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

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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) (Blahe 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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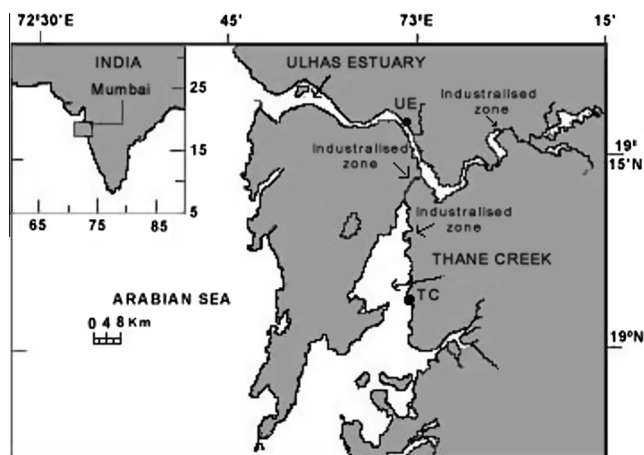


Fig. 1. Map showing the sampling locations in Mumbai [Thane creek (TC) and Ulhas estuary (UE)].

(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 SpectraAA 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 Euclidian 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:

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

where

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

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 $3.16 \times 10^6 \text{ m}^3/\text{d}$). 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 $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% HOAc , 6 h, $96 \pm 3^\circ\text{C}$, 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, $85 \pm 2^\circ\text{C}$, 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	

