

Diagenesis and bioavailability of mercury in the contaminated sediments of

Ulhas Estuary, India

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Abstract:

Sequential extraction of Hg was performed in a core collected from intertidal area in Ulhas Estuary in order to characterize the downward distribution and diagenetic behavior of Hg in a polluted estuary. Concentration of total Hg ranged between 0.46 and 6.40 $\mu\text{g g}^{-1}$ with significant decrease in surficial sediment as a result of closing of two Hg-cell based chlor-alkali plants. Results of sequential extraction showed that >65 % Hg was strongly bound to organo-sulfur and inorganic sulfide species that are not bioavailable. Flux of only 18.8 % of Hg was found compared to its depositing value on sediment-water interface. Hence, it is concluded that there is no significant diagenetic remobilization of Hg in Ulhas Estuary. This core also has been analyzed for ²¹⁰Pb geochronology. The estimated sedimentation rate is 0.31 cm y^{-1} in the present sampling region.

Key words: Ulhas Estuary, Mercury, Diagenesis, Bioavailability, Sedimentation rate

1. Introduction

The major environmental issues concerning metals in sediment are their potential availability to aquatic life (Bioavailability) and conditions under which they are remobilized (diagenesis). Processes that modify or alter particles in water bodies are known to influence particle-associated elements in several ways, such as altering the residence times (Santschi, 1984; Whitfield and Turner, 1987; Matty and Long, 1995), governing bioavailability (Elder, 1988), and determining the retention of particle-bound elements in the sedimentary record (Shaw et al., 1990). Bioavailable metals are defined as metals in such a biologically available chemical state that they can be taken up by an organism and can react with its metabolic machinery (Campbell et al., 1988). Many sediment bound metals are affected by the redox cycling of iron (Fe) and manganese (Mn) during early diagenesis and their concentrations tend to increase in the upper layer of sediment, producing higher concentrations near the sediment surface and lower concentrations at depth in the sediments (Berner, 1980). Though diagenesis alters the concentrations of other metals in the sediments as discussed above, opinions differ in case of mercury (Hg). These problems cannot be satisfactorily solved by trace metal analysis of the bulk sample alone. Hence, specific or sequential extraction techniques have been considered as a possible tool with which to assess trace element sources and the form in which they occur in sediments (Martin et al., 1987). Sequential extraction thus, allows us to understand the relative binding strengths of trace metals to the various solid phases by successive leaching with chemicals of increasing strength and selectivity (Kersten and Förstner, 1985). Hg has been a focus of extensive research due to its organic matter affinity, high toxicity, biomagnification capacity and difficulties in its control, and makes this element one of the most harmful metal to biota threatening both human and the ecosystem. Hg is known to be associated with particulate matter in aquatic systems and is considered a particle-reactive element. The behavior of particulate matter must therefore influence the geochemical cycle of Hg in aquatic systems. It has been shown that the industrial Hg once bound to the sediment is not redistributed rapidly (Nakanishi et al., 1989; Krom et al., 1994; Rood et al., 1995) which was supported by appearance of high Hg concentration in Ravenna lagoon (Italy) near Hg release area even after 25 y of closure of Hg releasing plant (Miserocchi et al., 1993) and in Thane Creek (western India) maximum peak was observed at the depth when maximum input of Hg took place from a chlor-alkali plant, which also coincides with the sedimentation rate (Jaiswar et al., 2008).

The Ulhas Estuary is a long aquatic ecosystem comprising a network of channels of various depths, mud flats, tidal marshes and isles. As a consequence, different environments are established, characterized by particular hydrodynamics and physical,

chemical and biological conditions. The estuary can be considered a natural chemical reactor in which material is constantly imported, transformed and exported. It is heavily affected by anthropogenic activities and by uncontrolled discharge of pollutants from both point and non-point sources. Rivers, streams, land runoff, waste water inputs, industrial discharges and the atmosphere are all pathways by which pollutants enter the estuary. Pollutants are cycled and distributed within the system according to patterns in water circulation and biogeochemical reactivity. Indeed, hydrodynamics, speciation, and interaction with suspended particles, bottom sediments and organisms are the key factors determining the distribution of contaminants and their retention in the estuary. Pollutants such as heavy metals have received considerable attention, but most processes leading to their distribution and accumulation in the estuary are yet to be completely understood. Detailed study of Hg concentration in water, suspended particulate matter (SPM) and sediment have been published (Ram et al., 2003), revealing heavy load of anthropogenic Hg on the sediment of Ulhas Estuary. However, diagenetic behavior of Hg and its bioavailability in the estuarine sediment is unknown.

The primary objective of this study was to evaluate the influence of early diagenetic processes on Hg in sediment. This is in pursuance of our earlier publication examining the content of Hg in waters, SPM and sediment at several locations in the Ulhas Estuary (Ram et al. 2003). For this study, sequential chemical extractions were used to determine Hg partitioning in sediments. Hg concentrations were measured in interstitial water and bulk sediment samples to provide additional insight into the effects of early diagenesis.

3. Materials and methods

3.1 Study site

The Ulhas River originates in western slopes of the Sahyadrian range in the state Maharashtra, India and after a westerly course of about 100 km through mountainous terrain, reaches Kalyan on the plains. From Kalyan onwards the river meanders through vast mudflats and extensive mangrove areas to join the Arabian Sea near Vasai through the Bassein Creek. Bhatsai and Kalu Rivers join the Ulhas in the upper tidal zone (Fig. 1). The high rainfall that the catchment receives during the monsoon period, leads to heavy runoff through these rivers to the Arabian Sea. These rivers have barrages constructed on them in the upstream that permit only limited river discharge (5×10^4 - 7×10^4 m³/d) into the estuary during the early dry season and becomes scanty after December.

