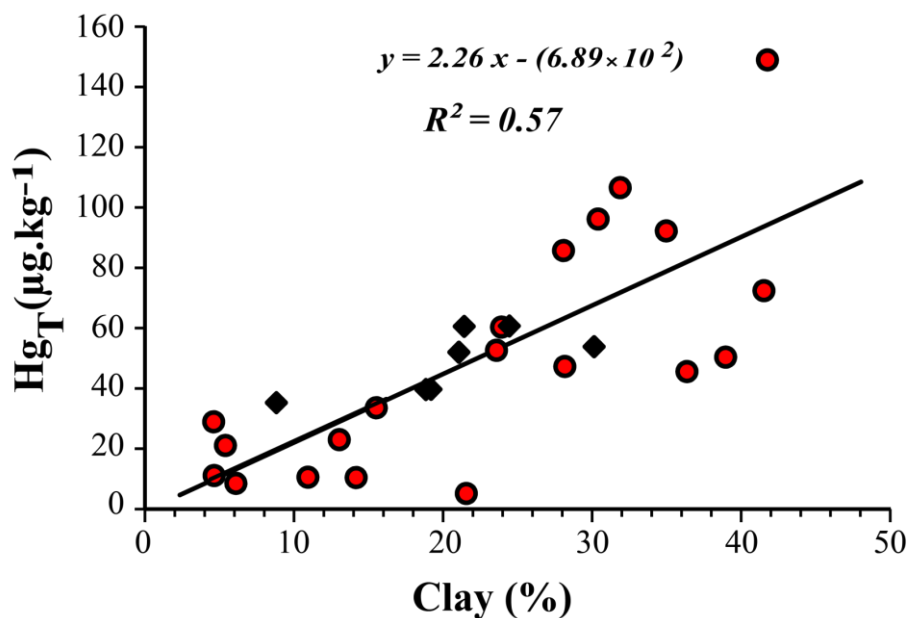


Figure SM2 Variation of Hg_T as a function of varying clay content in the sediment from the Mandovi(♦) and Zuari(●) estuaries .

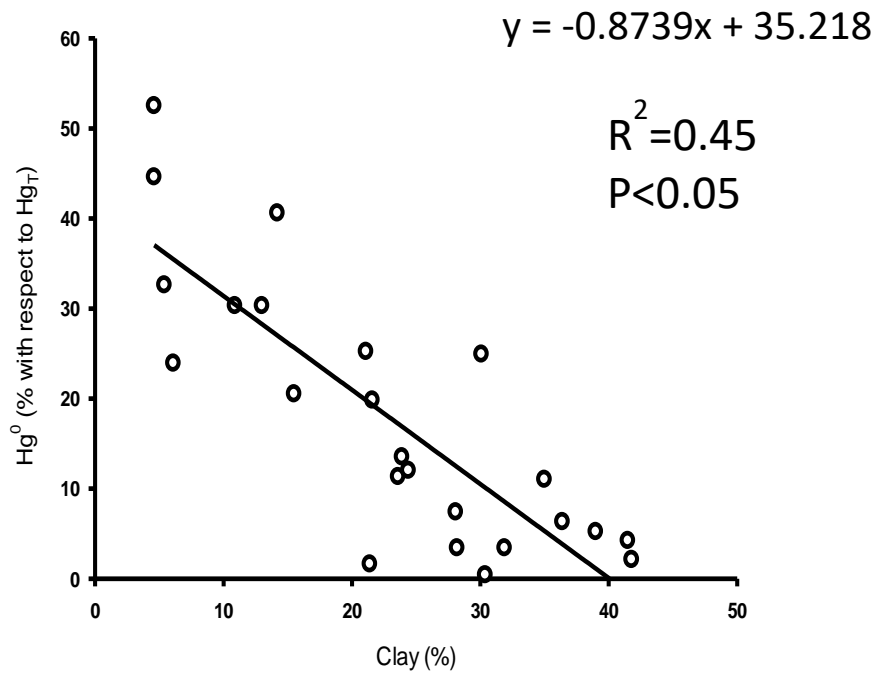


Figure SM3 Variation of Hg⁰ as a function of varying clay content in the sediment from the Mandovi and Zuari estuaries