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Seawater intrusion and re-suspension of surface sediment control mercury (Hg) distribution and its bioavailability in water column of a monsoonal estuarine system

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ABSTRACT

There is limited knowledge regarding seawater intrusion on Hg distribution in monsoon fed tropical estuarine systems during the dry season. This study examined the influence of re-suspension of sediment and intrusion of Hg bound SPM (by the tide) from the outside of an estuary in controlling distribution, mobility, and bioavailability of Hg within the estuarine systems during the dry season (February to May). This investigation was carried out in a monsoon-fed tropical estuarine system (Mandovi Estuary) in the central west coast of India. Total Hg concentrations in the water column showed an increasing trend from upstream to downstream of the estuary. The concentration of Hg in the water column of the estuary was much below the concentration recommended by the EPA for aquatic life ambient water quality. Dissolved Hg was found to associate mainly with the higher molecular weight fraction of dissolved organic matter (DOM). A significant portion of the total Hg in the water column was found to be associated with the suspended particulate matter (SPM). The average bio-accumulated Hg concentration in edible oyster was high (collected from the estuary) during the dry season compared to the monsoon period.

This study revealed that re-suspension of Hg associated finer sediment particle and intrusion of Hg bound SPM (by the tide) from the outside of an estuary increased bioaccumulation of Hg in the estuarine systems during the dry season. It is suggested that re-suspension and intrusion of Hg (due to tide) may increase Hg bioaccumulation in commercially important biological species from different tropical estuarine system during the dry period. The outcome of this research can be useful for policy makers to take proper decision to reduce and control Hg/toxic metals pollution (if any) in tropical estuarine system.

KEYWORDS: tropical estuarine system; oyster; mercury pollution; resuspension, particulate bound mercury; Mandovi Estuary

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INTRODUCTION

Estuarine ecosystems are the nursery grounds for numerous economically important biological species (Beck, et al., 2001; Sheridan and Hays 2003). Many commercially important biological species start their lives in estuaries, and part of their life cycles occurs in both fresh and saline waters. Estuaries are also utilized as pathways for different biological species during their migration (Able, 2005; Elliott, et al., 2007). Therefore, healthy estuarine ecosystems are important (Christensen, et al., 1996; Daily, 2003; Chakraborty et al., 2010). Knowledge of distribution and speciation of pollutants in estuarine system is necessary to control or reduce the impact of pollutants on the numerous economically important biological species. Estuaries in developing countries are more vulnerable to pollution due to rapid growing economy and industrialization in the countries (Varis, and Vakkilainen, 2001; Kennish, 2002; Isla, 2009; He, 2014). India is an industrial giant with one of the fastest growing major economies in the world (Chakraborty, 2017; Rose, 2016).

A large number of tropical rivers in India are fed by monsoon rains. Estuaries receive high river discharge during monsoon period (June to September) and very little or no river discharge during dry period (February to May). Pollutants in estuarine systems usually get diluted and flushed out from the estuaries during heavy rain periods. It has been reported that pollutants remain longer time in estuarine systems due to poor flushing during dry period (Bárcena, et. al., 2012; Sainz, et.al. 2004). Longer residency time of pollutants in an estuary may increase their bioavailability in the estuarine system during low river discharge time (Elbaz-Poulitchet, 2005, Chakraborty et al., 2016). The distribution and fate of pollutants within monsoon fed tropical estuaries during dry period are poorly understood.

Mercury (Hg), one of the priority pollutants by the international marine environmental protection agencies (Anthony and Breimhurst 1981; Tchounwou et al., 2012), has been reported to have negative effects on marine living resources (Rice 2014). This toxic metal has also been reported to show detrimental effects to human and ecosystem health (Clarkson, 1993; Tchounwou, et. al., 2003; Fitzgerald, et al., 2007; Selin, 2009). India, the third highest energy consumer (world ranking), is also the second highest Hg emitter in the world (Sloss, 2012). The distribution of Hg and its fate in tropical estuaries are poorly understood.

Biogeochemical processing of Hg in an estuarine system consists of a series of complex processes that Hg undergoes after entering (via atmosphere or river run-off) into an estuarine system. In general these are as follows (i) Hg undergoes complexation and reduction reactions with dissolved organic matter (DOM) and suspended particulate matter (SPM) in the water column. Mercury prefers to associate with DOM and sedimentary organic matter (SOM) of high molecular weight (Chakraborty

et al., 2014). However, minimal information is available on Hg-DOM and Hg-SPM interactions in tropical estuarine systems.

(ii) A part of Hg (from water column) gets precipitated as hydroxides, Hg-SPM, and Hg-DOM complexes from the overlying water column to the bottom sediment. (iii) A fraction of the total Hg (in water and sediment) undergoes reduction reactions and is returned to the atmosphere (the process is known as evasion). (iv) Precipitated Hg undergoes diagenetic changes and becomes an integral part of estuarine sediments. (vi) A portion of sedimentary and dissolved Hg in the presence of labile organic matter gets converted to methylmercury by sulfate-reducing bacteria in estuarine water and sediment respectively. However, the concentration of methylmercury in an estuarine water column (a dynamic system) is usually much less compared to the bottom sediment. There is minimal knowledge available in the literature on Hg distribution, speciation in tropical monsoon fed estuarine system. Inadequate flushing and prolonged residency period of Hg during the dry season in monsoon supported estuarine system is expected to intensify Hg bioavailability in the system.

The objective of this study was to test the hypothesis that re-suspension of Hg associated particle and intrusion of Hg bound SPM (by the tide) from the outside of an estuary may control distribution, mobility, and bioavailability of Hg within the estuarine systems during the dry season.