During dry season (October-May), the spring tidal range of about 4.5 m at the estuary mouth decreases to 2.8 m at 55 km inland (up to sampling location); the corresponding neap

tide ranges between 3.0 and 1.7 m respectively. The high tidal influence generates strong currents with peak speeds typically exceeding 1 m/s. The dry season tidal excursion of 5-15 km in the lower estuary (Bassein-Kasheli segment) decreases to 2-5 km in the inner estuary (upstream of Mumbra). The estuarine reach is at least up to 55 km inland during dry season. Temporal and spatial variation in salinity is significant. The estuarine flushing time has been estimated to vary between 73 and 211 tidal cycles during dry season suggesting the possibility of build-up of contaminants in the inner estuary. Though no information on the dynamics of the estuary is available for the monsoon period, the estuary is considered to be effectively flushed by the voluminous riverine flow and occasional floods (NIO, 1994; Ram et al., 2003). The Estuary receives effluent from multiple industries situated in Kalyan-Ulhasnagar belt and domestic sewage from surrounding localities. Consequently water quality of the estuary deteriorates as the dry season progress. Hence, pH decreases to 6.7, and dissolved oxygen decreases below 1 ml l⁻¹ in the inner estuary during low tide, the average concentration of PO₄³⁻-P (>2.5 μmol l⁻¹) and NO₃⁻-N (>30 μmol l⁻¹) is high in the inner estuary with abnormal levels of NO₂⁻-N (>20 μmol l⁻¹) and NH₄⁺-N (>5 μmol l⁻¹). Chlorophyll a concentration in inner estuary, where suspended particulate matter (SPM) is relatively low (5-30 mg l⁻¹) increases to >25 mg m⁻³. The outer estuary sustains low chlorophyll (<3 mg m⁻³) due to high SPM (100-700 mg l⁻¹) that results from the dispersion of the sediment from the bed and the mudflats by strong currents sweeping through the shallow outer region of the estuary (Ram et al., 2003). Accumulation of Hg in sediment of Ulhas Estuary has been reported (Srinivasan and Mahajan, 1989; Sahu and Bhosale, 1991; Ram et al., 2003) and its accumulation (upto 70 μg g⁻¹) in the inner Ulhas Estuary sediments was found to contaminate the coastal sediment off Bassein Creek significantly (Ram et al., 2003).

3.2 Field sampling

Intertidal area near Kalyan where fine grained sediments are actively accumulating were chosen as sampling site, because high concentration of sediment-bound Hg has been reported at the same location (Ram et al., 2003). Two cores were collected from same spot by pressing a pre-clean acrylic tube (I. D. 5.5 cm and O. D. 6.0 cm) in March 2002. One core (85 cm in length) was used for sequential extraction while other was used for the analysis of density, porosity and total Hg in the sediment. Overlying water was collected from sediment-water boundary layer directly in pre-cleaned plastic bottle. The core for sequential analyses was immediately sealed from both the ends and brought to the laboratory.

3.3 Sample processing

Precautions were taken during all sampling and processing steps to minimize potential contamination. Water used in all cleaning, processing and analysis steps was high purity Milli-Q distilled-deionized water. All acids and chemicals used during analysis were of low Hg content (E. Merck Germany). Core for sequential analyses was sectioned at 1 cm interval in a nitrogen-filled glove-bag. The sections were transferred to acid-cleaned 50 ml polyallomer centrifuge tubes and centrifuged for 15 min at 15,000 rpm (using a chilled centrifuge head) to separate the porewaters from the sediment (Matty and Long, 1995). After removing porewater, sediment samples were stored frozen in the centrifuge tubes. Leachate concentrations were converted to $\mu\text{g g}^{-1}$, using the dry mass equivalent (found by determining the dry/wet weight ratio of a separate aliquot of each sample). Porewaters were removed from centrifuged samples by syringe, filtered through acid-cleaned 0.45 μm Millipore membrane filter papers, acidified by Suprapure nitric acid to a $\text{pH} < 2$ and stored in polyethylene bottles. All water sample bottles were sealed in plastic bags and stored in refrigerator at 4 °C.

3.4 Sequential Extraction

Hg in various phases of the sediment was extracted using the selective chemical extraction procedure devised by Strunk (1991) and summarized by Matty and Long (1995). These procedures were specifically designed to prevent the reduction and subsequent loss of Hg from samples and were optimized to be effective, reproducible, and avoid resorption of leached Hg (Matty and Long, 1995). The extraction solutions, conditions and sediment phases theoretically affected for 1 g sample are summarized in Table 1.

The sediment samples were thawed in a refrigerator, but not dried. Aliquots of sediment were placed in acid-cleaned centrifuge tubes, weighed and treated with: (1) KCl to extract exchangeable Hg [EX fraction]; (2) NaOH to extract base-soluble Hg (BS fraction); (3) 1 N HCl to extract acid-soluble Hg [AS fraction]; (4) H_2O_2 and HNO_3 , followed by NH_4Cl in HNO_3 , to extract oxidizable Hg [OX fraction] (Matty and Long, 1995). Following each extraction the sediment was washed by adding 10 ml of Milli-Q water which was mixed into the sediment with a cyclo mixer, then centrifuged, and the water removed by pipetting. A set of blank for chemicals used for each fraction was treated in the same manner and was analyzed with the samples. Hg was not detectable in all the operational blanks.

3.5 Analytical Procedure

3.5.1 Solid fraction

The core collected for the analysis of total Hg in sediment was subjected to dry at < 60 °C until constant weight reached. Sediment density (ρ) was calculated on the basis of the percent water content (Berner, 1971). Porosity (ϕ) of sediment was assessed from the relation (Johnson et al., 1982):

$$\phi = (M_w/\rho_w) / (M_s/\rho_s) + (M_w/\rho_w) \quad (1)$$

Where, M_w is the weight of water lost, M_s is the weight of dry sediment, ρ_w is porewater density (1.025 g cm^{-3}) and ρ_s is the sediment dry density (assumed to be 2.6 g cm^{-3}).

Hg in solid phase was determined after acid digestion of powdered sediment (0.2 g) with aqua regia followed by oxidation by KMnO_4 (US EPA, 1979). Hg was analyzed by cold-vapor atomic absorption spectroscopy (CV-AAS) following its reduction to Hg^0 with NaBH_4 . Analyst-300 (Perkin-Elmer) atomic absorption spectrophotometer coupled with FIAS-400 and gold amalgamation preconcentration system was used for the detection of Hg. The precision determined with PACS-1 (NRC Canada) estuarine sediment standard was $\pm 5 \%$ and the detection limit was $0.005 \mu\text{g g}^{-1}$ (calculated as 3σ of the reagent blank).

