Post depositional memory record of mercury in sediment near effluent disposal site of a chlor-alkali plant in Thane Creek-Mumbai Harbour, India

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Abstract

A mercury–cell chlor-alkali plant operating at Airoli (eastern bank of Thane Creek) for 40 years, caused widespread contamination of the surrounding environment. Untreated wastewater from the plant was discharged to Thane Creek for several years. Thane Creek joins to Ulhas Estuary, an impacted estuary by mercury (Hg) released by several industries including two chlor-alkali industries by a narrow arm and opens to Arabian Sea through Mumbai Harbour. In order to understand historical record of anthropogenic Hg and its association to Al, Fe and total organic carbon (TOC), estimation of Hg, Al, Fe and TOC was made in surface sediments and cores from Thane Creek-Mumbai Harbour (Bay) and the adjacent coastal area. Though 70 % of the plant has been changed to membrane-cell based technology, surficial sediment in the vicinity of effluent release contain high concentration (up to 1.19 \( \mu g \) g\( ^{-1} \) dry wt) of Hg as compared to its background value (0.10 \( \mu g \) g\( ^{-1} \) dry wt). The contaminated creek sediments are prone to current-driven resuspension and are acting as a strong source of Hg to the sediment of coastal region. Several rocks and sediments from the catchment area were analyzed to find out natural background of Hg. High suspended load transported from catchment region provides natural dilution to the Hg contaminated Bay sediment. Lithogenic and anthropogenic Hg buried in marine sediments is quantified based on normalization with Al, Fe and TOC and inter-comparisons of results indicate comparable values obtained by using Al and Fe while discernible deviations are found when calculated by using TOC. The Hg profile in core from the effluent release site for which sedimentation rate has been established, is discussed in terms of progressive removal of Hg from the effluent after mid-1970s and partial changeover of the manufacturing process from Hg cell to membrane cell production subsequent to 1992. Based on reported sedimentation rate in the locality, maximum concentration (49.19 \( \mu g \) g\( ^{-1} \) dry wt) of Hg represents the year 1967, when the chlor-alkali plant started discharging its untreated effluent to the creek. Results indicate that more than 80 % of Hg settles in the vicinity of its discharge and once deposited in the sediment, it is not affected to any substantial degree by diagenesis.

Keywords: mercury; lithogenic concentration; anthropogenic deposition; deposition rate; enrichment factor
1. Introduction

Toxicity of mercury (Hg) has been known for over five decades following Minamata tragedy in Japan [1]. Hg is present in trace quantities in all parts of the environment as a consequence of emissions from both natural and anthropogenic sources. Environmental Hg levels have increased considerably worldwide since the on-set of the industrial age and past practices have left a legacy of Hg in landfills, mine tailings, contaminated industrial sites, soils and sediments. Estuaries and coastal marine regions form an essential link in the global biogeochemical cycling of Hg between the terrestrial environment - the major repository for atmospheric Hg [2,3], and the oceans. Burning of fossil fuels, effluent generated by Hg-cell based chlor-alkali plants and dumping of municipal wastes are the major sources of anthropogenic emission of Hg in the environment [4-9]. Approximately 5000 t of Hg is introduced in the Earth’s atmosphere every year through natural as well as anthropogenic sources [2]. Though the uses of Hg have reduced significantly in many industrialized countries as alternatives are commercially and competitively available, it is still used widely in less-developed regions or nations where regulations and restrictions on its use are less comprehensive or less well enforced with the major commercial use in chlor-alkali plants. In the aquatic systems Hg is trapped into the sediment by close relationship with organic matter, and Fe and Al oxides or sorbed onto the mineral particles [8]. Hence, sediments adjacent to the outfalls of chlor-alkali plants frequently contain high levels of Hg [7,10-15]. Some natural processes (water, soil and vegetation degassing, volcanic emissions) allow Hg to degas and to flow back into the atmosphere, creating an atmospheric dispersion and diffused deposition on the terrestrial and oceanic ecosystems [8].

Industrial Hg emission in India on an annual basis is estimated around 200 t out of which 100-150 t is contributed by chlor-alkali industry and 60 t by coal-fired thermal power plants [16]. Hg consumption in chlor-alkali industries in India has been reported to be at least 50 times higher than the global best companies and Hg losses as much as 47 g in the production of 1 t of caustic soda [17]. Although a limit of 0.01 mg l⁻¹ has been prescribed for the levels of Hg in the effluent of chlor-alkali plants in India, this is often exceeded and the concentration can vary from 0.03 to 15 mg l⁻¹ [18,19]. A few chlor-alkali plants are located around Mumbai (formerly called Bombay) and have been releasing their effluents to the Thane Creek-Mumbai Harbour (hereinafter termed as Bay) and the Ulhas Estuary. A detailed account of Hg enrichment of sediment in the Ulhas Estuary has been recently published [15].

