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Mercury enrichment in sediments of Amba estuary

Anirudh Ram*, M. A. Rokade & M. D. Zingde
Regional Centre, National Institute of Oceanography, Lokhandwala Road, 4- Bungalows, Andheri (w), Mumbai - 400 053, India
[E-mail: anirudhram@nio.org]

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Concentrations of Hg, total organic carbon (TOC), Al, Fe and Mn were determined in sediment of the Amba Estuary between the mouth and the head over a distance of 24 km in December and May during 1997-2002. Temporal and spatial changes in metal concentrations appear to be due to sediment movement associated with tidal movements. The Hg concentration varies in 0.05 -2.66 μg g^{-1} range and the profiles of its variation indicate Patalganga River that opens in the Amba Estuary is a major source of anthropogenic metal to the estuary. Geoaccumulation index and enrichment factor support Hg contamination of the estuarine sediment to a varying degree. Hg is not significantly correlated with TOC, Al, Fe and Mn in these sediments.

[Key words: Amba Estuary, mercury, geoaccumulation index, enrichment factor]

Introduction

Hg like other trace metals, discharged into estuaries and coastal waters through domestic and industrial wastes. It is generally present in association with particulates or has strong affinity for solid phases in the receiving waters making sediments its main repository in aquatic environment[1-2]. Prevailing distribution of Hg in sediments can be an indicator of extent of contamination in waste receiving areas[3-5]. Several factors including pre-industrial or lithogenic Hg content of sediments must be considered to interpret the present metal content at the site under assessment. Clay minerals, organics and Fe and Mn oxides in sediment also influence the concentration of trace metals including Hg in sediments[6]. Other major phases in sediments such as quartz and calcium carbonate which generally occur in relatively large particles are less efficient in binding trace metals and they dilute the trace metal bearing phases which are principally associated with fine-particle size fraction[7]. Marked variations in Hg content of sediments can therefore occur even in the absence of a local polluting source of Hg when the particle-size and mineralogy of sediment are heterogeneous.

Along the Indian coast high concentrations of Hg due to release of effluents from chlor-alkali industry have been reported in the Mumbai Harbour-Thane Creek (hereinafter referred as Bay)[8-10], Ulhas Estuary[10-12], Rushikulya Estuary[13-16] and the coastal area of Karwar[17]. Apart from Hg we have analyzed sediments from the Amba Estuary for total organic carbon (TOC), Al, Fe and Mn during dry season over the period 1997-2002 since Hg associates primarily with TOC and Fe and Mn oxides through adsorption and coprecipitation reactions in oxidized sediments[3] with organic matter typically being the overriding controlling solid phase[18]. This is the first report on the Hg content of the Amba Estuary that examines the factors influencing its distribution in the sediment through time series measurements. Due to the presence of a weir near Nagothane (Fig. 1), the monsoonal freshwater inflow in the estuary nearly ceases after October and the estuary is strongly tide dominated in the period November-June. The tidal exchange between the estuary and the sea is through the Mumbai Harbour and due to high tidal influence and strong currents[19] there is considerable exchange of sediment dispersed in the water column between the two water bodies. The sediment in the Mumbai Harbour has high anthropogenic Hg due to release of effluents from chloralkali industry as well as sewage[8-11]. The present study was also aimed at evaluating the impact of anthropogenic Hg in the harbour on the sediment of the Amba Estuary due to sediment exchange.

Study Area

Amba River originates in the western Ghats and follows a narrow and meandering course along her

*Corresponding author:

length of over 140 km before opening into the Mumbai Harbour (Fig. 1). The lower reaches of the river often referred to as the Dharamtar Creek is navigable upto Dharamtar for medium size crafts, under all tidal conditions, while, local country crafts navigate upto Gandhe during high tide. A Konkan type weir across the river near Nagothane impounds fresh water and there is no overflow after October rendering the estuary seawater dominated. The spring tidal range of 5.08 m at Rewas decreases to 3.35 m at Nagothane, while, the neap tidal range is about 1.0 m throughout the estuary. The high tidal displacements generate strong currents with the maximum current speeds exceeding 1 m s^{-1} in the lower estuary. The tidal excursion increases from 2.5-4 km at Nagothane to 7-10 km at Mankule. The cumulative flushing time (dry season) of the estuary varies from 6 to 23 tidal cycles depending on the tide[19]. The estuarine salinity is generally comparable with that of the Mumbai Harbour at least upto the Dharamtar (34-37 psu) during the dry season with some decrease in the inner segment due to seepage of water impounded within the weir[20] High tidal displacements disperse fine-grained bed material in water resulting in high and variable suspended particulate matter (SPM) in the estuary. The estuary receives treated effluent from a petrochemical complex directly in the segment off Mankule and several other industries via Patalganga River that opens in the Dharamtar Creek (Fig. 1).