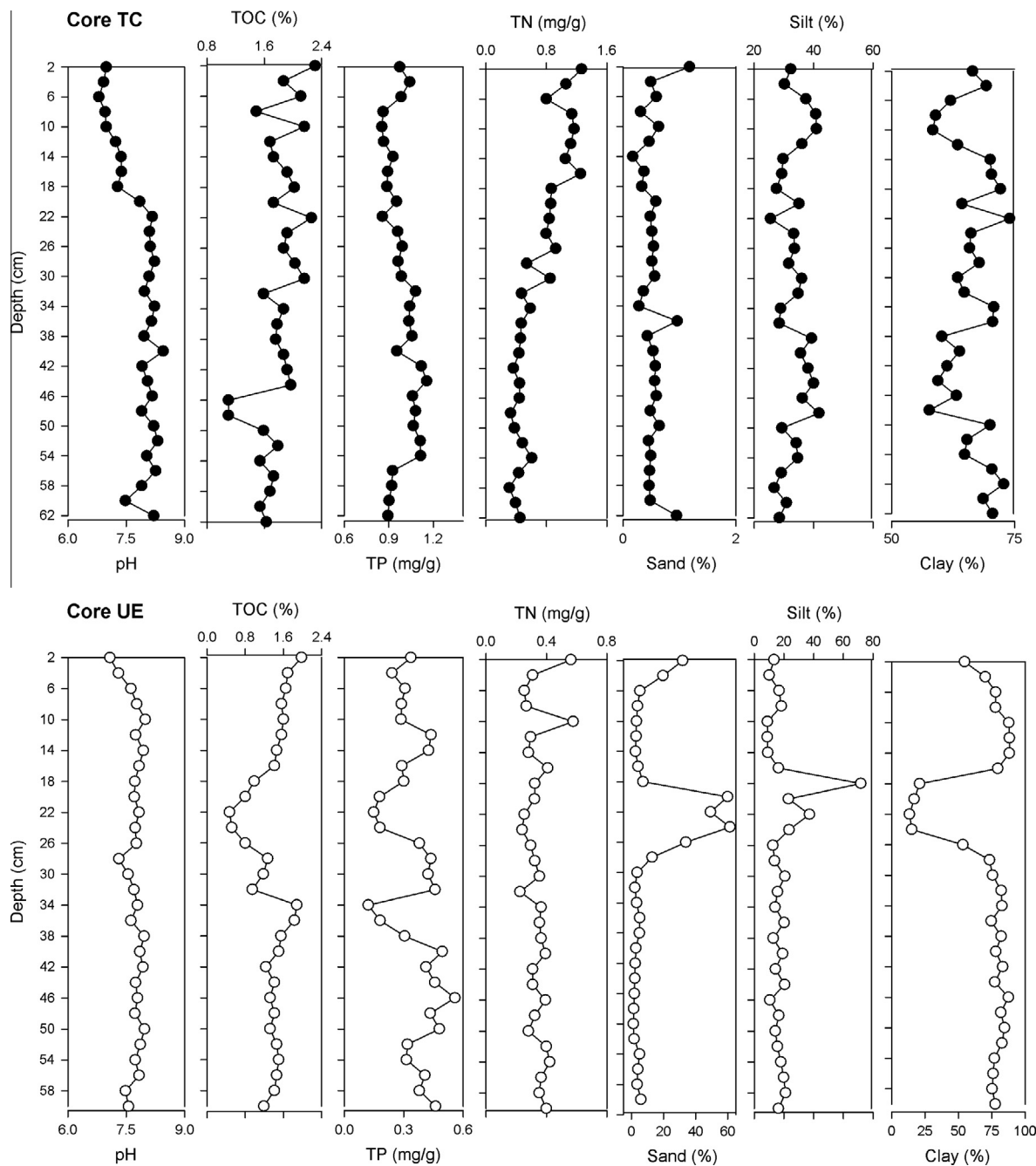


Fig. 2. Depth profiles of sediment components and organic matter in core TC and core UE.

and anthropogenic sources (coal based, metals and alloys, leather processing, electroplating, lead batteries, welding units, etc.) distributed throughout the upstream region of the estuary contribute to the metal load. Moreover, a barrage constructed upstream of the estuary restricts the river flow resulting in settling of suspended matter along with the adsorbed metals.

Speciation of heavy metals was performed on selected subsamples of the cores (Supplement Figs. S1 and S2). To better interpret the speciation data, factor analysis (FA) (Eigen values > 1, factor rotation and varimax normalization) was applied individually to each fraction.

(a) *Exchangeable fraction (F1)* corresponds to those metals that can be released by merely changing the ionic strength of the medium. FA resulted in three factors at each site. pH Strongly bonds

with Pb and Co (Fig. 5A1-2) at both the sites. Also, from the 3D plot, clay and OM appear in the vicinity. Therefore, clay and OM render sites for ionic exchange, thus supporting the initial interpretation of this fraction as exchangeable metal forming. On the other hand, Fe, which is mostly present in the residual form (90%), is placed farther away in both the plots. It is generally acknowledged that pH plays an important role in governing concentrations of soluble metals (Atkinson et al., 2007), but in this study no significant correlations are observed among all the elements and pH (Table 3). At soil pH above 6, Mn forms bond with OM, oxides and silicates whereby its solubility decreases. Mn availability and solubility is thus generally low at high pH and high OM content, while in acid soils with low OM content its availability is high. The solubility of Mn is also high in anaerobic conditions at pH above 6, as well as in