The Mandovi Estuary, located in the central west coast of India, was chosen as a representative of monsoon fed tropical estuary. During a tidal cycle in the Mandovi Estuary, the salinity remains almost constant (35 PSU) throughout the dry period (February to May) and varies from 8 to 22 PSU during the wet period (June to September) (Qasim&Sen Gupta 1981; Shetye et al. 1995) at the mouth of the estuary. The salinity range in this estuary is notably time-dependent and moves through different situations of stratification (riverine, highly-stratified, partially-mixed and well-mixed) as the river flow into the estuary varies from high in the wet season to negligible amounts at end of the dry season. Heavy precipitation and land runoff during monsoon (June to September) bring significant fluctuations in temperature, salinity, flow patterns, dissolved oxygen, and nutrients. The Mandovi Estuary becomes freshwater-dominated (Qasim&Sen Gupta, 1981) during the wet period. By the end of September, the effect of freshwater inrush gets reduced, and saline water intrudes further toward upstream regions.

In this work we studied the processes that control Hg distribution and bioavailability in the water column of the Mandovi estuary (a tropical estuarine system) during the dry season (with little or no river discharge).

2.1. MATERIALS AND METHODS

2.1.1.1. Study area and sampling

Samples were collected from the Mandovi Estuary, a tropical monsoonal estuary in the West Coast of India. The Mandovi Estuary is characterized by abundant runoff from river (approx. $258 \text{ m}^3 \cdot \text{s}^{-1}$) during wet monsoon period (June-September) and negligible runoff (approx $6 \text{ m}^3 \cdot \text{s}^{-1}$) during dry monsoon period (October-May) (Vijith et.al., 2009). As a result, this estuary acts as an extension of the river during wet period and an extension of the sea during dry period. This estuary is an example of mesotidal estuary where the tidal ranges are from 2.3 and 1.5m during the spring neap tides respectively (Manoj and Unnikrishnan 2009). Circulation in this estuary during dry period is dominated by tidal and wind induced currents and the extension of saline water was reported as far as 45 km inland from the mouth of the estuary (Manoj and Unnikrishnan 2009). High energy conditions prevail in the lower estuary during the monsoon and pre-monsoon seasons because of the consistent presence of Estuarine Turbidity Maximum (Rao et.al., 2011). On the basis of salinity the Mandovi Estuary falls under Partially Mixed Estuaries. The water, suspended particulate matter (SPM) and sediment samples were collected from ten stations (upstream to downstream on the basis of the salinity gradient) from the Mandovi estuary during spring tide in the month of February 2018. The detail descriptions of the sampling locations are given in Figure 1 and Table 1.

The surface and bottom water samples were collected by using Niskin samplers (Ocean Test Equipment Inc., Florida, USA). Salinity, pH and dissolved oxygen measurements were determined in-situ by using a portable multiparameter pH meter (Eutech CyberScan PCD 650 with ECFC7252203B pH electrode, Thermo Scientific) that were later compared with the CTD data (Seabird SBE 19plus Profiler CTD, USA).

Collected water samples (surface and bottom) were filtered through filter paper of $0.45 \mu\text{m}$ pore size (MCE membrane, MF-Millipore). Both the filtered and unfiltered samples were acidified (by using ultra-pure HNO_3 obtained from Merck, Germany), and transferred to pre-cleaned 500 mL Teflon bottles. A portion of filtered samples were also transferred to 60 mL amber colored bottles for dissolved organic matter (DOM) measurements and stored in ice box. Bottom water samples were collected in 5L pre-cleaned cans for SPM analysis and brought to the laboratory within 4-6 hours and filtered by using $0.45 \mu\text{m}$ filter paper (MCE membrane, MF-Millipore).

Sediment samples were collected using a stainless steel Van Veen grab. The top 0-5 cm of the sediment was carefully removed, stored in zip-lock bags at a low temperature. The sediment and SPM samples were freeze dried and homogenized in laboratory and stored in Teflon sample vials for further analyses.

Oyster samples were collected on a regular interval (monthly) for one year (Feb, 2015-Jan, 2016) from the two sampling locations (inter-tidal areas) from the same region, Goa, central west coast of India.

2.2.1.2. Texture analysis of sediment

A Particle Size Analyzer (LPSA from Malvern Mastersizer 2000, Worcestershire, UK) was used to analyze the texture of the sediment after separating the sand content by wet sieving by passing through 63 μ m sieve. Pump and stirrer speeds of the instrument were kept constant throughout the calibration and analysis of samples. Duke's latex and glass sphere standards were used in a range of 0.2-62 μ m for calibration of the instrument. Each sample were analyzed three times and the average value of the texture was considered when the standard deviation of $\pm 5\%$. A vivid description of the procedure has been described in the literature (Ramaswamy and Rao, 2006 and Chakraborty et al., 2015).

2.3.1.3. DOM analysis

The seawater samples were collected into acid-cleaned 30 mL glass vials and immediately frozen upright at -20°C . A Shimadzu TOC-LCPH analyzer was used to determine DOM (Dickson et al., 2007). DOM was analysed at 680°C following combustion catalytic oxidation method. Standardization was achieved using potassium hydrogen phthalate for DOM. A 5 point calibration curve was generated before each batch. Triplicate analysis was done for each sample. CRM (Deep Sea standard; 41–44 μM for total organic carbon) procured from University of Miami was run in each batch, and the accuracy of the analysis was $\pm 1 \mu\text{M}$.

The characterization of dissolved organic carbon in the water samples were carried out after filtration through 0.45 μ m filter paper (MCE membrane, MF-Millipore). The filtrates were used for the spectrochemical characterization of colored dissolved organic matter (CDOM) by using Spectroquant® Pharo-300 (Merck Millipore) UV-Vis spectrophotometer (Helms, et al., 2008; Peacock, et al., 2014). The spectrophotometer was regularly checked for accuracy of absorbance and wavelength. The calibration was done by using NIST-grey glass filters SRM 1930 and Holmiumoxide Solution Merck reference material for Spectroquant® PhotoCheck (Travis, et al., 2005). Every sample was scanned three times and the mean value was considered and the standard deviation of absorbance was ± 0.02 .