Materials and Methods

Surficial sediments from 7 stations marked in Fig. 1 were sampled in May and December between 1997 and 2002 using a van Veen grab. The samples after collection were transferred to clean polyethylene bags and frozen at -20°C until analysed. Prior to analysis, the sediment was dried below 60°C in an electric oven and powdered in an agate mortar. A weighed portion of the powdered sediment was digested in aqua regia for 2 min at 95°C followed by

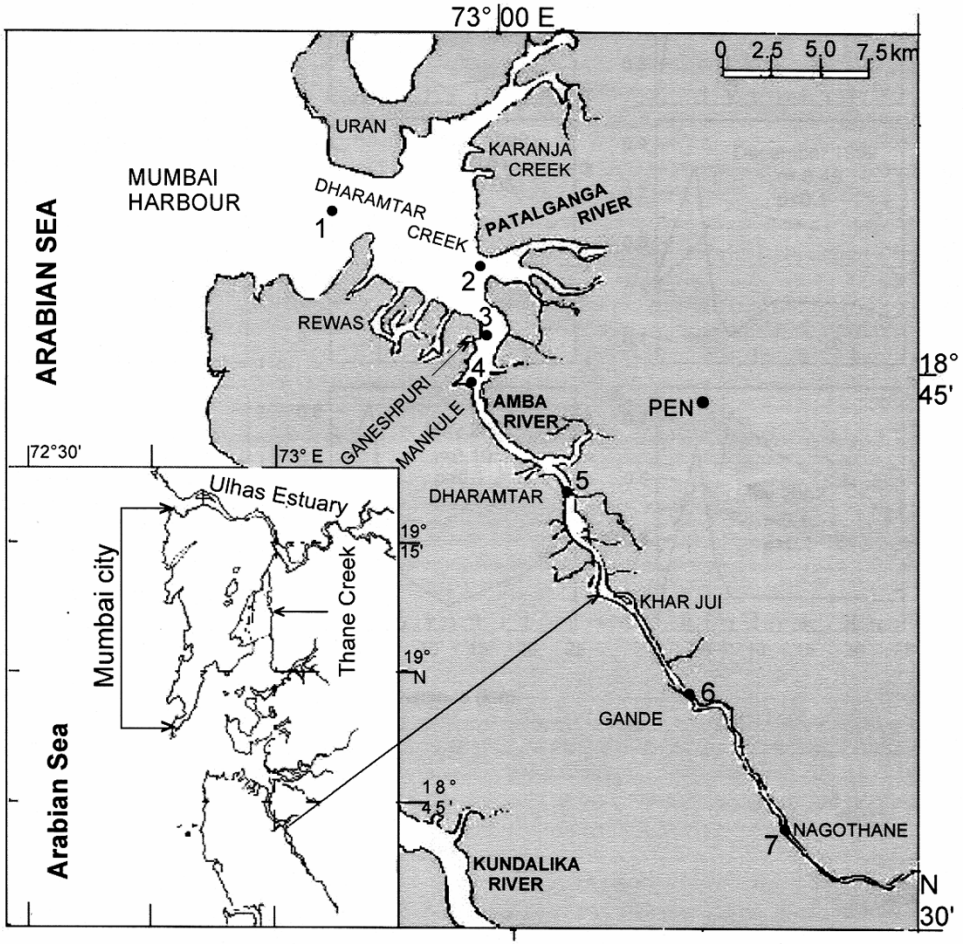

Fig. 1—Locations of sampling in Amba Estuary. Mumbai region is shown in the inset.

