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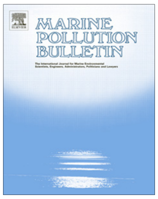

Baseline

Characterizing metal levels and their speciation in intertidal sediments along Mumbai coast, India

Lina L. Fernandes, G.N. Nayak *

Marine Sciences Department, Goa University, Taleigao Plateau, Goa 403206, India

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ABSTRACT

The present study investigated the concentration, distribution and speciation of metals (Fe, Mn, Cu, Pb, Co, Zn and Cr) in sediments of Mumbai region. Pearson's correlation matrix and cluster analyses showed good association of metals with grain size and organic matter. Factor analysis applied to the speciation data helped to identify the role of different sediment fractions in metal retention. The environmental risks of metals, evaluated by sediment quality guidelines, revealed some contamination in the region. However, the Individual and Global Contamination Factors and the Risk Assessment Code, suggested low risk to the aquatic environment, except of Mn in the creek sediments.

Mumbai city, in India, is an industrial hub comprising of textiles and petrochemicals, with its industrial units spanning around its creeks and estuaries. Thane creek (73°14′E, 19°14′N; 72°54′E, 19°17′N), adjoining Mumbai harbour, is a triangular mass of brackish water that opens to the Arabian Sea in the south. The creek is considered as an estuary during the southwest monsoon period when the land drainage and river runoffs are considerable. The area is extremely bio-productive and yields about 2 to 3 thousand metric tonnes of fish annually. At present, this zone harbours about 25 large, 300 medium and small scale industries that utilize hazardous chemicals. Ulhas River Estuary (72°55′E, 19°N; 73°E, 19°15′N) is mainly a monsoon fed river with its fresh water flow dwindling during the non-monsoon season. Several industries situated along the banks of the river add their effluents at various localities. Previous studies covering sediment, water and biota carried out along the coastal wetlands as well as the offshore areas of Mumbai, have noted increasing levels of mercury (Ram et al., 2003), polycyclic aromatic hydrocarbons (PAHs) (Blaha et al., 2011), metals (Fernandes et al., 2011) and declining abundance and diversity of flora and fauna (Quadros and Athalye, 2012). The vast mudflats present along the creek and estuary, render considerable fishery in the region. However, owing to the various anthropogenic activities, the substratum gets disturbed thereby greatly affecting the fishery species. Archeivala (1969) reported a decrease in spawning ground of the *Hilsa* fishery due to heavy pollution at the upper reaches of the estuary. Nath et al. (2003) observed degeneration in the ovarian cells of *Clarias batrachus* due to altered physico-chemical parameters of the wetlands. Moreover, mass fish kill has been frequently observed in the coastal waters (Rathod et al., 2002). Athalye et al. (2003) blamed the fuel gathering, reclamation, industrial and domestic pollutants and overfishing for deterioration of the estuary. The chemical forms rather than the total content, govern metal toxicity (Liu et al., 2007). Speciation analysis can provide information on the origin, mode of occurrence, and the biological and physicochemical availability of heavy metals (Shiowatana et al., 2001). Although trace element pollution is a key environmental problem in Mumbai, no study on metal speciation has been undertaken in the region. Therefore, the present study was carried out to determine the degree of sediment contamination and bioavailability of metals at the two sites.

Two sediment cores, one from Thane creek (TC-62 cm long) closer to the creek mouth and the other from upstream region of Ulhas estuary (UE-60 cm long), surrounded by industries (Fig. 1), were collected from the intertidal regions along the southeastern part of Mumbai. The cores were sampled at low tide, with the help of a PVC corer (150 cm length and 5 cm diameter) which was gently pushed into the sediment and retrieved. The geographical co-ordinates were determined by GPS.