2.4.1.4. Absorption spectra.

Water samples were filtered through 0.45 μ m filter paper (MCE membrane, MF-Millipore). The filtrates are used for the spectrochemical characterization of colored dissolved organic matter (CDOM) by using Pharo-300 Spectroquant (Merck Millipore) UV-Vis spectrophotometer as described in the literature (Helms, et al., 2008; Peacock, et al., 2014). The calibration was done by using well characterized humic and fulvic acid solutions (obtained from International Humic substances Society). The accuracy of the spectrophotometer was regularly checked by using NIST-grey glass filters SRM

1930 and Holmiumoxide Solution Merck reference material for Spectroquant® PhotoCheck (Travis, et al., 2005). Every sample was scanned three times and the mean value was considered and the standard deviation of absorbance was not more than ± 0.02 . The spectrum was scan over a range from 200 to 700 nm wavelengths with a 1nm interval in a quartz cell of 10mm. The spectral absorbance at 250, 364, 465 and 665 was used to calculate the E_2/E_3 and E_4/E_6 ratio as described in the literature (Chen et al., 1977 and Helms et al., 2008).

2.5.1.5. Pre-concentration of water samples for Hg analysis

Pre-concentration of Hg from the water samples were carried out using Ammonium pyrrolidinedithiocarbamate (APDC) (chelating agent) (Sigma-Aldrich) and methyl-isobutyl-ketone (MIBK) (Merck, Germany) as reagents following a slightly modified protocol described in Kremling and Petersen (1974) and Satyanarayana et al., (2006). Acidified 400mL of water samples (to a pH of 2.5 by using ultrapure HNO_3) was placed in a 500mL separating funnel. About 10 mL of 1% solution of APDC 15mL of MIBK were added, shaken for almost 4 minutes and kept. Organic layer was collected after 15 minutes to a 125mL separating funnel. The same procedure was repeated by adding 10mL APDC and 15mL MIBK to the aqueous layer for the complete extraction of Hg from the water sample. The Hg in the organic layer was back extracted by adding 200 μL of ultrapure HNO_3 , shaken and by adding 9.8mL of Milli-Q water after 15 minutes. Final volume of 10 mL aqueous layer containing Hg transferred to Teflon vials for further analysis. 1% of APDC solution was prepared and treated with 10 mL of MIBK in a separating funnel to remove all the possible contamination of Hg prior the experiment. The extraction procedure was performed completely in a clean environment. Separating funnels and storage vials are acid washed to limit Hg contamination. The aqueous Hg solution with known concentration was prepared in the laboratory to check the recovery. The recovery was $>98\%$.

2.6.1.6. Hg Analysis

Hg in pre-concentrated water samples, SPM, and sediment were analyzed by using Direct Mercury Analyzer (Tri-Cell DMA – 80, Milestone, Italy). The analysis in DMA–80 comprises of four steps, 1) thermal decomposition of the sample, 2) catalytic conversion/removal of unwanted species, 3) pre-concentration of Hg by a gold amalgamator, and 4) determination of the Hg by atomic absorption spectrophotometry. Oxygen was used as the carrier gas. The DMA-80 instrument was calibrated by using aqueous Hg standards. The working standards of Hg (aqueous) solution were freshly prepared in the laboratory before calibration. 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 $0.09 \pm 0.04 \text{ mg.kg}^{-1}$. After a satisfactory recovery (>98%), the calibration curve was used for Hg analysis in different matrices. Aqueous standard of Hg was prepared in the laboratory prior to analysis and used to check the calibration. An instrument blank and the aqueous Hg standard were run after every 10 samples. The standard deviation of absorbance was not more than $\pm 2\%$.

3.2. Results and discussion

The surface water salinity of the Mandovi estuary ranged from ~13 (at the upstream) to ~34 PSU (at the downstream) while the salinity of the bottom water ranged from ~14 (at the upstream) to ~35 PSU (at the downstream). Data suggest that the water column in the Mandovi estuarine system was vertically well mixed during the sampling time. It has been reported that the Mandovi estuary is a vertically well-mixed estuary and behaves like an extension of Arabian Sea during the dry season (February-May) (Manoj and Unnikrishnan., 2009; Varma et al. 1975; De Sousa 1977; Qasim&Sen Gupta 1981; De Sousa et al. 1981; Shetye et al. 1995). The pH of the estuarine surface water varied from 8.2 ± 0.1 to 7.3 ± 0.1 and that of the bottom water ranged from 8.3 ± 0.1 to 7.3 ± 0.1 . The surface waters in the Mandovi estuary was oxygenated and the dissolved oxygen (DO) concentration varied from 3.7 to 4.4 mg.L^{-1} , whereas, the DO value in bottom water ranged from 3.5 to 4.3 mg.L^{-1} . The small variation in DO concentrations in the surface and bottom water of the estuary also suggests that the water column of this estuary was well mixed during the dry season. The variations in salinity, pH, and DO data in the water column are presented in Table 1.

The concentration of SPM in the water column varied from the upstream to the downstream of the Mandovi estuary. The SPM concentration (6.9 mg.L^{-1}) at the upstream was much lower than the SPM concentration (22.6 mg.L^{-1}) at the downstream of the estuary (Table 1). A very similar observation has been proclaimed in the literature (Kessarkar et al., 2010). It has been described that the concentrations of SPM in the Mandovi estuary are generally low at the river-end locations, and typically increases towards the sea, and are highest at sea-end stations (Kessarkar et al., 2010). The highest concentration ($\sim 45 \text{ mg.L}^{-1}$) of SPM was determined at M2 station (the last station within the estuary). However, the SPM concentration in the water column was low (7.2 mg.L^{-1}) at M1 station which was explicitly placed outside of the estuary. Kessarkar et al (2010) have also published that estuarine turbidity maximum (ETM) appears at the sea-end stations (in the Mandovi estuary) during high river discharge time (June–September) and even at low river discharge time (February–May). The formation of ETM during June–September was due to the southwest monsoon and the latter characterized by a persistent sea breeze. Therefore, the high concentration of SPM in the water column of the Mandovi estuary at the downstream site was due to development of ETM due to the persistent sea breeze.