3.5.2 Overlying water and extracts

Total dissolved Hg analyses, including organic and inorganic species, were performed by a gold amalgamation preconcentration procedure, thermal desorption and cold vapour atomic absorption (CV-AAS) after cold oxidation of organic Hg compounds by a BrCl solution (Bloom and Crecelius, 1983). All sample solutions were analyzed by Analyst 300 (Perkin-Elmer) atomic absorption spectrophotometer coupled with FIAS-400 and gold amalgamation system. The carrier solution was 3.0 % (v/v) HCl prepared using low Hg content HCl (Merck Germany) and Milli-Q water. The reduction solution was 0.2 % (w/v) NaBH_4 prepared in 0.05 % (w/v) NaOH in Milli-Q water. Samples were also acidified to 1 % (v/v) HCl . Leachate concentrations were converted to $\mu\text{g g}^{-1}$, using dry mass equivalent (found by determining the dry/wet weight ratio of a separate aliquot of each sample).

Preconcentration of Hg in water samples was performed using the Perkin-Elmer Amalgam system accessory, which facilitates the measurement of lower concentrations of Hg. All readings (for total Hg in solid phase as well as in water) were taken in triplicate and mean concentration of three readings was calculated. Percent relative standard deviations (%RSD) of three replicates were < 3%. A 1 ml loop of sample in triplicate provides the detection limit of 0.002 $\mu\text{g l}^{-1}$ (3σ of the reagent blank).

3.5.3 ^{210}Pb analysis

Sections of the core collected for total Hg analysis were subject to ^{210}Pb analysis for estimating the sedimentation rate. ^{210}Pb in the sediment was determined by measuring grand-daughter ^{210}Po ($t_{1/2} = 138$ days) by following the standard procedure of Flynn (1968). Briefly, 2-3 g dried (< 60 °C) and powdered sediment was brought into complete dissolution in the presence of ^{208}Pb tracer by treating it with HF, HClO_4 , HNO_3 and HCl in a Teflon vessel. The solution was finally made in 60-70 ml of 0.5-0.6 M HCl and ascorbic acid was added to mask the Fe^{3+} ions in solution. The Po isotopes (^{210}Po and ^{208}Po) were then auto-plated onto a 1.5 cm diameter silver disc. The plating was carried out for 3-4 h during which the temperature of the solution was maintained at 65°C. After plating, the silver disc was rinsed with distilled water, dried and alpha activities of the Po isotopes (^{210}Po and ^{208}Po) were assayed using ion implanted surface barrier detector coupled to Octete plus Alphaspectrometer (EG & G-Ortec).

4. Results and Discussion

4.1 Sediment characteristics

Sediment density and porosity at sampling station in the estuary is presented in Fig. 2. The density of the sediment in Ulhas Estuary varied in the range of 0.73-1.5 g cm^{-3} while the sediment porosity which was high (0.90) in surficial sediment decreased systematically up to 30 cm depth and remains nearly constant at about 0.7 in the deeper depths. High sediment porosity has been reported to be associated with high percentage of fine silt and clay in the sediment (Berner, 1980; Devol and Archer, 1992; Ram and Zingde, 2000) and a marked decrease with depth is largely due to the combined effect of compaction and change in sediment texture (Berner, 1980).

Total concentration of Hg in the sediment (Fig. 3) varied (0.46 – 6.40 $\mu\text{g g}^{-1}$) in accordance with that reported earlier (Ram et al., 2003) from the same spot. However, concentration of Hg (0.46-0.79 $\mu\text{g g}^{-1}$) in surficial sediment of present study showed substantial decrease in its concentration compared to earlier studies (0.89-2.49 $\mu\text{g g}^{-1}$). This is because the earlier three cores (May 1997, January 1999 and May 1999) from same location were collected

prior to October 1999 when two Hg-cell based chlor-alkali plants were discharging their effluents ($48,000 \text{ m}^3 \text{ d}^{-1}$ of process and $6000 \text{ m}^3 \text{ d}^{-1}$ of domestic) since 1951 to the estuary, around 12 km upstream of present sampling location. Hence, substantial amount of Hg was added to the sediment of Ulhas Estuary, giving rise to its concentration in the sediment. Present core was collected on 5 March 2002, both the chlor-alkali plants have reportedly closed their Hg-cell based plants during 1999 (3 years before the core collection). Hence, the major source of Hg has been stopped resulting in decrease in Hg concentration in the surficial sediment of Ulhas Estuary. Despite the closure of the plants in 1999, which is three years prior to the collection of the core, Hg concentrations in surficial sediments (0-1 cm) remain high ($\sim 0.80 \mu\text{g g}^{-1}$) compared to its background level ($0.10 \mu\text{g g}^{-1}$; Ram et al., 2003) observed at the bottom of a core around 60 km away from the study area. This may be possibly due to the resuspension and remixing of contaminated sediment with low Hg containing sediment.

4.2 Hg in overlying water and extracts

Results of sequential extractions for Hg in the core along with total (bulk sediment concentration) and dissolved (porewater) Hg are presented in Fig. 3. Hg was not detectable in the exchangeable (EX) fraction of all sections of the core with the base soluble (BS) fraction that represents organic bound Hg, contributing to the extent of 5-11% to the total sediment Hg. Thus, sulfide and organic bound Hg accounts for more than 90 % of the total Hg. Similar results have been reported for sediment of the Laurentian Great Lakes (Matty and Long, 1995).