Metal concentration in sediments represents natural and anthropogenic components as both accumulate together in the sediment. Hence for a realistic assessment of metal pollution it is necessary to differentiate the two metal components. This poses problems because sedimentary metal loads can vary several orders of magnitude, depending on the mineralogy and grain-size of the substratum [20]. Normalization with an adequately selected parameter to compensate for natural variability of the metals in sediments is frequently used to detect and quantify anthropogenic metal contribution to the system. These techniques include grain size [21, 22], total organic carbon (TOC) [23,24], Fe [24-27], Al [28-32], Li [33], Sc [8]. Of these reference elements, Al is widely used because it is a major constituent of fine-grained aluminosilicates with which the bulk of the trace metals are associated and its concentration is generally not influenced by anthropogenic sources [20]. Many of these normalizing techniques have also been used for quantifying anthropogenic Hg in marine sediments but comparison using multiple reference elements is scanty.
High Hg burden in sediments of the Bay has been established [34] through the studies conducted in 1978 when environmental awareness in India was low and the industrial effluents entered the Bay without significant treatment. As a step towards reducing Hg fluxes to the environment, by mid 1980s the chlor-alkali units in India were required to treat the effluent to remove Hg and also shift from Hg-cell to diaphragm cell process in a phased manner. Hence, the Hg loads to the Bay through the effluent of the chlor-alkali industry would have decreased over the years since the past estimates of Hg accumulation in sediments of the Bay [34]. Hence, it was also of interest to investigate the sediment Hg profiles with respect to the changed scenarios of anthropogenic fluxes of Hg to the Bay. In this paper we also compare the normalization of Hg in the sediment of the Bay by using Al, Fe and TOC as reference element apart from deciphering the chronology of Hg deposition in sediment adjacent to the outfall of a chlor-alkali industry.

2 Materials and Methods

2.1 Sampling areas

Differential weathering of the interlayered soft tufts and resistant basaltic flows (Deccan Traps) by seawater has created several bays and creeks around Mumbai; the prominent among them being the Bay and the Mahim, Versova and Bassein Creeks (Figure 1). The Bay is under the high influence of semi-diurnal tides with the mean spring tidal range of 4 - 5 m. The flow within the Bay is ebb dominated along the western bank as against weak flood-dominated currents along the eastern segment [35]. The high terrestrial runoff during June-September (monsoon period) associated with heavy precipitation (mean rainfall: 2000-2800 mm y⁻¹) causes efficient annual flushing of these creeks thereby substantially improving their ecological quality [36].

The vast intertidal mudflats that get exposed during low tide sustained rich and luxurious mangroves in the past; however, due to pressures of development, these habitats have been either destroyed or severely degraded. Sparse vegetation in the coastal belt and extensive development, which includes surface quarrying of the basaltic ridges, provides a large amount of lithogenic flux into the Bay apart from the transport of longshore sediments from the southeast [37].

Mumbai and Jawaharlal Nehru (JN) ports located within the Bay (Figure 1) are the major gateways for India’s import and export and handle over 4.5 x 10⁷ t of cargo annually, which includes crude oil and its products, fertilizers, rock phosphate, sulphur, food grains, metals, chemicals, containerized cargo etc. Mumbai City with a human population density of 25,000 persons km⁻² [38] and the satellite townships together generate 3.16 x 10⁶ m³ d⁻¹ of domestic sewage out of which about 2.8 x 10⁶ m³ d⁻¹ enters marine waters, largely untreated [39]. Nearly 8 % of industries of India are located around Mumbai in three large industrial clusters around Thane, Kalyan and Patalganga. A variety of industries, including a chlor-alkali plant at Ghansoli (Figure 1) from the Thane industrial zone have been releasing their effluents-largely untreated in the past, in the Bay. Sewage-associated loads of dissolved solids, suspended particulate matter (SPM), BOD, N, P, Cu, Zn and Pb to the coastal water of Mumbai have been quantified and their impacts on marine ecology have been investigated [38,40]. Typically, the sewage receiving creeks are characterized by abnormally high and tide dependent levels of PO₄³⁻-P, NO₃⁻-N, NO₂⁻-N, NH₄⁺-N and chlorophyll a, variable dissolved oxygen (DO) falling to zero at low tides in some instances and markedly high and tide-dependent populations of pathogens [36]. The concentrations of selected heavy metals in water, sediment and organisms have also been reported [15,34,37,41-44].
2.2 Sampling

Extensive sampling of surficial sediment (1-5 cm) in the subtidal (using a van Veen grab) segment (between stations 7 and 23) in the Bay (Figure 1) was conducted during November-December 1996 (post-monsoon) and May-June 1997 (pre-monsoon). The routine monitoring at stations 1 to 6 (inner Bay) and 21 to 23 was continued till May 2000. Sediment cores from shallow stations (1 to 4 and 8) were obtained by pressing a pre-cleaned acrylic tube (outer diameter 6 cm and inner diameter 5.5 cm) in the bed and carefully retrieving it, while, a gravity corer was employed for deeper stations 21, 23 and R (16°59.0' N, 73°2.5' E; not shown in Figure 1). The sediment contained in the acrylic tube was carefully pushed out on a clean glass plate using an acrylic plunger and sectioned at every 1 cm interval. The surficial sediment as well as the core sections were transferred to clean polyethylene bags and frozen at -20°C until analysis. Several rocks and sediment samples were also collected from the catchment of the Bay. All samples were homogenized, dried at < 60 °C in an electrical oven and powdered in an agate mortar pestle.