Total dissolved organic matter (DOM) (that includes organic matter in SPM and the dissolved organic carbon) concentration in the Mandovi estuarine water varied from ~1.3 to ~1.7 mg.L⁻¹. The high concentration of DOM was found (1.7mg.L⁻¹) at the mid of the estuary, and low concentration (1.3 mg.L⁻¹) at the downstream region of the estuary. The low concentration was due to increasing bacterial degradation at the seaward stations. It is relevant to mention that the SPM concentration in the water column was always much higher than the DOM concentration at each station. The differences between the SPM and the DOM concentration in the water column indicated that a significant fraction of the SPM was composed of inorganic complexes (dominated by Fe/Mnoxyhydroxide) during the sampling period. The presence of rich Fe ore in the adjacent landmass is the reason Fe-oxyhydroxide was probably one of the primary components of the SPM in both the estuarine systems.

An exercise was also carried out to characterize the DOM of the Mandovi estuary using a UV-Visible spectrophotometer. The distribution of different molecular weight size fraction of DOM in the estuarine water column was investigated by comparing the E₂/E₃ ratio. It has been reported that the molecular size of DOM is inversely correlated with the E₂/E₃ ratio (De Haan and De Boer, 1987). Relatively, a high value of E₂/E₃ (ranging from 0.57 to 0.77) was noted in the estuarine water sample obtained at the middle and seawards part of the estuary. The lowest value of E₂/E₃ (~0.57) was detected in the midstream region (Table 2). These observation (based on E₂/E₃ ratio) suggest that high molecular weight fraction of DOM prevail in the midstream of the estuary. However, the molecular weight of DOM decreased at the downstream of the estuary. The presence of low molecular weight DOM at the downstream was probably due to increasing bacterial degradation at the seawards stations (Qasim&Sen Gupta 1981). Nevertheless, the quantitative information on the change in molecular weight of the DOM (from different parts of the estuary) could not be done in this study.

3.1.2.1. Variation of Total Mercury (Hg_T) in the estuarine waters

Concentrations of total Hg (Hg_T) in the water column of the Mandovi estuary (from upstream to downstream) varied from 40.8±2.0 pM to 201.4±10.1 pM. Total Hg concentrations showed an increasing trend from upstream to downstream of the estuary. Bhat et al., (2014) reported that total Hg concentrations in the Mandovi estuary varied from 349 to 847 pM. Table SM1 displays a comparison of total Hg concentration in the Mandovi estuary with other estuaries from the different parts of the world. Based on these data the concentration of Hg in the water column of the Mandovi estuary was below the Hg concentration recommended by the EPA for aquatic life ambient water quality (<https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table>).

3.2.2.2. Variation of dissolved mercury (Hg_D)

Concentrations of dissolved Hg (Hg_D) in the Mandovi estuary varied from 7.0 ± 0.3 to 48.1 ± 2.4 pM. Concentrations of Hg_D (obtained in this study) are comparable to the Hg_D level reported in different pristine estuarine systems in the different parts of the world (presented in Table SM1).

There was no statistically significant relationship existed between the concentration of Hg_D and the concentration of organic matter (OM) in the water column.

Dissolved Hg-DOM complexes were further characterized by UV-Vis spectroscopy. The concentration of Hg_D was found to be more with DOM with low E_2/E_3 (i.e., higher molecular weight fraction of DOM) values (Figure 2a). This observation suggests that Hg_D preferred to associate with higher molecular weight fraction of DOM. It has been reported earlier that Hg prefers to enrich with higher molecular size cut-off fraction of DOM (Chakraborty et al., 2014, 2015). Figure 2b shows that variation of Hg_D with E_4/E_6 ratio (indicator of HA/FA ratio) of the DOM. It was observed that Hg_D in estuary gradually increased with increasing E_4/E_6 ratio (i.e. increasing HA/FA ratio). However, quantitative estimation of HA and FA are required to understand the variation in concentration of dissolved Hg in the estuarine water column.

3.3.2.3. Variation of mercury associated with Suspended Particulate Matter (Hg_{SPM})

A significant portion of the total Hg (Hg_T) in the water column was found to be associated with the suspended particulate matter (SPM) in the Mandovi Estuary. Mercury associated with the SPM revealed an increasing trend as moving from the upstream to the downstream of the estuary (the similar variation was observed in SPM concentration of the water column). The low concentration of Hg associated with SPM (Mean \pm SEM $348.1 \pm 67.0 \mu\text{g.kg}^{-1}$ Mean concentration = $348.1 \pm 94.7 \mu\text{g.kg}^{-1}$) was observed in the upstream (where the salinity varied from 13.1-15.9 PSU) region of the estuary. The highest concentration of Hg associated with SPM ($Hg\text{-SPM}$) (Mean \pm SEM $694.1 \pm 75.5 \mu\text{g.kg}^{-1}$ Mean = $694.1 \pm 130.8 \mu\text{g.kg}^{-1}$; and Median value = $676.4 \mu\text{g.kg}^{-1}$) was found in the downstream (where the bottom water salinity varied from 30.9 to 34.9 PSU) region. Figure 2c shows that the distribution coefficient (K_D = concentration of dissolved Hg/concentration of Hg associated with SPM) of Hg linearly increased with the increasing SPM concentration in the estuarine water.

This increasing concentration of the SPM bound Hg in the water column towards the downstream of the estuary (during dry period) raised two relevant questions. (i) Was the intrusion of seawater (tide) responsible for bringing SPM bound Hg from the coastal areas and accountable for the high concentration of Hg_T and $Hg\text{-SPM}$ in the water column of the estuary? (ii) Was re-suspension of fine particles (due to wind and tide) from the bottom sediment responsible for high Hg_T and $Hg\text{-SPM}$ in the water column of the estuary? In order to answer these questions further analysis were carried out.