In the laboratory, the cores were sub-sampled at 2 cm intervals; the pH was measured by a calibrated pH meter and then immediately refrigerated at 4 °C until further analysis. The pipette analysis by Folk (1974) was used for obtaining sand, silt and clay fractions. The dried samples were pulverized using an agate mortar and pestle and used for organic matter analysis, total and sequential extraction of trace metals. Total organic carbon (TOC) was determined by Walkley and Black (1934) method, modified by Gaudette et al. (1974). For the analyses of Total Phosphorus (TP) and Total Nitrogen (TN), a standard procedure (Grasshoff, 1999) was employed. For total elemental concentration, the sediments

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* Corresponding author. Tel.: +91 832 6519059 (O), +91 832 2458468 (R), +91 9822725032 (M); fax: +91 832 2451184.

E-mail addresses: nayak1006@rediffmail.com, gnnayak@unigoa.ac.in (G.N. Nayak).

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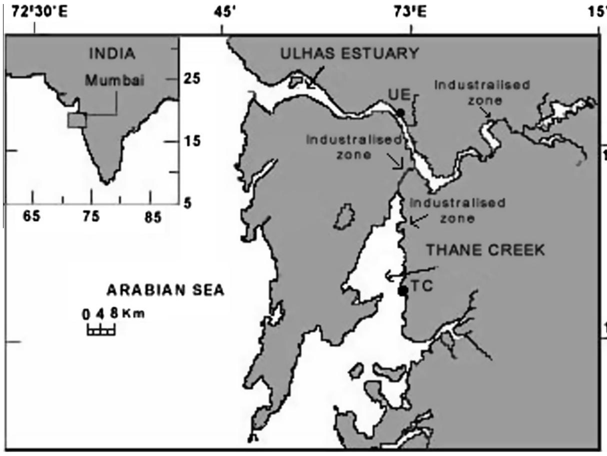

Fig. 1. Map showing the sampling locations in Mumbai [Thane creek (TC) and Ulhas estuary (UE)].

(300 mg) were digested using a combination of concentrated HNO_3, $HClO_4$ and HF (Jarvis and Jarvis, 1985), diluted with deionised water and then aspirated into the flame. To evaluate the effectiveness of the digestion procedure, in addition to blanks and replicates, a certified reference material (BCSS-Marine Sediment Reference Material for Trace Metals and Other Constituents) from the National Research Council, Canada was also included in the analytical procedure. The percent recoveries were 86–91% for Fe, Cu and Al; 87–92% for Mn and Co; 80–85% for Pb and Zn; 90–95% for Cr; 82–90% for Ca, respectively, with a precision of +6%. Chemical speciation of trace metals in selected samples (17 subsamples in core TC and 16 subsamples in core UE) were analysed using Tessier's sequential procedure (Tessier et al., 1979). The description of the five fractions as well as the operating conditions used for each extraction is illustrated in Table 1a. The total and the various forms of the metals were determined using Atomic Absorption Spectrometer SpectrAA 280 FS manufactured by Varian with acetylene–air flame atomization (F-AAS) for Fe, Mn, Co, Cu, Cr, Pb and Zn. For Al and Ca, nitrous oxide–acetylene flame was employed. The recovery rates of the metals, obtained by sequential extraction procedure, were judged by comparing the sum of the five fractions with the total metal concentration (Table 1b). All the apparatus used in the chemical analyses were acid cleaned and dried.

The mean, standard deviation and range of the studied variables as well as the associated background values are summarized in Table 2a and b and plotted in Figs. 2 and 3. In core UE, distinct variations are seen between the depths of 26 and 20 cm, wherein some elements show an increase (Ca, Mn, Co and Cr) whilst others show a decrease (Al, Cu, Pb and Zn). This observation may be related to the grain-size variations (Williams et al., 1994). Higher sand content seen in this part of the core, probably due to high monsoonal runoff, might have led to the lower concentration of some of the elements. In core TC, most of the elements studied display surface increment, while in core UE only Pb demonstrates an increase. This is contrary to expectation as core UE being closer to anthropogenic sources of pollution (industrialized area) than core TC (no major industries present) receives higher metal input. The observed high metal content may be linked to the differences in organic matter (OM) content and salinity at the two sites. Core TC shows higher OM content than core UE indicating that OM effectively forms metal complexes (Jambers et al., 1999). Marine water intrusion into the creek region results in higher salinity (28 ppt, Quadros and Athalye, 2012) in contrast to the estuary (14 ppt, Mishra et al., 2007) which receives more of freshwater from the upstream Ulhas River. Therefore, the increase in salinity from the freshwater to the marine zone favors the adsorption of trace metals on particulates, induces flocculation, and encourages the aggregation and deposition of sediments in the region.