4.2.1 BS fraction

BS fraction (base-soluble) that represents organic (humic and fulvic acid) bound Hg varies in accordance to its concentration in the bulk sediment (Fig. 3) with good positive correlation ($r^2 = 0.82$; $p = <0.0001$) (Fig. 4). Though its concentration was comparatively low (5-11 %) compared to its total concentration in sediment (Fig. 5), its affinity to organic matter is proved by the study of sequential extraction method in present study. A strong correlation has been reported between the distribution of organic matter and Hg in numerous types of sediments (Langston, 1982; Rada et al., 1989; Coquery & Welbourn, 1995; Gagnon et al., 1997; Ram et al., 2003; Hissler & Probst, 2006; Ullrich et al., 2007). Our study contrasts with that of Matty and Long (1995) in which they reported the absence of BS Hg below the redox zone. However, it is well in agreement with that of Strunk (1991) who found that the BS fraction contributed significant amounts of Hg to deeper sediments at several locations of Lake Superior. It also explains identical and suitability of extraction method followed in present study in line with that used by Strunk (1991). However, it differs with the sequential extraction results

of Bono, (1997), who has reported 50-80 % of the Hg found in Saguenay fjord sediment associated with organic matter extractable by a 1 N NaOH solution.

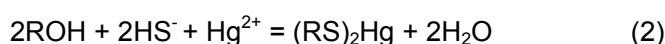
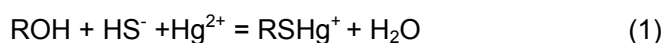
4.2.2 AS fraction

Results of the AS (Acid soluble) (Fe and Mn oxides) indicate no correlation ($r^2=0.02$; $p=0.56$) with its total concentration (Fig. 4) in the bulk sediment and varies in the range <0.005 - $0.036 \mu\text{g g}^{-1}$. Only a small percentage of Hg (about 1.5 %) in the core is bound to Fe and Mn oxides even in the surficial sediment (Fig. 5) unlike in the sediment of the Laurentian Great Lakes where the Hg concentration was relatively high in the AS fraction above the Mn redox horizon (Matty and Long, 1995). Hence, Fe and Mn oxihydroxides do not significantly influence the total Hg content of sediment in our core. It has been reported that Hg has relatively low affinity for oxide surfaces and the bonds between Hg and oxide surfaces are less stable compared to those of other metals (Forbes et al., 1974). Overlying water of Ulhas Estuary is overwhelmed with organic matter received from several industrial as well as domestic wastes and dissolved oxygen during dry season nears zero during low tide in the vicinity of sampling location (NIO, 1994). Hence, the sediment of the sampling area is expected to be anoxic even in the surface segment up to the such an extent that reduction of Mn and Fe oxides will be taking place. As Fe oxides begin to dissolve under reducing conditions, Hg may be readily released and escape either to the overlying water or towards downward depending upon diagenetic condition (Gagnon et al., 1997). Once in solution, Hg may be re-adsorbed (Shoham-Frider et al., 2007) to residual organic matter or Fe sulphides (FeS and FeS_2). Comparatively high concentration of Hg in AS fraction down the core may be bound to acid volatile sulphide minerals (AVS) (Morse, 1994). As Hg extractable by 1N HCl is considered potentially bioavailable (Morse et al., 1993), though the sediment contain high concentration of Hg, much of the Hg in the core and probably in sediment of the Mumbai region may not be available for biological uptake. On the basis of diffusion model, Merritt and Amirbahman, (2007) have explained that the document suggesting that in presence of an external perturbation, the sediment solid phase serves as a large re-supply reservoir for the porewater Hg pool is an odd suggestion. It has been suggested that little Hg repartitioning occurs following either tidal resuspension (Heyes et al., 2004) or dredging (Bloom and Lacorsa, 1999).

4.2.3 OX fraction

Maximum (0.42 - $5.07 \mu\text{g g}^{-1}$) Hg is present in OX (oxidizable fraction), which represents sulphide and organic (other than humic and fulvic acid) fraction (Fig. 3). About 65-95 % of Hg in the core sediment is associated with the OX fraction (Fig. 5). Hg in OX fraction strongly correlates (Fig. 4) with its total concentration in bulk sediment supporting the hypothesis that

once Hg is fixed to the active sites of sediment, it is not altered by any diagenetic changes in Ulhas Estuary. It has been concluded that in sulphidic sediments, sulphide can out-compete other ligands for Hg complexation because of the extremely high formation constant of Hg-S complexes (Dyrssen and Wedborg, 1991). This study sounds enough to answer whether the oxidative release of Hg from pyrite could have a significant impact on the concentration of the potentially bioavailable fraction. Previous work has shown that sulphide produced from dissimilatory sulphate reduction is rapidly incorporated into both Fe sulphides and organosulphides (Dyrssen and wedborg, 1991). The overall reactions for formation of solid-phase Hg complexes can be written as:



Though the sulphide chemistry of Ulhas Estuary is not known, the results of sequential extraction in sediment of Ulhas Estuary suggest that organic matters and sulphides mainly control the mobility of Hg in present core.

4.2.4 Hg in porewater

Porewater appears to be a bridge between solid phase sediment and overlying water and concentration of chemical constituents in porewater represents several diagenetic processes occurring in different type of sediments. Hence, the concentration of chemical constituents in porewater are of greater importance in terms of their availability to cause contamination in aquatic organisms. Hg concentration in the porewaters (PW) of our present study varies from $<0.002 \mu\text{g l}^{-1}$ to $0.83 \mu\text{g l}^{-1}$ with insignificant contribution ($<0.1 \%$) to the bulk sediment Hg content (Fig. 3) and is consistent with values found in porewaters of the Saguenay Fjord (Gagnon et al., 1997). Dissolved Hg peak in this core is observed at the sediment-water interface where Hg may be released as a result of organic matter degradation (Matty and Long, 1995), which is relatively higher (2-4%) in the surficial sediment of the study area (Ram et al., 2003). Its vertical distribution is not correlated with total Hg in the solid phase ($r^2 = 0.09$; $p = 0.27$). The lack of covariance between Hg in the dissolved and solid phases has already been noted in sediments from other areas (Bothner et al., 1980; Gagnon et al., 1997). Relative high concentration of Hg in porewater of the top few centimeters is most likely the result of oxidative release of organic-bound Hg facilitated by benthic macrofauna (Bothner et al., 1980; Gobeil and Cossa, 1993) particularly polychaetes, which are abundant in the Ulhas estuary (NIO, 1994; Ram et al., 2003). Concentration of dissolved Hg in the overlying water