Figure 3a shows the variation of δC^{13} in sediments against δC^{13} ($\delta C^{13}Sed$) in SPM ($\delta C^{13}SPM$) from three different major tropical estuaries (Mandovi, Zuari, and Godavari Estuaries) during the dry period. Data were acquired from the literature (Sarma, et al., 2012; Shynu, et al., 2015). There was a robust positive relationship between the $\delta C^{13}Sed$ and the $\delta C^{13}SPM$ during the dry period in the estuaries. Therefore, it is proposed that the SPM in the water column of the Mandovi estuary was due to re-suspension of the finer particles (silt and clay particles) from the surface sediments. Figure 3b shows that the rivers discharge (for monsoon fed rivers) become negligible during the dry period of the year. Therefore, it is suggested that intrusion of seawater in the estuaries and re-suspension of the fine particles from the surface sediment was probably responsible for the SPM in the water column of the estuary.

It was proposed that there should be a relationship existed among the Hg associated with SPM and the Hg in the finer particles of the surface sediments. The concentration of Hg in the surface sediments was low and ranged from 38.8 ± 1.8 to $80.1 \pm 3.6 \mu g.kg^{-1}$. However, the concentration of Hg in the SPM of the water column varied from 281.1 ± 1.4 to $876.2 \pm 9.2 mg.kg^{-1}$. There was no significant relationship between the concentration of Hg in the SPM and the total sedimentary Hg concentration (Figure SM 1). The concentration of Hg in the SPM was much higher than the total Hg in the surface sediment.

If we assume that the SPM were made up only by the finer particles of the sediments then the concentration of Hg in the finer sediment did not match the SPM concentration (Table SM 2). Hence, the question why is there excess Hg in the water column of the Mandovi estuary remains. The probable sources of Hg the estuary are discussed below.

3.4.2.4. Probable sources of Hg associated with SPM in the Mandovi estuary

The ratio of Hg concentration in the SPM and the sedimentary Hg concentration gradually increased from the upstream towards the downstream of the estuary (Figure 3c). The concentration of Hg from anthropogenic sources in the Mandovi Estuary (determined by subtracting the Hg concentration in the finer particles of the sediments from the Hg concentration in the SPM) gradually increased with increasing salinity of the water column (upstream to downstream) (Figure 3d). The water column in upstream of the estuary was found to have much less concentration of Hg associated with SPM.

These observations confirm that there was intrusion of Hg associated SPM in the water column in the Mandovi Estuary (by seawater) during the dry season. This finding indicates that monsoon fed tropical estuary may face incursions of pollutants by seawater during the dry period. During post monsoon period, dark black powder was collected from the adjacent beaches (as shown in Figure SM2) of the

Mandovi River. The concentration of Hg in this black powder was found to be $200.5 \pm 5.0 \mu\text{g.kg}^{-1}$. The physical appearance of the black powder looked very similar to that of the fine particles of coal. The SEM images also support that the black powder was coal particles (Figure SM2b and c). The concentration of Hg in the coal sample (obtained from the nearby area of the Mormugao Port Trust) was $\sim 210 \pm 15 \mu\text{g/kg}$. The sources of this coal could be from the Mormugao Port Trust where ~ 25 million tons of coal — evenly spread across a standard football field. The transportation of coal via road, rail, and river has been reported to deteriorate the environment of Goa (<https://indianexpress.com/article/india/coal-on-move-25-tonnes-a-minute-is-choking-go-a-more-is-on-the-way-4904963/>). However, further investigation is required to identify the sources of this fine black particle associated with high concentration of Hg.

3.5.2.5. Bioaccumulation of Hg by filter feeders in the estuary during dry period

This study demonstrated that re-suspension of finer particles of estuarine sediment and inclusion of Hg associated with SPM (containing high concentration of Hg) (by tide) was responsible for high total Hg concentration of the overlying water column during dry period in the estuary. This process is expected to increase mobility and bioavailability of Hg in an estuarine system. Minimal river discharge and poor flushing is expected to increase residence time of Hg in the estuary and raise the possibility of filter feeders to get exposed to Hg (associated with SPM) during low river discharge period.

Therefore, further investigation was carried out to check the intra-annual variation in Hg bioaccumulation in edible oyster (species) from the same estuarine system. Figure 4 shows the variation in bio-accumulated Hg concentration in the oyster during dry and wet seasons. It is interesting to note that the average bio-accumulated Hg concentration was high during the dry period in two sampling stations from the same estuarine region. The average concentrations of bioaccumulated Hg (in oysters) during dry season at St. 1 and St. 2 were $76.2 \mu\text{g.kg}^{-1}$ and $48.2 \mu\text{g.kg}^{-1}$ respectively (presented by red and blue lines in Fig. 4a). The average concentrations of bioaccumulated Hg were $33.4 \mu\text{g.kg}^{-1}$ and $46.7 \mu\text{g.kg}^{-1}$ during the wet period (presented by red and blue lines in Fig. 4b). This observation clearly suggests that mobility and bioavailability of Hg may increase during the dry season due to re-suspension of finer particles and intrusion of Hg bound SPM in monsoon fed tropical estuaries. However, the concentrations of Hg in the edible oysters (in this study) were below the permissible limit.

Conclusions

Major tropical (monsoon fed) estuaries are surrounded by industrial estates all over the world. The health of these estuaries faces pressure from these industries. Estuaries, the nursing ground for many

commercially important biologically species, receive huge amount of treated and untreated effluent/sewage/ pollutants throughout the year. The high river discharge and flushing removes pollutants from the estuaries during monsoon period. However, poor flushing during dry season (pre-monsoon) increases the residence time of pollutants. This study described the distribution of Hg in estuarine water column and sediment. This study revealed that re-suspension of Hg associated particle and intrusion of Hg bound SPM (by tide) from the outside of an estuary may increase mobility and bioavailability of Hg within the estuarine systems during dry season.