Cluster analysis (CA) employing Eucledian method and Pearson's correlation matrix (Table 3a and b) were performed at each site, to investigate the relationship among the elements. Core TC, Fig. 4a, displays three clusters, (I) silt, TP, Co, Cr, Pb; (II) subdivided into two clusters (a) Fe, Al, TN, Zn, Cu and (b) Ca, Mn, sand, TOC and (III) Clay, pH. In case of core UE (Fig. 4b), three clusters are identified, (I) Mn, Fe, silt, sand, Ca, Cr, Co; (II) Al, TN, TOC, Cu, Pb, Zn and (III) Clay, TP, pH. The main reason for the considerable difference in the clusters at the two sites might be due to the different types of polluted substances, arising from the different industries and human activities present along the sites. From Table 3, strong correlations are seen between OM and the trace elements.

An ecological risk factor (E_r^i) (Hakanson, 1980; Zhu et al., 2008) has been computed, given by the following equation:

$$E_r^i = T_r^i \cdot C_f^i \qquad (1)$$

where

$$C_f^i = C_s^i / C_n^i \qquad (2)$$

where C_f^i: contamination factor of metal i; C_n^i: pre-industrial records in sediments; C_s^i: detected concentration values; T_r^i: toxic-response factor of a given metal; E_r^i: ecological risk coefficient. In this study, the metal background values are taken from Fernandes (2013) and Taylor (1964). To estimate the possible environmental consequence of the metals, the mean metal values have been compared with sediment quality guidelines (Supplement Table S1) developed by the US National Oceanic and Atmospheric Administration (Long and MacDonald, 1998) and US Environmental Protection Agency (Perin et al., 1997). From Table 4, the sediments are found to be contaminated with metals and can thus contribute to sediment toxicity, especially in core UE, which receives high inputs of domestic and industrial wastewater (about 3.16×10^6 m^3/d). Both the natural

Table 1
(a) Sequential extraction scheme of Tessier et al. (1979). (b) Recovery rates of metals obtained from sequential extraction.

Step	Fraction	Extraction reagents/conditions
(a)		
1	Exchangeable – (F1)	8 ml $MgCl_2$, pH 7, 1 h, room temperature, continuous agitation
2	Acid-soluble (Carbonates) – (F2)	8 ml NaOAc, pH 5, 5 h, room temperature, continuous agitation
3	Reducible (Fe–Mn oxide bound) – (F3)	20 ml of 0.04 M $NH_2OH.HCl$ in 25% HOAc, 6 h, 96 ± 3 °C, occasional agitation
4	Oxidizable (Organically bound + sulphide bound) – (F4)	3 ml of 0.02 M HNO_3 + 5 ml of 30% H_2O_2, pH 2, 2 h, 85 ± 2 °C, occasional agitation. Add 3 ml of 30% H_2O_2, repeat 3 h, cool and then add 5 ml of 3.2 M NH_4OAc in 20% HNO_3, 0.5 h, room temperature, continuous agitation
5	Residual – (F5)	$HF:HNO_3:HClO_4$ = 7:3:1, dryness, again $HF:HNO_3:HClO_4$, 1 h, 2 ml conc. HCl, dryness, 10 ml 50% HNO_3, make up to 50 ml with distilled water

Elements	Fe	Mn	Cu	Pb	Co	Zn	Cr
(b)							
Recovery (%)	95–99	85–95	90–94	92–98	102–114	96–105	90–95