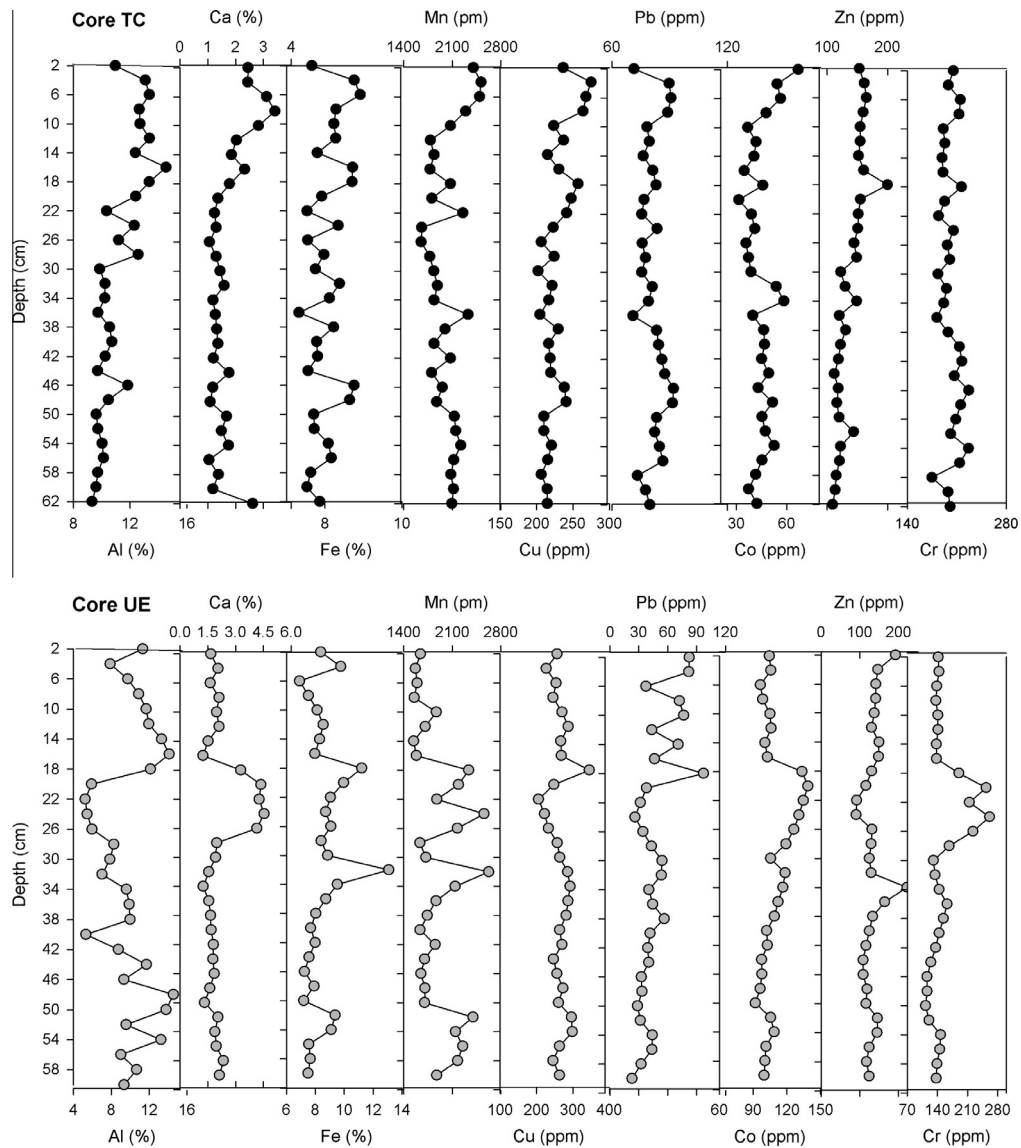


Fig. 3. Depth profiles of selected metals in core TC and core UE.

Table 2

Descriptive statistics of Thane creek and Ulhas estuary with respect to (a) Sediment components and organic matter and (b) metals.

Site		pH	TOC (%)	TP (mg/g)	TN (mg/g)	Sand (%)	Silt (%)	Clay (%)		
<i>(a)</i>										
Thane Creek	Mean	7.80	1.80	0.98	0.70	0.53	33.43	66.04		
	SD	0.49	0.28	0.09	0.31	0.20	4.58	4.57		
	Range	6.80–8.45	1.1–2.31	0.85–1.16	0.31–1.27	0.17–1.18	25.52–41.84	57.68–74.00		
Ulhas Estuary	Mean	7.71	1.35	0.35	0.34	11.70	18.44	69.86		
	SD	0.21	0.36	0.11	0.08	17.38	11.54	22.69		
	Range	7.08–7.99	0.47–1.98	0.12–0.56	0.23–0.58	1.26–61.35	8.79–71.34	13.44–88.24		
Site		Fe (%)	Mn (ppm)	Cu (ppm)	Pb (ppm)	Co (ppm)	Zn (ppm)	Cr (ppm)	Al (%)	Ca (%)
<i>(b)</i>										
Thane Creek	Mean	8.06	2025	227	81.50	44.92	139	201	11.19	1.71
	SD	0.44	235	19.08	5.84	7.76	21.34	13.06	1.48	0.64
	Range	7.32–8.92	1653–2518	202–275	71–92	31.50–66.75	109–200	175–227	9.31–14.54	1.05–3.42
Ulhas Estuary	Mean	8.56	1902	264	95	109	133	307	9.80	2.18
	SD	1.28	317	27	38	13	26	76	2.71	0.94
	Range	6.91–13.09	1545–2626	206–345	46–195	92–139	91–222	225–523	5.24–14.59	1.24–4.54
Fernandes, 2013 ^a		7.83	2290	110	41	49	100	90	12.49	2.81
Taylor, 1964 ^b		8.56	1500	100	5	48	100	200	8.76	6.72

Bold values indicate higher contents.

^a Background values.

^b Background values.