2.3 Analytical procedures

The concentration of total Hg was measured by cold vapor atomic absorption spectroscopic technique (CV-AAS) following the standard procedure [45]. A weighed portion of the powdered sediment was digested in aqua-regia followed by oxidation with KMnO₄. Varian Spectra 300 with VGA-76 attachment was used with sodium borohydride as the reductant. The precision of the method was 2.7 % at the concentration of 2.37 µg g⁻¹ dry wt Hg (10 replicates) of estuarine sediment. For the estimation of Al and Fe, the sediment was digested with concentrated HF, HClO₄ and HNO₃ [46]. The residue remaining after evaporation of acids was dissolved in dilute HCl and the metals analyzed by flame AAS (Varian Spectra 300). Air-acetylene was used for Fe analysis whereas nitrous oxide-acetylene was used for the analysis of Al. TOC was estimated titrimetrically by the procedure of Walkey & Black [47]. Estuarine sediment having TOC concentration of 2.2 % was analyzed to check the precision of the method which was found to be ± 4.4 % (10 replicates).

Quality of the results of sediment analysis was ascertained by analyzing certified reference materials (BCSS-1 and PACS-1, NRC, Canada) with each digestion set and the results are given in Table 1. Results obtained on certified reference materials were satisfactory. Acids and chemicals used during the analysis were of low Hg content (E. Merck, Germany). The water used in cleaning, processing, and analysis steps was high purity Milli-Q distilled-deionised water (DW).

3 Results and Discussion

3.1 Hg in surficial sediments

The concentration of Hg in the Bay sediments (Table 2) decreases markedly in the post-monsoon (November-December) probably due to high SPM of low Hg content associated with the runoff during monsoon. The SPM in the runoff to the Bay that has increased with high rate of development in the region and quarrying of basaltic ridges [37] is mainly derived from the catchment. A yearly load of 8.4 × 10⁵ m³ of fine-grained sediment that is transported to the Bay largely during monsoon is spread fairly uniformly over the 240 km² area of the Bay by oscillating tidal movements [48,49]. This fine-grained sediment is mainly of terrestrial origin and would have low Hg content in view of the low concentration of Hg (<0.005-0.14 µg g⁻¹ dry wt) in soil and rock sampled from several sites in the
catchment of the Bay and the surrounding region, spread over an area of roughly 6400 km² (Table 3). Because of their basaltic origin, the catchment strata have high concentrations of Fe (11.3-31.9 %) and Al (6.6-55.3 %). There is good positive correlation between Hg and Fe (r = 0.64; p < 0.001), however, there is no significant correlation between Al and Fe (r = -0.13; p < 0.1) and Hg with Al (r = 0.17; p < 0.1) in these samples. Under dynamic environment, the native bed sediment of the Bay (with high Hg content) disturbed by the tidal scour mixes with the load (with low Hg content) delivered through the land runoff resulting in depressed Hg levels in the sediment during November-December. However, with the withdrawal of monsoon during October, the lithogenic flux of low Hg content to the Bay nearly ceases leading to enhanced levels of Hg in the sediment during May-June. Dilution of native SPM with the load associated with runoff leading to depressed burden of Hg has been reported for Hackensack Meadowlands of northeastern New Jersey [50].

The trend of variation of Hg in the sediment of the Bay (Figure 2) has remained comparable over the period 1996-2000 with relatively high levels confined to the inner zone upstream of station 7 and a decrease in the seaward direction. Recent estimate suggests that the Bay received around 239 kg of Hg through sewage annually and 750-1000 kg y⁻¹ through the effluent of the chlor-alkali unit at Ghansoli in the inner Bay (Figure 1) until 1992 with marked reduction subsequently due to phased change over to diaphragm cell production of caustic [39]. Apart from these loads the transport of SPM with high Hg content (1.13-6.43 µg g⁻¹; dry wt) from the Ulhas Estuary [15] to the head Bay to which it is connected through a narrow arm (Figure 1) would possibly contribute to the sediment of the inner Bay. Marked time lag in the occurrences of high and low tides between the Bay and the Ulhas Estuary facilitates such a transfer. The time lag also results in a low energy field at the head of the Bay inducing the settlement of SPM particularly in the dry season when the freshwater discharge through the Ulhas Estuary is insignificant [35,51]. This is supported by the sediment accumulation rate which is high (1.46 cm y⁻¹) in the inner Bay and decreases considerably (0.44 cm y⁻¹) in the outer segment [44]. Considerable variation in the concentration of Hg in sediment at the same station (Figure 2) in the inner Bay during different monitoring events is probably due to movement of the sediment associated with tidal action and high turbulence created by the Ulhas Estuary discharge during monsoon. The distribution of Hg within the Bay downstream of station 7 is fairly uniform (Table 2) with the absence of marked spatial trends due to good sediment mixing. The Hg content of the surficial sediment of the inner Bay at stations 1, 2 and 3 is much lower (0.21-1.19 µg g⁻¹ dry wt) than found (6.23-8.21 µg g⁻¹ dry wt) in 1978 [34]. Treatment to the effluent of the chlor-alkali unit that has been progressively enforced over the years, apart from decrease in consumption of Hg with changeover to membrane cell process since 1992 is probably the major factor responsible for the observed decrease in levels of Hg in the surficial sediment during the present study. The sewage released in the Bay has increased from 3.5x10⁵ m³ d⁻¹ in 1978 to the present of 1.1x10⁸ m³ d⁻¹ thereby increasing the sewage-associated Hg loading at least by 3.5 times [39]. The impact of incremental increase in sewage-associated Hg is not translated in increase in Hg content of the Bay sediment primarily because of inherent high Hg in sediments due to release of Hg-containing effluent of the chlor-alkali industry in the past because of which it is difficult to identify relative small increase in concentration due to rising sewage discharges.