oxidation with KMnO4. The concentration of total Hg was measured by cold vapour atomic absorption spectroscopy (CV-AAS) following standard procedure[21] on Varian Spectra 300 with VGA-76 attachment. All acids and chemicals used during the analysis were of special grade with low Hg content (E. Merck, Germany). The precision of the method was 2.7% at the concentration of 2.37 μg g^{-1} Hg (10 replicates). The validity of the results was ascertained by analyzing reference standard PACS-1 (NRC, Canada). The measured concentration for PACS-1 was within 4.40 -4.80 μg g^{-1} as against the certified value of 4.57 ± 0.16 μg g^{-1}. For the estimation of Al, Fe and Mn, the powdered sediment sample was brought into solution[22] by digesting with concentrated HF, $HClO_4$ and HNO_3 and the residue remaining after evaporation of acids was dissolved in dilute HCl. Mn and Fe were estimated using air-acetylene and Al by nitrous oxide-acetylene as oxidant, by flame AAS. The validity of the results was checked by analyzing the reference standard PACS-1 (NRC, Canada) along with the samples. The results were within 3 %, 7 %, and 2 % of the reported value for Al (13.08%), Fe (6.80%), and Mn (461 μg g^{-1}) respectively. TOC was analyzed titrimetrically by the procedure of Walkely and Black (1934)[23].

Results and discussion

The distribution trend of Hg in sediment along the Amba Estuary over the period 1997 - 2002 illustrated in Fig. 2 indicates two prominent features: (i) all profiles have a distinct peak at station 2 and (ii) there is considerable variation in the Hg concentration at the same station during different sampling events. The concentration of Hg in sediment at station 1 compares well with the values reported for the Mumbai Harbour. Elevated concentration of Hg (6.23 - 8.21 μg g^{-1}) in sediment of the inner Bay is known to occur due mainly to the release of effluents from a chlor-alkali plant[8]. The concentration of sediment Hg decreased in the seaward direction with