was also high ($0.35 \mu\text{g l}^{-1}$) but in the range of the concentration reported earlier (Ram et al., 2003). The concentrations of porewater Hg in 60-70 cm segment of the core are much higher ($0.35\text{-}0.54 \mu\text{g l}^{-1}$) than predicted from the thermodynamic solubility of HgS ($0.03 \mu\text{g l}^{-1}$) suggests that HgS precipitation is not limiting its solubility. Based on cinnabar solubility model, Benoit et al. (1999) have explained that in the presence of excess HgS (solid) dissolved Hg increases with increasing sulfide concentration. The formation of polysulfide as well as organic complexes has been suggested to explain the presence of porewater metal concentrations largely exceeding values predicted from the thermodynamic solubility of metal sulphides such as HgS (Matty and Long, 1995; Gagnon et al., 1997). Hg can form stable, soluble complexes with sulphide and polysulphide species (HgS_2^{2-} , HgHS_2^- , $\text{Hg}(\text{HS})_2$, etc.) which may dominate in sulphidic seawater (Paquette and Helz, 1995).

4.2.5 Sedimentation rate

The variation of $^{210}\text{Pb}_{\text{excess}}/\text{Al}$ with depth is shown in Figure 6. The ^{210}Pb activity in the core shows three independent events at the segments (0 to 10), (15 to 25) and (40 to 50) cm respectively indicating that the depositional flux of ^{210}Pb is not uniform throughout the core. So we can not use constant rate of supply (CRS) model. Being an intertidal area, the environment is dynamic and the re-suspension of fine particles and re-deposition of the coarser particles raising sediment could have taken place in three independent events.

Assuming the constant initial concentration (CIC) model (Krishnaswami et al., 1971), the sedimentation rates for the three events are 0.34 cm y^{-1} , 0.25 cm y^{-1} and 0.34 cm y^{-1} . An average rate could be 0.31 cm y^{-1} . Hence, an average rate of 0.31 cm y^{-1} has been used for the entire core.

4.2.6 Fluxes of Hg

Hg Concentration in porewater ($0.83 \mu\text{g l}^{-1}$) is greater than that in the overlying water ($0.35 \mu\text{g l}^{-1}$), suggesting that diffusive fluxes of Hg may be occurring from porewater into overlying estuarine water. To evaluate whether the diagenetic processes could lead to significant post depositional redistribution of Hg, we estimated vertical diffusive flux by applying Fick's first law of diffusion (Berner, 1980). The diffusion flux J is expressed as:

$$J = -\phi D_s (\delta C / \delta Z) \quad (2)$$

Where, J is the diffusion flux, ϕ is porosity, D_s is the whole-sediment diffusion coefficient, and $(\delta C/\delta Z)$ is the concentration gradient, Z being positive in the downward direction. Bulk sediment diffusion coefficient (D_s) was calculated from the molecular diffusion coefficient for Hg in seawater (D_0) by using the equation $D_s = \phi^2 D_0$ (Ullman and Aller, 1982). We used the value $5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for D_0 (Gobeil and Cossa, 1993) and 0.80 for (ϕ) (Fig. 2). The concentration gradient was calculated from the total dissolved Hg concentration in the overlying water and porewater collected from the first sediment sampling interval (0-1 cm, thus, $\Delta Z = 0.5 \text{ cm}$). Flux value calculated was $0.039 \text{ } \mu\text{g cm}^{-2} \text{ y}^{-1}$. This flux represents only about 18.8 % of the present accumulation rate ($0.207 \text{ } \mu\text{g cm}^{-2} \text{ y}^{-1}$) of Hg derived from anthropogenic inputs at the sediment surface, estimated by using equation:

$$f(\text{Hg}) = \rho \cdot (C_i - C_0) \cdot s \quad (3)$$

where $f(\text{Hg})$ is the Hg flux in $\mu\text{g cm}^{-2} \text{ y}^{-1}$, ρ is the sediment density in g cm^{-3} , C_i is the Hg concentration at depth i in $\mu\text{g g}^{-1}$, C_0 is the background Hg concentration ($0.10 \text{ } \mu\text{g g}^{-1}$) (Ram et al. 2003) and s is the sedimentation rate expressed as cm y^{-1} (Cundy and Croudace, 1995; Marins et al., 1999).

The sedimentation rate of 0.31 cm y^{-1} (Fig. 6), in situ sediment density of 0.97 g cm^{-3} (Fig. 2) and Hg concentration of $0.79 \text{ } \mu\text{g g}^{-1}$ in surficial sediment were used in this calculation. Thus, the diagenetic redistribution of remobilized Hg within the sediment column subsequent to its accumulation seems insufficient to induce significant variations with depth of Hg concentration in the solid phase. Thus, diagenetic remobilization of Hg does not appear to be significant in the sediment of Ulhas Estuary. The upward flux of $0.039 \text{ } \mu\text{g cm}^{-2} \text{ y}^{-1}$ is higher compared with the flux rate calculated by Gobeil and Cossa (1993) for the sediment of the Laurentian Trough (2.6 %), which may be attributed to the variation in environmental conditions among the two sites.