Although the inner Bay receives large volumes of sewage, the TOC content of the sediment is < 5 % and decreases to around 2.5 % at station 23, nearly 25 km off the coast (Figure 2). This indicates only a small built-up of TOC in the open-shore area over the expected background of 1-1.5 % estimated based on the dated cores [44]. Evidently, the built-up of TOC in the sediment is not commensurate with the increasing fluxes of organic matter thereby implying its efficient scavenging
by benthic organisms as well as enhanced rate of mineralization. This is supported by high macrobenthic biomass with populations dominated by polychaetes, decapods, amphipods and isopods [51] and the total count of bacteria in the Bay sediments (2.2x10^6 colonies g^-1; dry wt) which are very high, and in water (10^9-10^10 l^-1) far exceeds the number reported for the Chesapeake Bay [52].

3.2 Hg in sediment cores

3.2.1 Anthropogenic Hg in core 2

We have used Al, Fe and TOC as reference elements to facilitate inter-comparison of anthropogenic Hg deposited in the sediment of core 2 obtained from the effluent disposal site of the chlor-alkali plant at Ghansoli (Figure 1). Depth-wise distribution of Hg, TOC, Al and Fe in this core is illustrated in Figure 3a. The concentration of Hg in each 1 cm section of the core was normalized separately to Al, Fe and TOC (Figure 3b). This procedure yields metal enrichment factor (EF) which was calculated as:

\[
EF = \frac{([\text{Hg}]/[\text{M}])_{\text{sample}}}{([\text{Hg}]/[\text{M}])_{\text{background}}} \quad (1)
\]

Where \((([\text{Hg}]/[\text{M}])_{\text{sample}}\) refers to the total concentration of Hg measured in the core sample (µg g^-1 dry wt) and \((([\text{Hg}]/[\text{M}])_{\text{background}}\) the geochemical background; M being the total concentration of either Al, Fe or TOC. For ease, the EF values for Hg thus obtained are referred as \(EF_{\text{Hg Al}}, EF_{\text{Hg Fe}}\) and \(EF_{\text{Hg TOC}}\) in the discussion to follow. The cores 1, 2, 3 and 8 from the inner Bay have high concentration of Hg even in the bottom sections (0.32-1.00 µg g^-1; dry wt) compared to the Hg content in the catchment sediment (Table 3) and hence probably have anthropogenic component making them unsuitable for \((([\text{Hg}]/[\text{M}])_{\text{background}}\). This difficulty was overcome by using the values from the bottom section of the core 23 from the area where sedimentation rate of 1.4 cm y^-1 has been reported [53]. Hence the sediment at the bottom of this core was deposited about 116 year in the past and represents near lithogenic concentrations of constituents. The background concentrations used for all calculations are Hg = 0.10 µg g^-1 (dry wt), Al = 4.9 % (dry wt), Fe = 4.2 % (dry wt) and TOC = 1.0 % (dry wt). The Hg concentration of 0.10 µg g^-1; dry wt is marginally higher than its average concentration in the catchment soil (<0.005 – 0.10 µg g^-1) but compares well with the bottom section of core R (Figure 11) obtained from the coastal Arabian Sea about 300 km southeast of Mumbai. At the sedimentation rate of 0.21 cm y^-1 reported for a core obtained from the same site [53], the sediment of the bottom section of core R dates to the year 1542 and hence centuries prior to the significant use of Hg in the subcontinent. The EF profiles with the three reference elements appear similar in Figure 3b but there are differences in magnitude. The \(EF_{\text{Hg Al}}\) is 4-20 % greater than \(EF_{\text{Hg Fe}}\), while, \(EF_{\text{Hg TOC}}\) is 22 – 50 % smaller in the upper 27 cm segments and variable (-17 % to 11 %) below this depth. The distinct low \(EF_{\text{Hg TOC}}\) in the upper 27 cm of core 2 is due to increase in anthropogenic TOC in sediment in recent years.