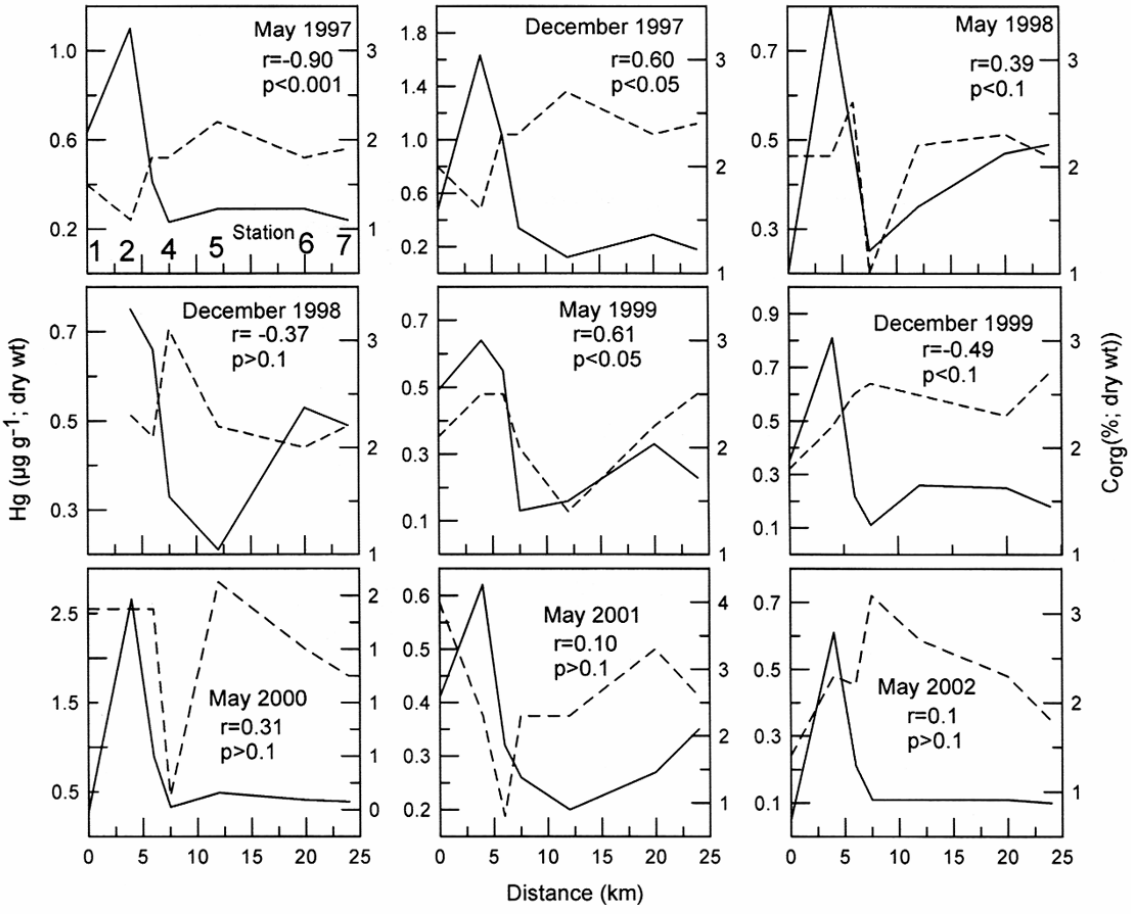

Fig. 2—Concentration of Hg (-) and C_{org} (---) in surficial sediment of Amba Estuary during different sampling events.

the sediment in the harbour area having concentrations[8] of 0.17 - 0.61 μg g^{-1}. A more recent study[24] has indicated marked decrease in the concentration of sediment Hg in the inner Bay due to change-over of the Hg-cell based caustic soda and chlorine manufacturing process to diaphragm cells. The concentrations in the harbour area however, had not decreased and varied in 0.12-0.75 μg g^{-1} range. Hence, tidal exchange of sediment between the Mumbai Harbour and the Amba Estuary could lead to high concentrations of Hg in the latter. The concentration of Hg in sediment of the Amba Estuary varies in the range 0.05-2.66 μg g^{-1}. The consistent high concentration of Hg at station 2 (0.57-2.66 μg g^{-1}) which is within the estuary suggests that the transport of sediment from the Mumbai Harbour is not the prominent source of Hg to the estuary. Station 2 is at the confluence of the Amba and Patalganga Estuaries and relative low concentrations at station 1 and in the segment upstream of station 2 indicate that the outflow of the Patalganga is the major and consistent source of Hg to the Amba Estuary. Several industries located at Rasayani about 25 km inland release effluents in the Patalganga Estuary. However there is no known source of Hg such as chlor-alkali unit among the industries at Rasayani. Further investigations are needed to identify the source of this anthropogenic Hg.

The concentration of sediment Hg in the Amba Estuary varies randomly without discernible trends with considerable fluctuation even at a given location during different sampling events. Thus for instance, the concentration of Hg at station 7 varies between 0.10 and 0.49 μg g^{-1} for sampling done in the same month (May) in different years. Such variations which are also evident for Al, Fe and Mn (Fig. 3) are probably due to sediment movement common to shallow estuaries with unconsolidated substratum, experiencing strong currents. Maximum current speeds exceeding 1 m S^{-1} are recorded in the estuary at least upto Dharamtar during dry season[19]. These currents disperse the fine-grained bed material of the