Table 3

Pearson's correlation matrix for different variables in (a) Thane creek (n = 31) and (b) Ulhas estuary (n = 30).

	pH	TOC	TP	TN	Sand	Silt	Clay	Fe	Mn	Cu	Pb	Co	Zn	Cr	Al
TOC	-0.21	1.00													
TP	0.39**	-0.25	1.00												
TN	-0.71**	0.45**	-0.53**	1.00											
Sand	0.03	0.21	0.07	-0.02	1.00										
Silt	-0.18	-0.20	0.31	0.02	-0.04	1.00									
Clay	0.18	0.19	-0.32	-0.02	0.00	-1.00	1.00								
Fe	-0.44*	-0.23	-0.05	0.25	-0.34*	0.25	-0.24	1.00							
Mn	-0.43*	0.12	0.00	0.07	0.36*	-0.15	0.13	0.06	1.00						
Cu	-0.67**	0.02	-0.20	0.45**	-0.13	0.19	-0.19	0.69**	0.42*	1.00					
Pb	-0.10	-0.43*	0.35*	-0.20	-0.28	0.49**	-0.48**	0.67**	0.13	0.50**	1.00				
Co	-0.23	0.02	0.43*	-0.02	0.16	0.14	-0.15	0.24	0.46**	0.30	0.32	1.00			
Zn	-0.61**	0.45**	-0.44*	0.74**	-0.28	-0.12	0.14	0.45**	0.10	0.63**	-0.04	0.04	1.00		
Cr	0.01	-0.35	0.35*	-0.22	0.01	0.39*	-0.39*	0.42*	0.15	0.31	0.77**	0.39*	-0.06	1.00	
Al	-0.66**	0.18	-0.45**	0.73**	-0.28	0.11	-0.09	0.67**	-0.08	0.66**	0.19	-0.15	0.80**	0.05	1.00
Ca	-0.76**	0.21	-0.35	0.60**	0.15	0.21	-0.22	0.36*	0.47**	0.53**	0.17	0.26	0.42*	0.07	0.48**

TOC	-0.21	1.00													
TP	0.04	0.06	1.00												
TN	-0.14	0.50**	0.02	1.00											
Sand	-0.22	-0.61**	-0.53**	-0.18	1.00										
Silt	0.01	-0.43*	-0.26	-0.20	0.20	1.00									
Clay	0.16	0.68**	0.54**	0.24	-0.87**	-0.66**	1.00								
Fe	-0.12	-0.33	-0.29	-0.20	0.22	0.37*	-0.36*	1.00							
Mn	0.13	-0.48**	-0.27	-0.13	0.30	0.36*	-0.41*	0.62**	1.00						
Cu	0.19	0.33	0.10	0.25	-0.57**	0.31	0.28	0.34	0.23	1.00					
Pb	-0.22	0.33	-0.14	0.28	-0.12	0.26	-0.04	0.32	-0.18	0.31	1.00				
Co	-0.06	-0.66**	-0.58**	-0.25	0.74**	0.53**	-0.84**	0.66**	0.57**	-0.05	0.05	1.00			
Zn	-0.26	0.72**	-0.32	0.43*	-0.26	-0.22	0.31	0.14	-0.11	0.39*	0.39*	-0.12	1.00		
Cr	-0.03	-0.68**	-0.56**	-0.27	0.89**	0.39*	-0.88**	0.32	0.45**	-0.33	-0.09	0.88**	-0.27	1.00	
Al	0.12	0.52**	0.21	0.27	-0.58**	-0.06	0.48**	-0.28	-0.34	0.48**	0.25	-0.56**	0.28	-0.59**	1.00
Ca	0.00	-0.80**	-0.41*	-0.30	0.85**	0.45**	-0.88**	0.27	0.46**	-0.41*	-0.15	0.80**	-0.48**	0.91**	-0.58**

* p < 0.05.
** p < 0.01.