Following the approach of Shotyk et al. [54] we calculated lithogenic Hg (Hg_{\text{lithogenic}}) with Al, Fe and TOC as reference elements as follows:

\[
[Hg]_{\text{lithogenic}} = [M]_{\text{sample}} \times ([Hg]/[M])_{\text{background}} \quad (2)
\]
Where $[\text{Hg}]_{\text{lithogenic}}$ is in units of $\mu g \, g^{-1}$ dry wt, $[M]$ refers to the concentration of either Al, Fe or TOC and $([\text{Hg}]/[M])_{\text{background}}$ is the background composition. Anthropogenic Hg was then calculated as:

$$[\text{Hg}]_{\text{anthropogenic}} = [\text{Hg}]_{\text{total}} - [\text{Hg}]_{\text{lithogenic}} \quad (3)$$

The profiles of lithogenic Hg calculated using Al and Fe illustrated in Figure 3c are comparable with decrease in the concentration of Hg over the period 1962-97 and follows the pattern of the Al profile. It appears that the lithogenic flux reaching the Bay has progressively become coarser over the depositional history. Querying of basaltic ridges which boosted with demand and rampant urbanization along the eastern shore of the Bay are the major causes for changes in the sediment texture [43]. The lithogenic Hg profile with TOC as reference element is significantly different from the other two and indicates apparent increase in $[\text{Hg}]_{\text{lithogenic}}$ over the depositional age of the sediment (Figure 3c). The $[\text{Hg}]_{\text{lithogenic}}$ profile mimics the TOC profile which reflects its (TOC) anthropogenic build-up in the sediment making it unsuitable as a reference element for core 2. Anthropogenic profile calculated using three reference elements provides similar results (Figure 3d) as that of EF values. Good positive correlations are evident with the combinations of all three normalizing elements (Figure 4a) because the decrease in TOC into the sediment is relatively small as compared to increase in anthropogenic Hg in percentage terms. The plots in Figure 4b indicate positive relationship for lithogenic Hg calculated using Al and Fe as reference elements but correlations are negative and less well defined with TOC as the reference element. The correlation of anthropogenic Hg is almost same (Figure 4c) as in the case of EF (Figure 4a) which is due to the reason explained above.

3.2.2 Cumulative, anthropogenic Hg (CAHg)

In order to estimate the inventory of total anthropogenic Hg per unit area of the sediment core, the mass of anthropogenic Hg ($[\text{Hg}_A]$) in units of micrograms ($\mu g$) per section was obtained from the relation:

$$[\text{Hg}_A] = [\text{Hg}]_{\text{anthropogenic}} \times \rho \times V \quad (4)$$

Where $\rho$ is the dry bulk density of the sediment (g cm$^{-3}$) and $V$ is the volume of the individual section of the core (cm$^3$). The CAHg was then determined by summing the mass of anthropogenic Hg in each section of the core:

$$([\text{Hg}_A]_T = \sum_{i=1}^{n} [\text{Hg}_A]_i \quad (5)$$

The value obtained by above calculation was multiplied by appropriate factor to determine the mass of anthropogenic Hg deposited per square meter of the sediment. CAHg calculated for core 2 using
Al (8.13 g m\(^{-2}\)) is similar to that obtained using Fe (8.14 g m\(^{-2}\)) and TOC (8.10 g m\(^{-2}\)) (Figure 5). In this calculation no age dating of sediment core is required and calculation of cumulative, anthropogenic deposition of the other trace metals of environmental interest can be made [54].

### 3.2.3 Anthropogenic Hg in other cores

The distribution of Hg, TOC, Al and Fe in other cores is shown in Figures 6-11. The profiles reveal significantly higher Hg concentrations in surface layers of cores obtained from the open coast (cores 21, 23, R), while, the depth distribution of Hg in cores from the Bay (cores 1, 3, 8) indicates its uneven deposition. Based on the background concentration of 0.10 µg g\(^{-1}\) dry wt of Hg, the cores 1, 3, and 8 have anthropogenic contribution up to the depth of burial. The lithogenic and anthropogenic concentrations of Hg in sediment of these (Bay) cores obtained following the procedure discussed above are given in Table 4. This table indicates comparable average lithogenic and anthropogenic Hg with Al and Fe as reference elements but vary markedly with TOC as the normalizing element as in case of core 2 for reasons discussed earlier. CAHg calculated for the Bay cores (Figure 5) other than core 2 is comparable with relatively high value for core 1 which is from the site of higher sediment deposition rate [44]. The Figure 5 indicates that more than 80 % of the anthropogenic Hg in the effluent of the chlor-alkali industry entering the Bay is buried in sediment in the vicinity of the input as expected [14, 55].