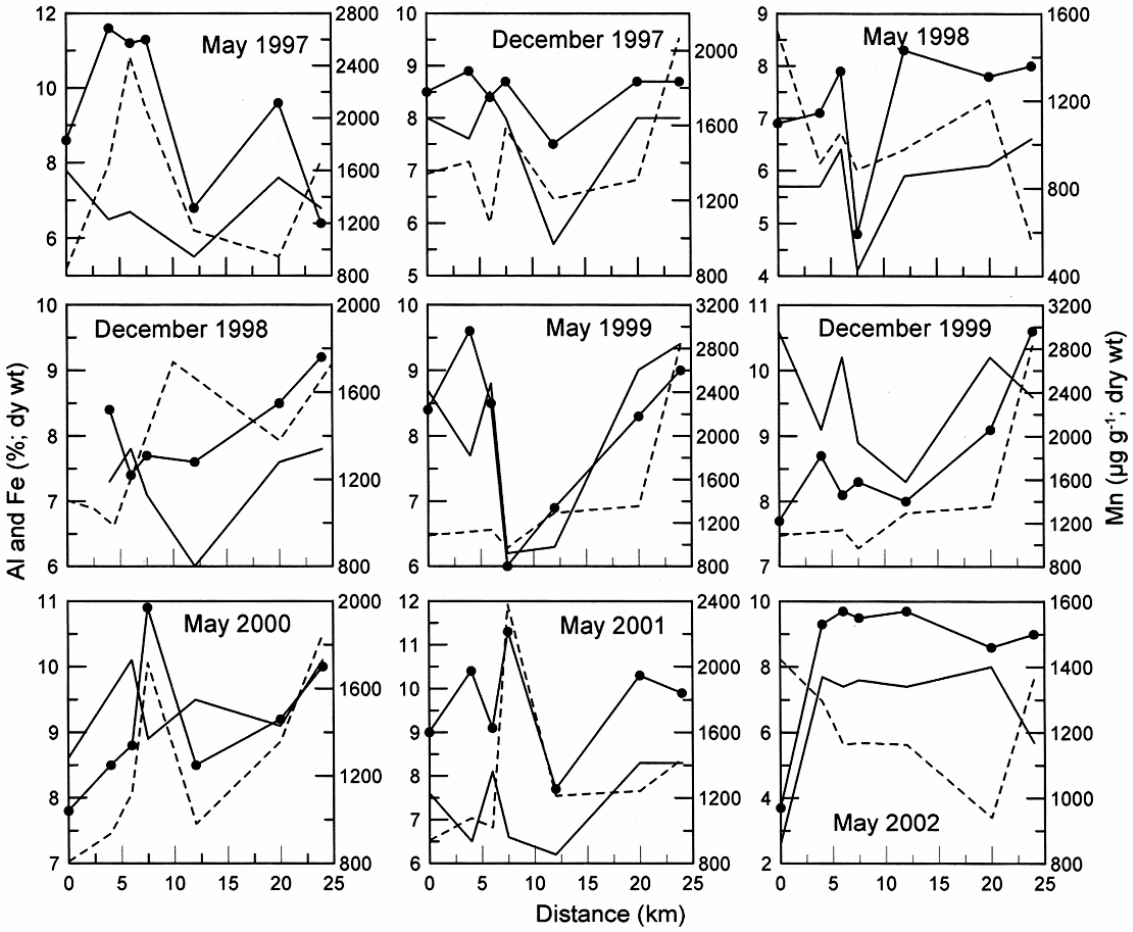

Fig. 3—Concentration of Al (-), Fe (-•-) and Mn (---) in surficial sediment of Amba Estuary during different sampling events.

estuary in water resulting in high and variable SPM (100-400 mg l^{-1}) with marked high values in the bottom water; being closer to its source[20]. Under high tidal excursion (2.5-10 km) this load is transported over long distances and may settle there around tidal slacks. The sediment movement would be even higher during monsoonal floods. There are instances such as in the nearby Ulhas Estuary where the sediment is eroded from the inner segment and transported downstream by river runoff[12]. The high tidal excursion also facilitates transport and distribution of Hg from the Patalganga plume throughout the Amba Estuary. In estuaries, salinity incursion gives an indication upto which a pollutant released in the saline reaches may exert an influence[25]. The high salinities (26-37 psu) between the mouth and the weir in the Amba Estuary during December-May[20] suggest that the Hg load transferred via the plume of the Patalganga Estuary is distributed throughout the Amba Estuary. The minimum in the Hg profiles generally falls at stations 4-5 (Fig. 2). This is also the segment of low Al and/or Fe content of sediment (Fig. 3) and is due to coarse-grained substratum in this zone of the estuary[26].

Concentration of TOC in the sediment of the Amba Estuary rarely exceeds 2% (Fig. 2) which is in conformity with its general distribution pattern in marine sediments off Mumbai-Bassein[12,23,27]. In the dated cores[27] from the coastal Arabian Sea off Mumbai the concentration of TOC in sediment deposited decades prior to urbanization and industrialization of the region, the TOC was around 1.5%. It therefore, appears that the organic carbon entering the estuary through natural and anthropogenic sources is effectively consumed by benthic organisms or mineralized and there is no significant accumulation of TOC in sediment over the years though the effluent loading has progressively increased on the estuary[26]. Close association of Hg with TOC has been reported in several instances[3, 28-30]. In the nearby Ulhas Estuary, Hg is positively correlated with TOC rather than with Al, Fe and Mn[12]. Such a relationship between Hg and TOC in the Amba Estuary which was good (negative) in May 1997 systematically decreased in the subsequent sets (Fig. 2). Hg - TOC relationship is not significant even when all the values are pooled together. Hg is also not significantly correlated with Al, Fe or Mn in individual sets as well as for pooled values. The distinct troughs in Al and Fe profiles in mid-estuary (stations 4-5) is due to the coarse sediment in this area which is frequently dredged for use as construction material[26]. The concentrations of Al, Fe and Mn in the estuarine sediment are in the range reported for basalts of the region[31] which is the major source of SPM in the Amba Estuary.