4.2.7 Diagenesis of Hg in sediment of Ulhas Estuary

This work provides more insight to explain the binding of Hg with organic matter and almost negligible role of Fe and Mn oxides in controlling the diagenetic behavior of Hg in a polluted estuary and also a new information on the mobility of Hg. Our results explain that Hg behavior in the sediment of Ulhas Estuary is probably influenced by sulfide mineral formation especially at deeper depths. Intrusion of seawater takes place beyond the sampling location in Ulhas Estuary during dry season. Seawater contains high concentration of sulfate. Hence, sulfate is readily available for the reduction in the estuary by microorganisms. Sulfate reducing bacteria (SRB) mediate methylation of inorganic Hg in aquatic sediments (Gilmour et al., 1992)

and these organisms produce sulfide as a byproduct of their metabolic activity (Benoit et al., 1999). Sulfate both stimulates CH₃Hg production and enhances the activity of SRB in sediments (Gilmour et al., 1992; Benoit et al., 1999). Hg in the sediment of Ulhas Estuary showed most of the Hg (71-97 % of total Hg) was strongly bound to organic and sulphide (BS+OX) compounds. This Hg is neither available nor accessible directly to biota, nor is it available to methylation process (Benoit et al., 1999; Bloom et al., 2003; Shoham-Frider et al., 2007). Sulfide minerals are excellent scavengers of divalent cations of Hg, Pb, Zn and Cd (Jean and Bancroft, 1986). It is likely that in the sediment of Ulhas Estuary the organic fraction decomposes and Hg is re-adsorbed mostly by the sulfidic fraction (Shoham-Frider et al., 2007). Anthropogenic Hg once incorporated in the sediment in the form of organic complexes and HgS can remain unaltered for several years (Krom et al., 1994; Benoit et al. 1999; Ravichandran, 2004; Merritt and Amirbahman, 2007). Sediments having strongly reducing conditions at the surface can only release detectable amounts of Hg to the water column (Bothner *et al.*, 1980; Gobeil and Cossa, 1993).

5. Conclusion

Sequential extraction analysis was performed on Ulhas Estuary sediments for studying the partition behavior of Hg bound to various chemically separate phases. Geochemical studies of Hg in sediment performed to understand the diagenetic behavior of Hg has allowed us to decide the following conclusions: (1) The downward variation of Hg indicates that the Hg concentration in surficial sediment of Ulhas Estuary has decreased compared to its concentration reported in earlier studies. This is due to the closing down of two Hg-cell based chlor-alkali industries which were releasing their effluent to the Ulhas Estuary. (2) Sequential extraction of Hg indicates that 71-97 % of Hg is organic and sulfide bound and results indicate that very low concentration (about 1.5 %) of Hg is Fe and Mn bound. Hence, Fe and Mn oxyhydroxides have no control on the concentration of Hg in Ulhas Estuary. Only 18.8 % of the present deposition of Hg flux out from sediment to the overlying water. Though the Hg concentrations are high in sediments, the partition chemistry data indicates that the Hg in sediment of Ulhas Estuary is logically not bioavailable.

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Legend to the figures

Fig . 1. Sampling location in the Ulhas Estuary

Fig. 2. Depth-wise variation of sediment density and porosity in Ulhas Estuary

Fig. 3. Concentration of Hg in different leachates of sequential extraction

(BS) Base soluble fraction, (AS) Acid soluble fraction, (OX) Oxidizable fraction,
(PW) Porewater

Fig. 4. Correlation of Hg in different fractions with its total concentration in bulk sediment

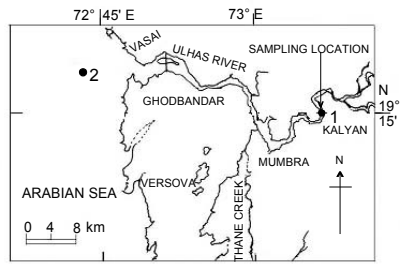
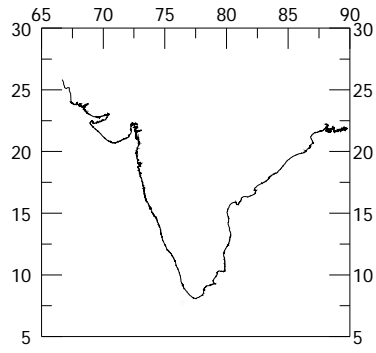
Fig. 5. Percentage of Hg in different leachates with respect to total Hg concentration in bulk sediment

Fig. 6. Variation of $^{210}\text{Pb}_{\text{excess}}$ in sediment of Ulhas Estuary as a function of depth

Table 1

Summary of procedure adopted for sequential chemical extraction of Hg using wet sediment (1 g).

Step	Chemical phase	Sediment phase	Extraction solution	Condition
1	Exchangeable (EX)	Clay minerals	15 ml 10 % KCl	20°C 1 h
2	Base soluble (BS)	Humic and fulvic acids	10 ml 0.1 N NaOH	20°C 30 h
3	Acid soluble (AS)	Fe and Mn oxides	10 ml 1.0 N HCl	20° 6 h
4	Oxidizable (OX)	Organics and sulfides	7 ml 30 % H ₂ O ₂ , 2 pH + 2 ml 0.02 N HNO ₃ then add 4 ml 2.0 M NH ₄ Cl in 20 % HNO ₃ then add H ₂ O dilute to 25 ml	50°C 5 h 20°C 1 h