In addition, the average bio-accumulated Hg concentration in edible oyster was high during the dry period in the estuary. Re-suspension and intrusion of Hg increased Hg bioaccumulation in commercially important biological species during the dry period. This research describes an important process of monsoon fed tropical estuaries which can be useful for policy makers to take proper decision to reduce and control Hg/toxic metals pollution(if any) during dry period.

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Captions and Legends

Figure1: The sampling locations from the Mandovi estuary, Goa, central west coast of India.

Figure2: Variation of dissolved Hg concentrations as a function of a) E_2/E_3 ratio; b) E_4/E_6 ratio of the CDOM and c) Variation of distribution coefficient (K_D) as a function of SPM concentrations in the water column of Mandovi estuary.

Figure3: a) Variation of δC^{13} in sediments against δC^{13} in SPM from three different major tropical estuaries (Mandovi, Zuari and Godavari estuaries) during the dry period. The data were put together from Sarma, et al., 2012 and Shynu, et al., 2015; b) Average monthly variation in River discharge from the monsoon fed tropical rivers along the Indian Coast; c) Variation in $[Hg_{SPM}]/[Hg_{sed}]$ ratio in different sampling locations along the Mandovi estuary and d) Variation in Hg concentration from other sources with respect to the salinity of the water column in the Mandovi estuary.

Figure4: The intra-annual variation of bio-accumulated Hg concentration in the oysters from the similar estuarine region. (a) shows the variation during the dry and (b) wet periods.

Table Legends

Table 1: Sampling Locations, environmental parameters (pH, salinity, DO) total organic carbon (TOC), suspended particulate matter (SPM) of the water column and sediment texture, in the Mandovi estuary, Central west Coast of India.

Table 2: Spectral ratios of CDOM (E_2/E_3 and E_4/E_6), sedimentary Hg concentration and Hg (total, dissolved and SPM) concentrations in water column of the Mandovi estuary, Goa, Central west Coast of India.

Research Highlight

- Seawater intrusion may change Hg distribution & bioavailability in tropical estuary

Table 2: Spectral ratios of CDOM (E_2/E_3 and E_4/E_6), sedimentary Hg concentration and Hg (total, dissolved and SPM) concentrations of the water column from the Mandovi estuary, Goa, central West Coast of India

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Sampling Station	E_2/E_3	E_4/E_6	Hg _{Dissolved} (pM)	Hg _r (pM)	Hg _{SPM} ($\mu\text{g}\cdot\text{kg}^{-1}$)	Hg _r ($\mu\text{g}\cdot\text{kg}^{-1}$) (Sediment)
M1	0.64	3.43	22.8 \pm 1.1	106 \pm 5.3	676.4 \pm 20.3	66.7 \pm 3.0
M2	0.64	1.94	16.9 \pm 0.8	201.4 \pm 10.1	573.0 \pm 22.9	66.6 \pm 3.0
M3	0.60	2.80	26.6 \pm 1.3	124.6 \pm 6.2	832.9 \pm 25.0	43.6 \pm 2.0
M4	0.63	3.63	48.1 \pm 2.4	91.7 \pm 4.6	391.9 \pm 19.6	57.1 \pm 2.6
M5	0.57	2.33	41.6 \pm 2.1	106.7 \pm 5.3	537.7 \pm 21.5	43.6 \pm 2.0
M6	0.77	1.91	7.0 \pm 0.3	41.4 \pm 2.1	323.5 \pm 16.2	59.2 \pm 2.7
M7	0.67	1.91	14.0 \pm 0.7	72.3 \pm 3.6	876.2 \pm 35.0	80.1 \pm 3.6
M8	0.67	2.00	20.1 \pm 1.0	64.3 \pm 3.2	415.0 \pm 16.6	38.8 \pm 1.8
M9	0.62	4.00	12.6 \pm 0.6	40.8 \pm 2.0	281.1 \pm 14.1	78.7 \pm 3.6

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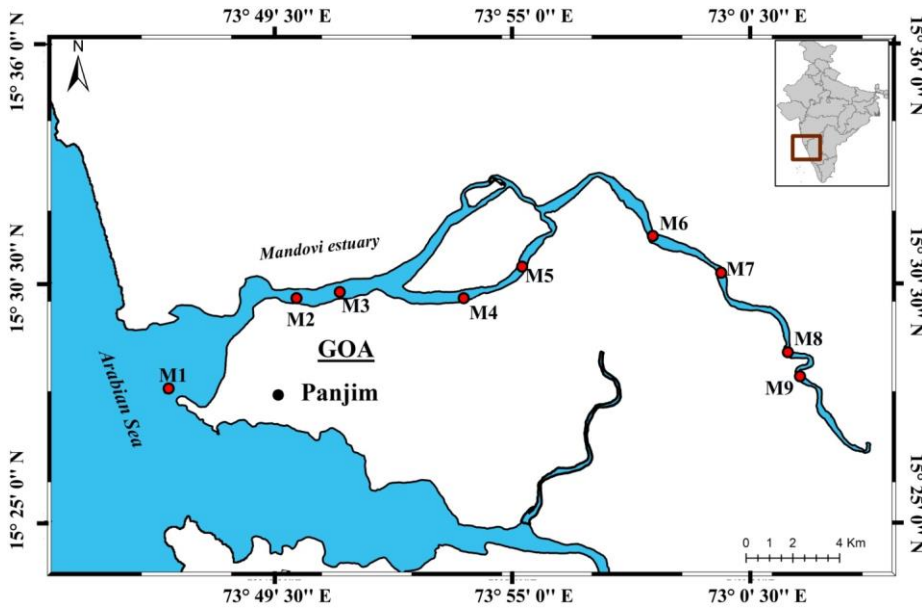