Geoaccumulation index (I_{geo})

The degree of Hg contamination in the sediments of the Amba Estuary is estimated based on the index of geoaccumulation (I_{geo}). I_{geo} is defined by the relation $I_{geo} = \log_2 C_{Hg}/1.5B_{Hg}$ where C_{Hg} is the measured concentration of Hg in a sediment sample and B_{Hg} is the background value. The factor 1.5 is used to compensate for possible disparity with respect to background due to lithological variation. I_{geo} consists of seven grades or classes, with I_{geo} of 6 indicating almost a 100fold enrichment above background value[32]. Average shale value[33] as well as the regional background[12,34] have been frequently used to estimate I_{geo}. We have used the Hg concentration of 0.10 μg g^{-1} reported in sediment deposited off Mumbai-Bassein in the pre-industrialized period[12,24] as the background in our calculations. The average Hg concentration in rock and soil of the catchment of the region is also close to this value[24]. Based on I_{geo} (Fig. 4) we conclude that the estuarine segment between stations 3 and 7 is moderately contaminated whereas that at station 2 is strongly polluted with Hg.

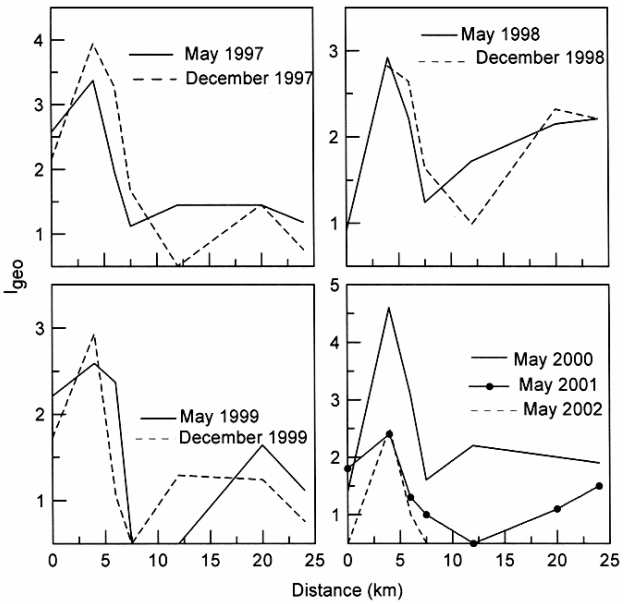

Fig. 4—Geoaccumulation index (I_{geo}) of Hg in sediment of Amba Estuary.

Normalization and Enrichment Factor (EF)

In order to compensate for grain size effect that has considerable baring on the concentration of contaminants in sediments, normalizing with conservative element such as Al, Fe, Sc, Rb and Li measured in the same sample is often adopted[35-41]. By using Al and Fe as a grain-size proxies we calculated the EF using the equation EF= $([Hg]/[M])_{sample}/([Hg]/M)_{back}$. The $([Hg]/[M])_{sample}$ refers to the total concentration of Hg measured in the sample ($\mu g\ g^{-1}$) and $([Hg]/[M])_{back}$ to the geochemical background. $([Hg]/[M])_{back}$ value was obtained from the previous background values (Hg = 0.10 $\mu g\ g^{-1}$; Al = 4.9%; Fe = 4.2%) defined for the coastal sediment of Bassein-Mumbai[12,24].

The EF for Hg is high at station 2 (EF_{Al}, 4.0-13.9; EF_{Fe}, 2.3-13.0) and is >1.5 in rest of the estuary (Fig. 5). Considering several factors influencing trace metal concentration in sediments it is suggested that a value of EF $\leq$1.5 may be considered to be due to crustal material or natural weathering[42-44]. Hence, a considerable fraction of Hg in sediment of the Amba Estuary is of anthropogenic origin. Thus the trend of variation of concentration of Hg, I_{geo} and EF indicates Patalganga Estuary as the important source of anthropogenic Hg to Amba Estuary. Fig. 5 reveals consistently lower EF with Fe as the normalizing element than when calculated with Al. Al being a major constituent of aluminosilicates occurring abundantly in marine sediments is generally not influenced by anthropogenic sources[40]. On the other hand the concentration of Fe in sediments can be influenced by diagenetic processes as well as anthropogenic addition in certain cases. Digenetic mobilization of Fe in the sediment of the Amba Estuary is unlikely in view of good oxidizing conditions in the bottom water[20], strong currents that keep the surface sediment well-ventilated and the absence of accumulation of TOC in sediments which invariably occurs in anoxic coastal sediments. Handling of large quantities of iron ore at Dharamtar Port and spillages during such operations which are