### 3.2.4 Chronology of anthropogenic Hg deposition

The study area from where the cores were collected is age-dated using \(^{210}\)Pb excess inventories [42,44,56], which allows us to estimate variations in anthropogenic Hg with time. The high concentration of Hg in sediment up to the depth of burial in the Bay cores is not due to disturbed sediment as concluded based on \(^{210}\)Pb profiles and excess \(^{210}\)Pb inventories for cores from the same area [42,44]. The 50 cm long core 2 obtained off the effluent release location of the chlor-alkali industry reveals a profile having high content of Hg in the 28-44 cm segment with the maximum concentration of 49.19 µg g\(^{-1}\) at 44 cm (Figure 3a). Sedimentation rate of 1.46 ± 0.13 cm y\(^{-1}\) is reported by Sharma et al. [44] for a sediment core from the same site. Applying this rate of sediment accumulation for core 2, the highest concentration of Hg at 44 cm coincides with the year 1967 (Figure 3a) when the chlor-alkali industry went into commercial production. The nature of the Hg profile suggests that the industry continued to release high loads of Hg up to about 1978. The enforcement of treatment to the effluent to remove Hg in a phased manner by the State Pollution Control Board that was established in mid-1970s, is clearly reflected in decreasing concentration of Hg (0.82-3.25 µg g\(^{-1}\)) in the sediment deposited after 1978. A distinct decrease in Hg burden in the 8-12 cm section (0.82-0.92 µg g\(^{-1}\)) roughly coincides with the partial changeover of the manufacturing process by the industry from Hg cell to membrane cell production in 1992. The subsequent increase in concentration in the 0-6 cm segment (1.27-1.49 µg g\(^{-1}\)) though minor, indicates an enhancement in the Hg flux through the effluent of the industry during 1993-97. Historical evaluation of Hg accumulation in aquatic sediments has been made elsewhere based on Hg profiles and sedimentation rates derived from \(^{210}\)Pb dating [7,50,55]. A good agreement of the sedimentation rate derived based on \(^{210}\)Pb and the historical events of release of Hg from the chlor-alkali industry at Ghansoli suggests that the assumption of low rate of remobilization and redistribution of Hg within the sediment as compared to its deposition at the sediment surface [57] is valid for the Bay.
The average sedimentation rate of 0.63 cm y\(^{-1}\) established for the coastal area of Mumbai [44] when applied to the 40 cm long core 21 obtained from the same site, indicates a gradual increase in the Hg concentration (0.14-1.79 \(\mu\)g g\(^{-1}\)) above the 25 cm segment corresponding to the year 1957. This gradual rise in Hg concentration prior to the functioning of the chlor-alkali industry is due to general increase in domestic and industrial effluents to the Bay. The western coast of the Bay saw accelerated industrial development with the setting-up of two refineries in 1957-60 which released their effluent in the Bay and continued to do so when these studies were conducted. With rapid industrial growth during 1950-65 the coastal strip of the Bay that was until then underdeveloped, was rapidly transformed into densely populated urban agglomerate. The concentration of Hg in sediment below 25 cm depth in core 21 that averages at 0.14 \(\mu\)g g\(^{-1}\) represents the background and compares well with the value reported by Ram et al. (2003) [15] for the coastal sediment of the Arabian Sea off Bassein about 50 km North of Mumbai. Acceleration in Hg deposition upward of 16 cm in core 21 corresponds to the year 1972 after the Hg flux to the Bay increased with the establishment of the chlor-alkali industry in 1967. A similar profile of Hg concentration decreasing with depth is also evident in core 23 though the overall content of anthropogenic Hg is considerably low due to the distance from the Hg sources.

The enrichment of Hg (0.15-0.24 \(\mu\)g g\(^{-1}\)) in the top 10 cm compared to the rest of the core (0.06-0.13 \(\mu\)g g\(^{-1}\)) is seen in core R obtained from a location around 300 km southeast of Mumbai. For a duplicate core collected from the same site and at the same time a sediment accumulation rate of 0.21 cm y\(^{-1}\) has been reported [53]. Hence, Hg accumulation in the sediment seems to have commenced in late 1950s and accelerated after 1970. The coastal belt south of Mumbai is industrially underdeveloped and human settlements are sparse because of which the lithogenic flux to the coastal sediment would be relatively free from anthropogenic Hg. Hence, this incremental increase of Hg in more recently deposited sediment in core R can be due to general enhancement of anthropogenic Hg in the environment, atmospheric fallout from burning of fossil fuel etc [5] or transport of Hg-enriched fine particles of the Mumbai coast under the influence of coastal circulation. There are instances of transport of particulate Hg over long distances by currents [5,58].

Depth profiles of Al and Fe (Figures 3, 6-11) indicate the absence of dramatic variations in concentrations over their depositional history though subtle trends are seen in some cores. A steady increase in the Al concentration with depth in cores 2 and 3 (Figures 3 and 7) and a reverse trend in core 8 (Figure 8) are the result of modified Bay dynamics due to human-induced changes in morphology. The flux of Fe to the Bay however, seems to have remained grossly comparable at a given site. The low Al content of 4.6-5.0 % in the bottom 10 cm of core 23 from the Arabian Sea has doubled in the surface sediment over the depositional period of about 116 year (Figure 10). The corresponding increase in Fe content is from 4.1% to 9.9 %. Fe and Al vary directly with good correlations in cores 1 (r=0.99; p< 0.001), 2 (r=0.77; p< 0.0001), 3 (r=0. 47; p< 0.0001), 23 (r=0.93; p< 0.001) and R (r=0.84; p< 0.0001). Al and Fe profiles over the depositional history of 456 year in the dated core R are indicative of an episodic event around 1816 wherein their flux to the coastal area decreased sharply. The minimum in the TOC profile also coincides with this event (Figure11).