Figure 1

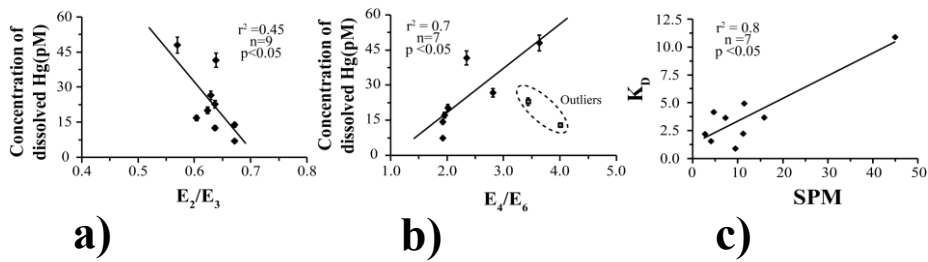


Figure 2

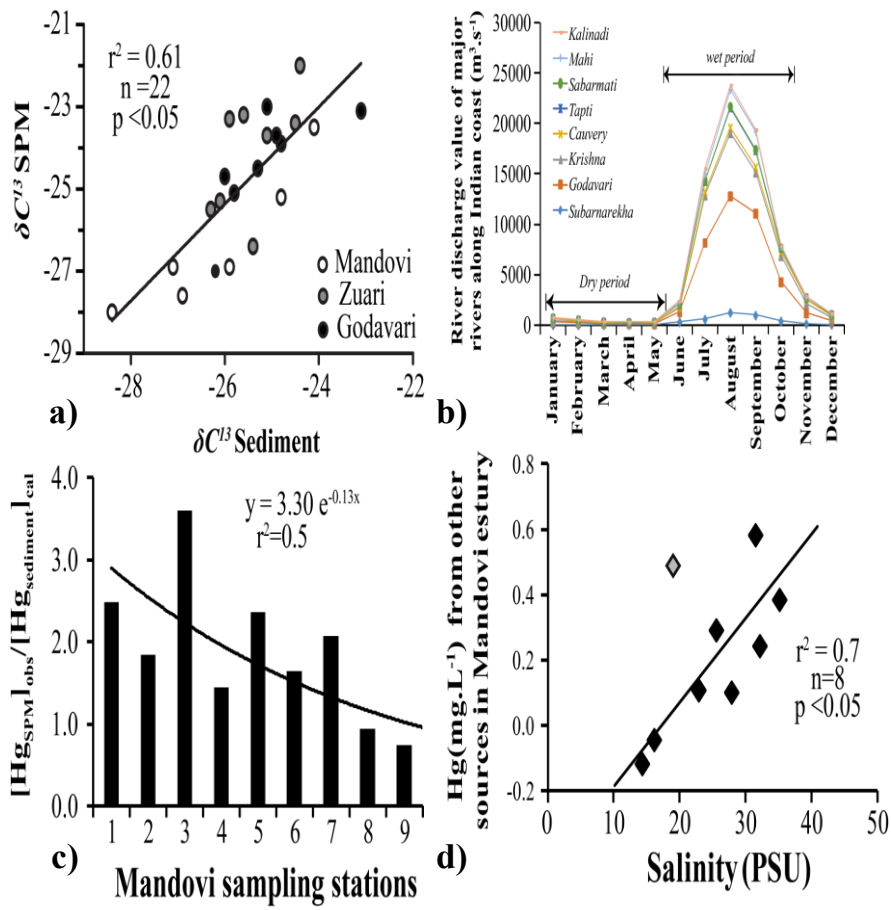


Figure 3

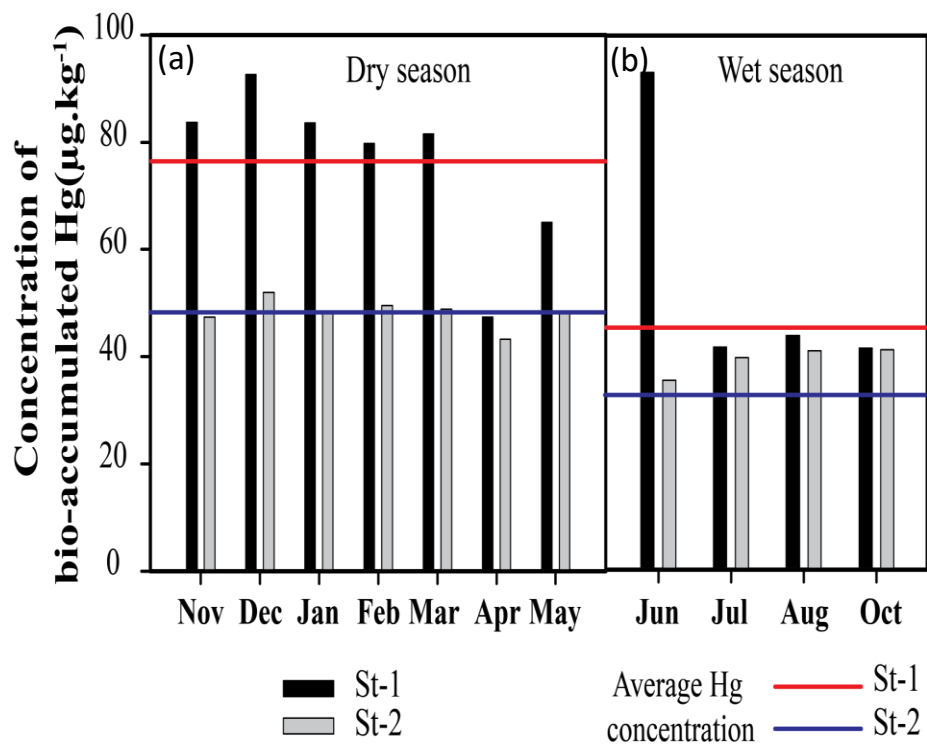


Figure 4

Supporting information

Seawater intrusion and re-suspension of surface sediment control mercury (Hg) distribution and its bioavailability in water column of a monsoonal estuarine system

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Figure SM 1: Variation of mercury associated with SPM (Hg_{SPM}) with respect to sedimentary mercury ($Hg_{Sediment}$) concentration in the Mandovi estuary, Goa, Central west coast of India.