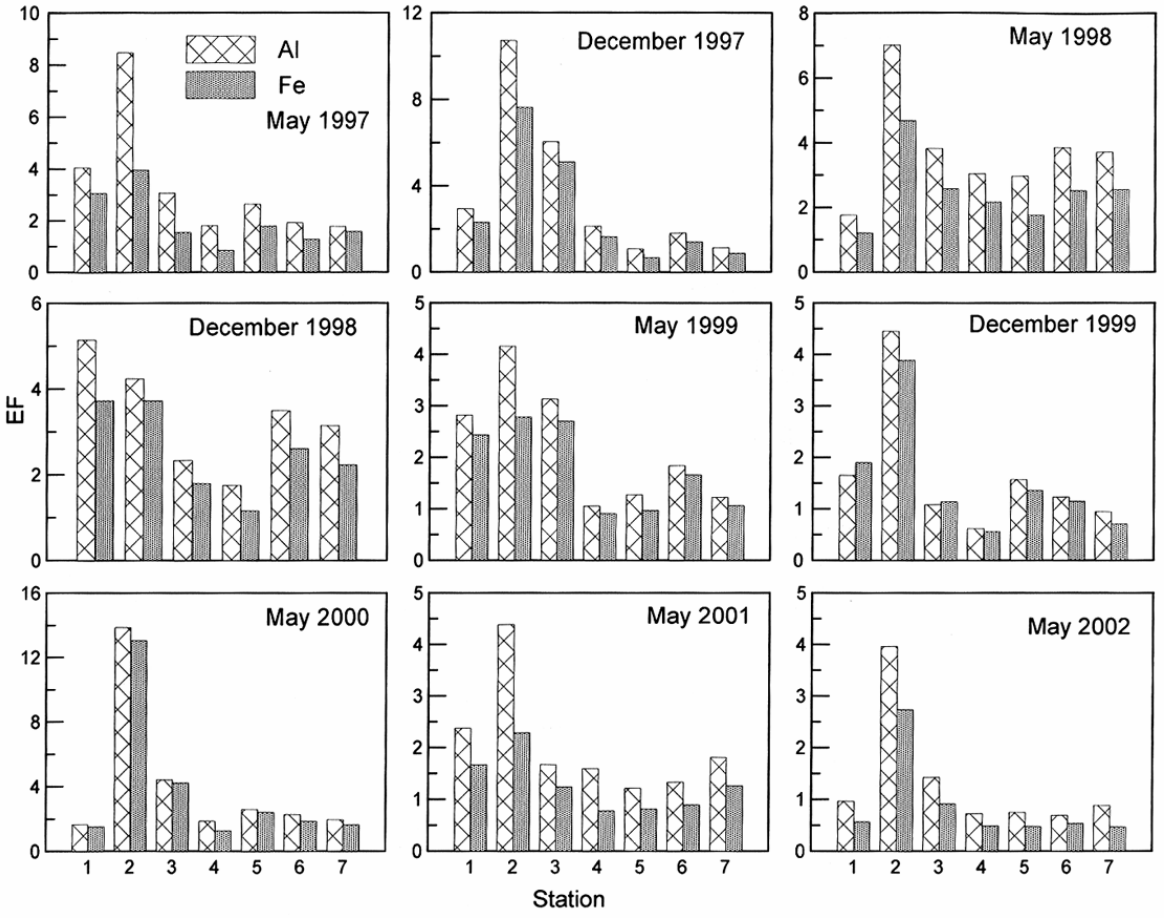

Fig. 5 — Enrichment factor (EF) of Hg in sediment of Amba Estuary.

common could be the major source of anthropogenic Fe to the estuary leading to relatively low EF with Fe as the reference element. Available information indicates that about 3.4×10^6 t of iron ore in various forms was handled at the Dharamtar Port during 2003-04[45].

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