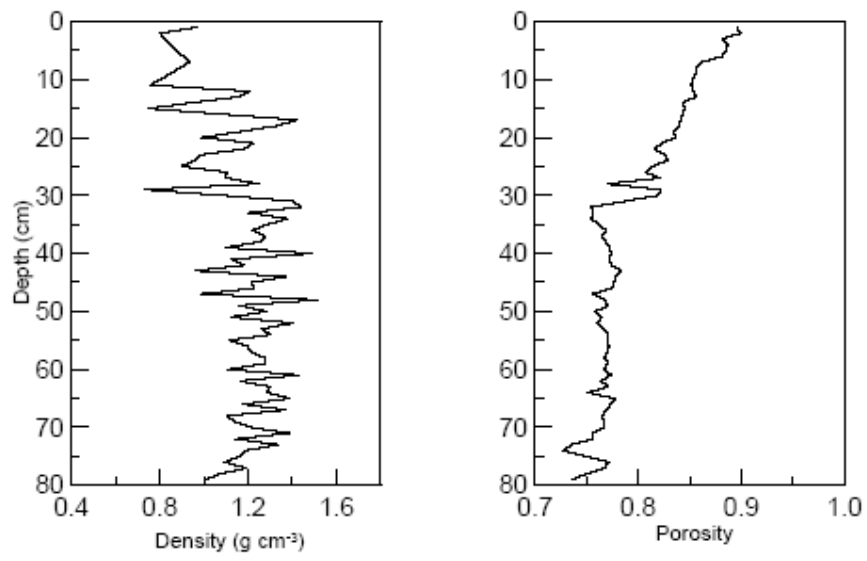


Fig. 2

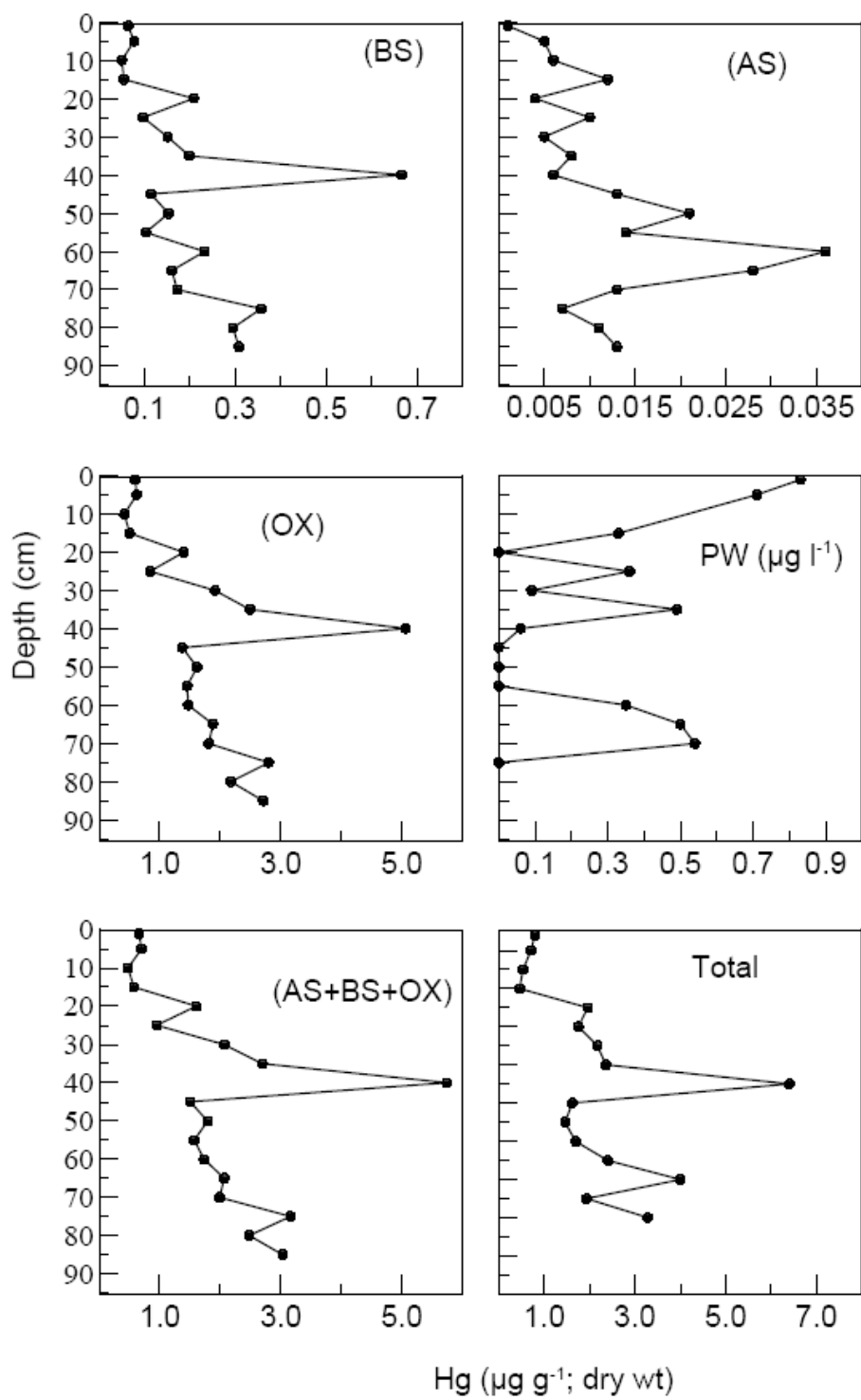


Fig. 3

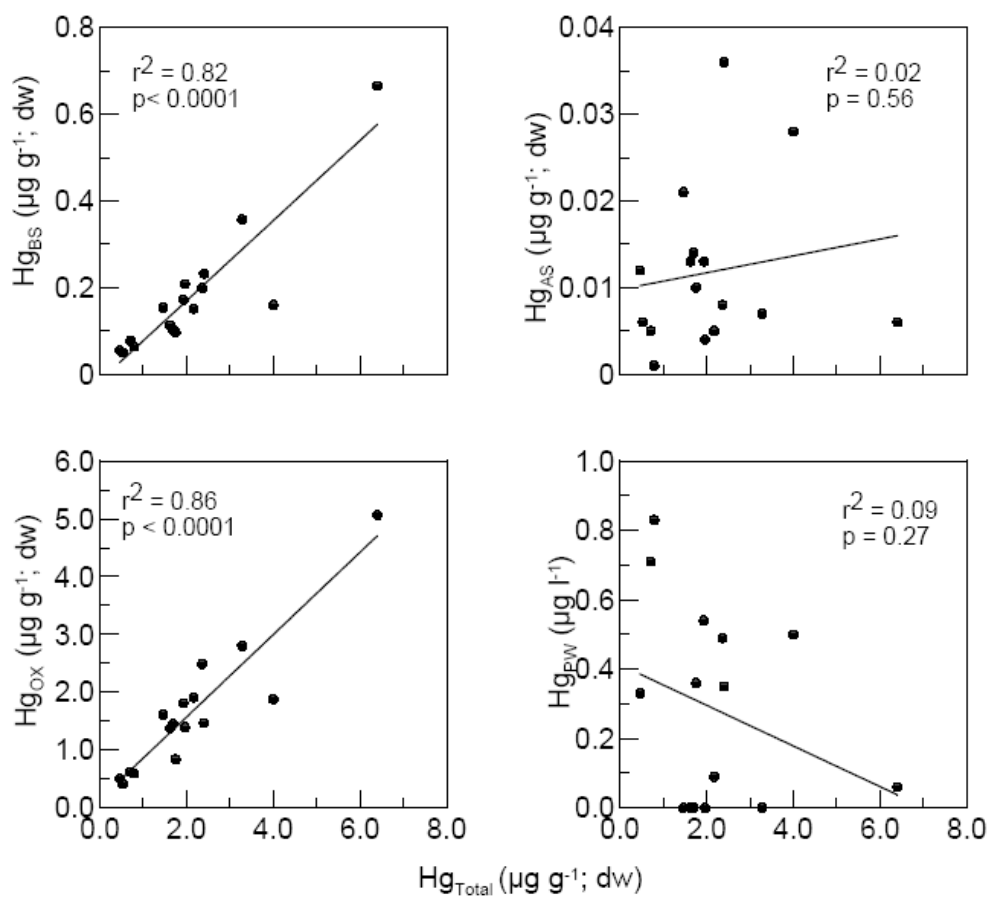