With the above results it is evident that large quantity of sediment (8.4 x 10\(^5\) m\(^3\) y\(^{-1}\)), transported to the Bay acts as a natural diluent for contaminants of the Bay sediments. Decreasing trend of Al towards the surface in core 2 (Figure 3a) from the Bay and reverse trend in the core 23 (Figure 10a), which was collected around 25 km away from the shore indicates that the coarser sediment settles in the Bay during slack period whereas the fine clay particles with higher Al content
get carried away from the Bay by low tidal currents and settle in the open shore region where the tidal current is comparatively low. Hence, Al content in surficial sediment of open shore region increases with time. Thus the Bay functions as natural filter for coarse sediments.

3.2.5 Hg deposition rate

Using the sedimentation rate (1.46 cm y$^{-1}$) reported by Sharma et al. (1994) [44] and the concentration of Hg in cores 1, 2 and 3 we calculated the Hg deposition rate in the Bay sediment by using the equation:

$$f(\text{Hg}) = \rho.(\text{C}_i-\text{C}_0).s$$

where $f(\text{Hg})$ is the Hg flux ($\mu g \text{ cm}^{-2} \text{ y}^{-1}$), $\rho$ is the sediment density (g cm$^{-3}$), $\text{C}_i$ is the Hg concentration at depth i ($\mu g \text{ g}^{-1}$), $\text{C}_0$ is background value of Hg (0.10 $\mu g \text{ g}^{-1}$) and $s$ is the sedimentation rate (1.46 cm y$^{-1}$) [59,60]. The Hg deposition rate (Figure 12) ranges from 1 $\mu g \text{ cm}^{-2} \text{ y}^{-1}$ to 50 $\mu g \text{ cm}^{-2} \text{ y}^{-1}$ in core 2. Presuming an average rate of deposition of Hg (0.82 $\mu g \text{ cm}^{-2} \text{ y}^{-1}$) in the surficial sediment of cores 1-3 for the 60 km$^2$ area of the inner Bay (stations 1-6) the yearly burial rate of Hg in sediments of this segment amounts to 490 kg.

We assessed the total Hg buried in the sediment of the Mumbai region over the natural background (0.10 $\mu g \text{ g}^{-1}$) from its concentration and the depth of contamination in sediment, density of sediment (0.7 g cm$^{-3}$), and area of the region (estimated from the Naval Hydrographic Chart Nos. 2016 and 255). These calculations indicate that the sediments in the Bay and the coastal area of Mumbai-Bassein have burden of 52.2 and 37.3 t of anthropogenic Hg up to the depth of contamination.

3.2.6 Relationship between TOC and Hg

Hg in the surficial sediments and in cores 1 ($r=0.44; p<0.01$) and 3 ($r=0.60; p<0.0001$) from the Bay is positively correlated with TOC in accordance with several literature reports [8,15,61-64]. High affinity between Hg and TOC in the Bay suggests the occurrence of adsorbed inorganic Hg species to organic coatings on fine particles [65]. In core 2 the TOC decreases with the depth in the sediment as expected but the concentration of Hg increases in the same direction due to effluent-associated Hg of the chlor-alkali industry as discussed earlier resulting in a negative relationship between the two ($r=-0.47; p<0.001$). The correlation of Hg with Al and Fe in the surficial sediment is significant ($r=0.62; p<0.05$) and ($r=0.82; p<0.001$) respectively during October 2000. Similar association of Hg with Fe during October has been reported for the nearby Ulhas Estuary [15]). However, no significant correlation of Al and Fe with Hg is evident for most cores. High correlation between Hg and TOC indicates that the distribution of Hg is not dependent on granulometry, but is dependent on the organic load [66]. The Hg transported to the Bay through land runoff during monsoon is probably in the form adsorbed on the Fe flocks under highly oxic conditions [67,68]. Gagnon et al. (1997) [64] have shown that significant fraction (up to 70 %) of total Hg in the oxic layer of fjord sediments is associated with Fe-hydroxides.
4. Conclusions

The signature of anthropogenic Hg associated with the effluent of a chlor-alkali industry released to the Bay is seen in the sediment profile of a core obtained about 25 km from the shoreline though the concentrations are significantly lower than in the Bay cores. Dilution of native sediment of the Bay by runoff-associated lithogenic flux of low Hg content during monsoon leads in marked seasonal changes in the Hg level in surficial sediments. A pronounced decrease in Hg concentration from 6.23-8.21 μg g⁻¹ in 1978 to 0.21-1.19 μg g⁻¹ in 1996-2000 in sediment of the inner Bay is attributed to progressive control on Hg released by the chlor-alkali industry. The highest concentration of Hg (49.19 μg g⁻¹) at 44 cm depth in core 2 obtained from the vicinity of the effluent outfall of the chlor-alkali industry coincides with the year 1967 when the unit went into commercial production and the nature of the Hg profile suggests that the industry continued to release high loads of Hg up to about 1978. Decrease in consumption of Hg due to partial changeover of the manufacturing process by the chlor-alkali unit is clearly reflected in decrease in sediment Hg deposited after 1992. Hg in these sediments seems to be associated with TOC with no significant correlation with Al and Fe. The EF is considerably high for core 2 with about 80 % of the effluent-Hg load buried in the sediment in the vicinity of release. Lithogenic Hg computed using Al and Fe as reference elements are more or less comparable but differ when normalized with TOC. The average anthropogenic Hg calculated with Al, Fe and TOC as reference elements agrees to within 0 - 0.5 % for cores 2, 23 and core R. This difference is 1.9 - 6 % for other cores with Al and Fe but increases to 11 - 22 % with TOC as reference element. Cumulative anthropogenic Hg ranges from 0.41 to 8.14 g m⁻² with pronounced accumulation in the vicinity of effluent discharge. The Hg deposition rate in core 2 varies from 1.28 μg cm⁻² y⁻¹ at the surface section to 50.17 μg cm⁻² y⁻¹ in sediment deposited around 1967 when the chlor-alkali unit went into production. The anthropogenic Hg buried in the sediments of the Bay and the coastal area of Mumbai is estimated at 52.2 and 37.3 t respectively. The approaches used in this investigation to calculate EF as well as lithogenic and anthropogenic Hg in marine sediments of the Mumbai region support the use of Al as the preferred reference element followed by Fe. The results deviate markedly with TOC as the normalizing element probably due to its anthropogenic addition and alteration as a part of diagenesis.