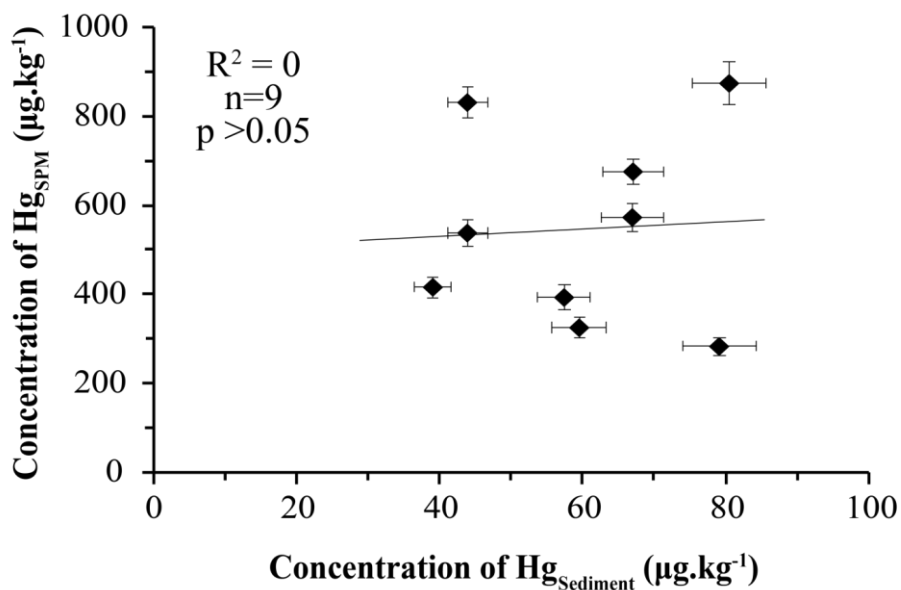
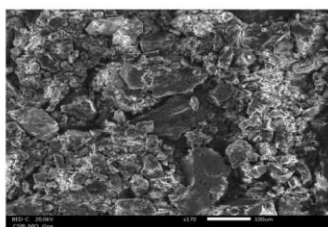


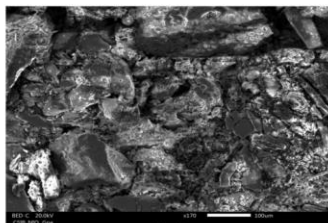
Figure2: a) Image captured along the beach near to the Mandovi estuary, central west coast of India; b) Scanning electron microscope(SEM) image of Coal sample (usually transports to Goa) and c) SEM image of Black material collected from the beach near to the Mandovi estuary, central west coast of India.



(a)



(b)



(c)

Table SM1 The concentrations of mercury associated with particulate matter $Hg_{SPM}(\mu g.kg^{-1})$ and dissolved Hg_D (pM) in the estuaries from the different parts of the world and the Mandovi estuary.

Name of the River/Estuaries	$Hg_{SPM}(\mu g.kg^{-1})$	Hg_D (pM)	References	Name of the River/Estuaries	$Hg_{SPM}(\mu g.kg^{-1})$	Hg_D (pM)	References
Tinto-Odiel Estuarine System (Gulf of Cádiz, Spain)				New Jersey Harbor Estuary			
Tinto estuary, Apr-98	60.2-1123.3	8.3-33	Cossa et al.,2001	Surface water	786.0	5.0	Balcom et al.,2008
Odiel estuary, Apr-98	140.4-6519.2	29.1-199.6			605.8	1.8	
Huelva Ria, Apr-98	361.1-902.7	7.0-9.5			84.2	3.8	
Gulf of Cádiz, Apr-98	80.2-421.2	2.1-3.8			409.2	3.21	
Riou Mort River,France				Bottom water	1175.4	4.8	
1999	253-2890	0.5-14.0	Schäfer et al.,2006		1035	1.9	
2000	185-847	1.5-15.0		204.6	4.5		
2001	107-1120	4.5-20.4		760.2	4.1		
2002	187-3040	4.0-22.9		190.6	2.5		
2003	113-1910	4.5-11.5		676.4	22.8		
Siberian estuaries and adjacent arctic coastal waters					573.0	16.9	
Lena	30	5.4	Coquery et al.,1995	Mandovi	832.9	26.6	Data in the present study
	210	4.5			391.9	48.1	
	110	3.2			537.7	41.6	
	320	3.2			32.5	7.0	
	350	3.5			876.2	14.0	
Laptev sea	410	6.8		415.0	20.1		
	1670	10.8		281.1	12.6		
Surface Waters of the English Channel							
	680	3.4	Cossa and Fileman1991				
	460	2.7					
	510	3.2					
	730	4.2					
	400	1.5					

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Table SM2:

Predicted concentration of sedimentary Hg ($\mu\text{g.kg}^{-1}$) based on composition of sediment texture in sediment samples collected from the central west coast of India, Mandovi estuary, Goa.

Sample ID	100%clay	75% Clay+25% silt	80%clay+20%silt	70% clay+30% Silt	
M1	272.9	45.0	43.4	46.7	50.1
M2	311.0	38.6	37.3	39.7	42.5
M3	231.5	48.7	47.6	49.9	52.1
M4	271.4	40.4	39.7	41.2	42.6
M5	227.4	51.1	49.7	52.5	55.3
M6	313.6	39.0	37.6	40.4	43.2
M7	423.5	36.8	34.2	39.5	44.8
M8	440.2	32.7	30.7	34.7	38.6
M9	379.7	40.5	37.7	43.4	49.0

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