Fig. 4

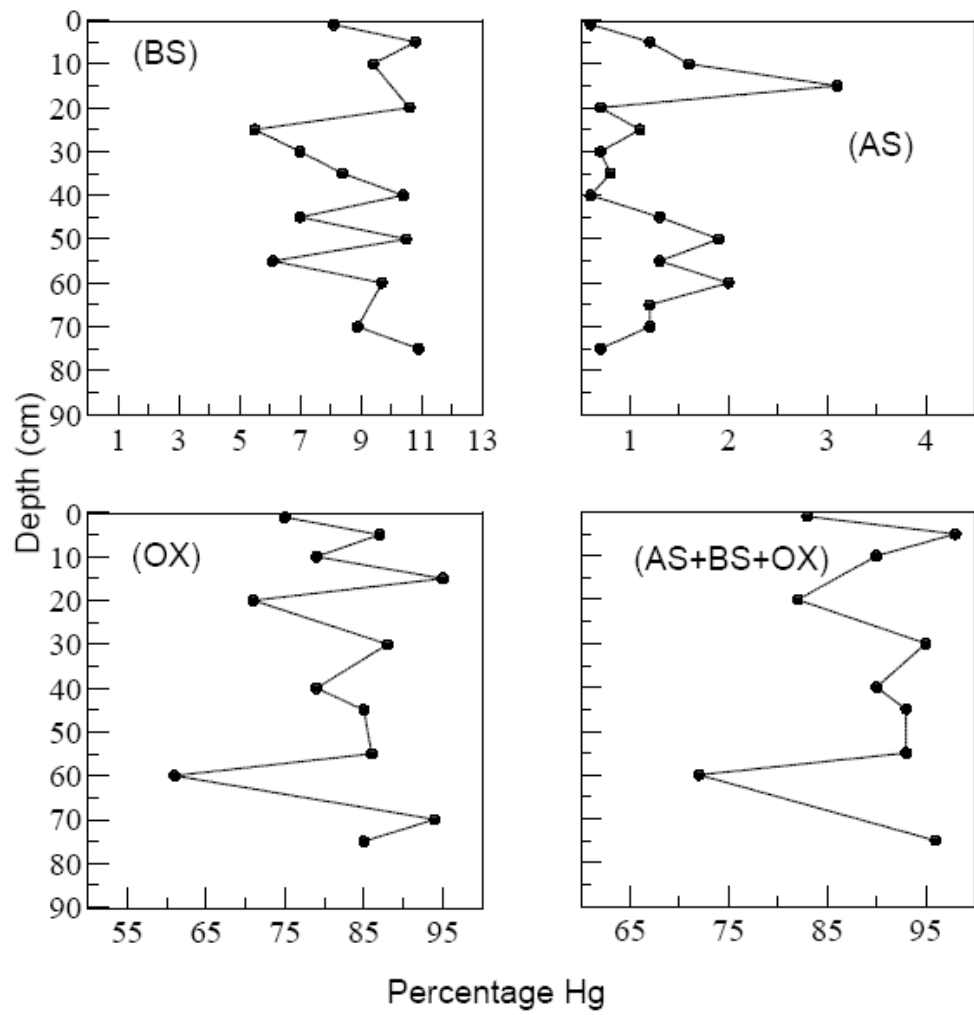


Fig. 5

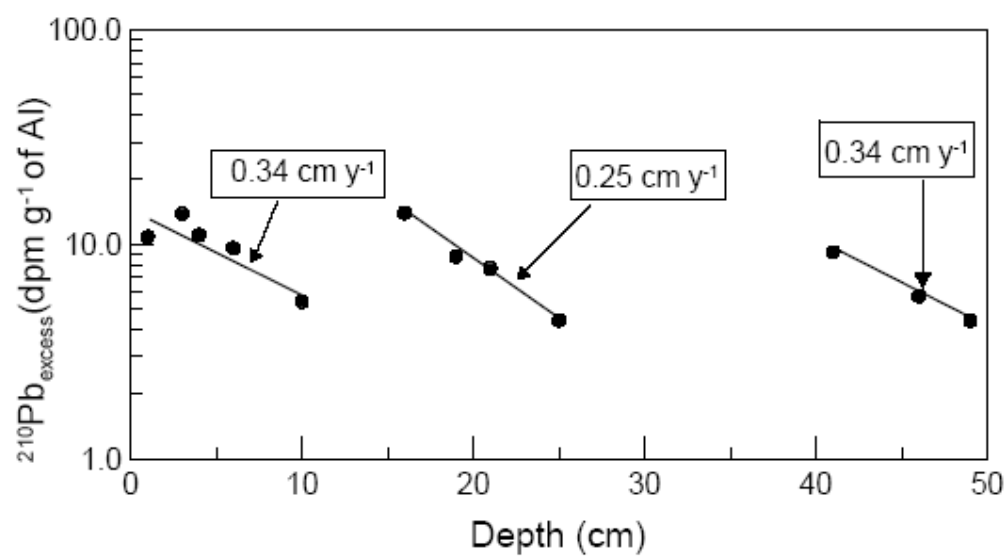


Fig. 6