Acknowledgement

We are thankful to Dr. S. R. Shetye, Director, National Institute of Oceanography and Mr. R. V. Sarma, Scientist-in-Charge, Regional Centre, National Institute of Oceanography, Mumbai for providing facilities to conduct the research work.

References


Legend to the figures

Fig. 1: Location map and sampling stations in the Bay and off Mumbai.

Fig. 2: Variation of Hg (µg g⁻¹; dry wt) and TOC (%) in surficial sediment with distance from the Bay mouth.

Fig. 3: (a) Depth-wise variation of Hg (µg g⁻¹; dry wt) and TOC, Al and Fe (%; dry wt); (b) enrichment factor (EF) of Hg; and (c) lithogenic and (d) anthropogenic concentration of Hg (µg g⁻¹; dry wt) in sediment of core 2 calculated using Al, Fe and TOC as reference elements.

Fig. 4: Comparison of (a) EF; and (b) lithogenic and (c) anthropogenic concentrations of Hg (µg g⁻¹; dry wt) in core 2 using Al, Fe and TOC as reference elements.

Fig. 5: Cumulative, anthropogenic Hg deposition (g m⁻²) in cores 1, 2, 3 and 8 calculated using Al, Fe and TOC as reference elements.

Fig. 6: (a) Depth-wise variation of Hg (µg g⁻¹; dry wt) and TOC, Al and Fe (%; dry wt) in sediment of core 1; and (b) EF of Hg calculated using Al, Fe and TOC as reference elements.

Fig. 7: (a) Depth-wise variation of Hg (µg g⁻¹; dry wt) and TOC, Al and Fe (%; dry wt) in sediment of core 3; and (b) EF of Hg calculated using Al, Fe and TOC as reference elements.

Fig. 8: (a) Depth-wise variation of Hg (µg g⁻¹; dry wt) and TOC, Al and Fe (%; dry wt) in sediment of core 8; and (b) EF of Hg calculated using Al, Fe and TOC as reference elements.

Fig. 9: (a) Depth-wise variation of Hg (µg g⁻¹; dry wt) and TOC, Al and Fe (%; dry wt) in sediment of core 21; and (b) EF of Hg calculated using Al, Fe and TOC as reference elements.

Fig. 10: (a) Depth-wise variation of Hg (µg g⁻¹; dry wt) and TOC, Al and Fe (%; dry wt) in sediment of core 23; and (b) EF of Hg calculated using Al, Fe and TOC as reference elements.

Fig. 11: (a) Depth-wise variation of Hg (µg g⁻¹; dry wt) and TOC, Al and Fe (%; dry wt) in sediment of core R; and (b) EF of Hg calculated using Al, Fe and TOC as reference elements.

Fig. 12: Hg deposition rate (µg cm⁻²y⁻¹) in sediment cores 1, 2 and 3.
Table 1 Concentration of Hg (µg g⁻¹; dry wt), Al, Fe (%; dry wt), and precision based on the analyses of certified standards.

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<th>PACS-1</th>
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<td>Fe (%; dry wt)</td>
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</tr>
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<td>Observed</td>
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<tr>
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Table 2. Concentration of Hg (µg g⁻¹; dry wt) and C_{org}, Al, Fe (%; dry wt) in sediments of the Bay during post- and pre-monsoon.

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<td></td>
<td>Hg C_{org} Al Fe</td>
<td>Hg C_{org} Al Fe</td>
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Table 3. Concentration of Hg (µg/ g; dry wt) and Al, Fe (%; dry wt) in soil and rock from the catchment of the Bay and Ulhas Estuary.

<table>
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Table 4. Concentration of lithogenic and anthropogenic Hg (µg g⁻¹; dry wt) calculated using Al, Fe and TOC as reference element. Average value given in parenthesis

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Fig. 1
Fig. 2
Fig. 4
Fig. 5
Fig. 6
Fig. 7
Fig. 8
Fig. 9
Fig. 10
Fig. 11
Fig. 12