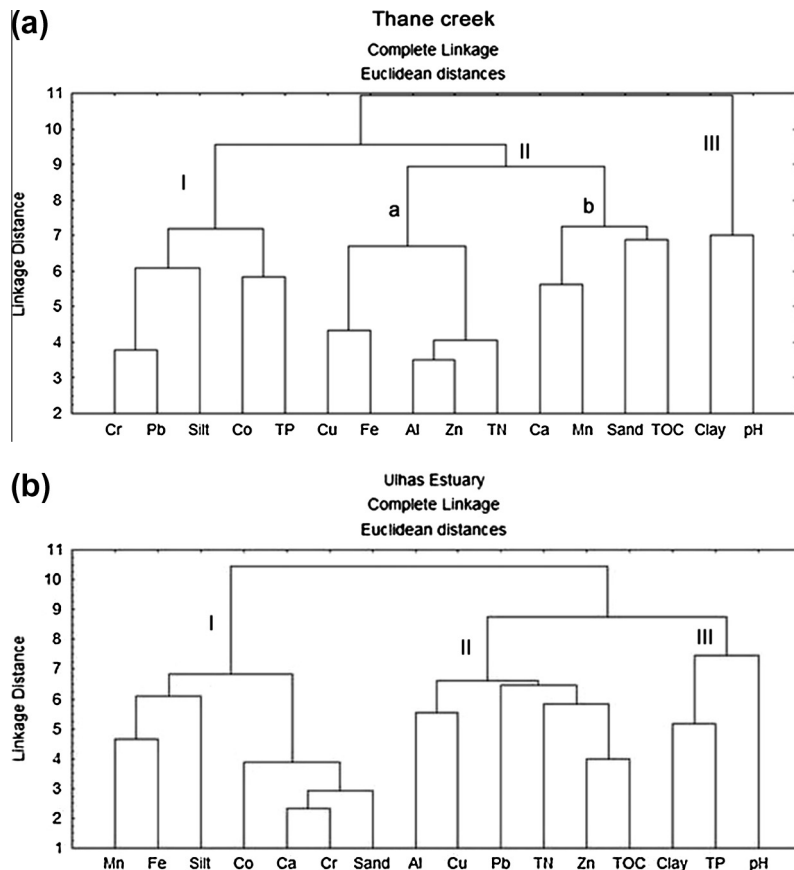


Fig. 4. Dendrogram plots for core TC and core UE.

Table 4

Average values of Ecological Risk index, Individual and Global Contamination factors and Risk Assessment Code of selected elements in Thane creek and Ulhas estuary.

Elements	Thane Creek				Ulhas Estuary			
	Ecological Risk Factor	Individual Contamination Factor	Global Contamination Factor	Risk Assessment Code	Ecological Risk Factor	Individual Contamination Factor	Global Contamination Factor	Risk Assessment Code
Fe	–	0.07	5.37	0.31	–	0.07	2.33	0.30
Mn	–	2.92		31	–	0.70		20
Cu	10.34	0.24		4.27	12.02	0.11		3.36
Pb	9.94	0.78		24	11.56	0.55		15
Co	–	0.75		23	–	0.34		7.75
Zn	1.39	0.46		11	1.33	0.44		6.84
Cr	4.48	0.15		3.49	6.81	0.12		3.45

aerobic conditions at pH below 5.5 (Pendias and Pendias, 2001). In the present study, the sediment pH ranges from 6.80 to 8.45 in core TC and from 7.08 to 7.99 in core UE. Therefore, there is a lesser tendency of this metal to solubilise.

(b) *Carbonate Fraction (F2)* shows the amount of elements that would be released into the environment if the conditions became more acidic (Okbah et al., 2008). In Fig. 5B1–2, better associations are seen among Ca, Mn and Zn in core UE than in core TC. This may be because of the higher residence time of more polluted water at the inner part of the estuary as compared to the water near the creek mouth. As already mentioned, core UE was sampled from the upstream region of the estuary surrounded by industries while core TC was collected closer to the creek mouth. The co-precipitation with carbonate minerals is of importance for a number of metals, including Zn (Alloway, 1990). High Pb concentrations are seen in this fraction, probably as bound to carbonates (Izquierdo et al., 1997). Carbonate-bound Mn includes that which is chemisorbed or coprecipitated with calcite and related carbonate minerals. The present result indicates that considerable amount of Mn would be released into the environment if the conditions became more acidic (Yuan et al., 2004).

(c) *Fe-Mn oxide fraction (F3)* includes the metal oxides/hydroxides soluble under slightly acidic pH, as well as the metals associated with reducible amorphous Fe–Mn Oxy-hydroxides (Velimirovic et al., 2011). Metals from this fraction are released into the system with a pH decrease and if sediments change from oxic to anoxic condition (Turki, 2007). As expected, in this fraction Fe and Mn oxides are grouped together (Fig. 5C1–2), particularly with Mn and Zn, which are the most extractable elements in this step at both the sites. Fe and Mn oxides are reported to be the main carriers of Zn from the fluvial environment to the lagoonal one (Li et al., 2001), as they easily undergo adsorption phenomena (Hem, 1977). Further, the higher association of Pb observed in this fraction may be due to the higher stability constant of Pb-oxides (Fan et al., 2002).

(d) *Organic matter/Sulphide Fraction (F4)* represents the amount of metals bound to the OM and sulphides that would be released into the environment if conditions became oxidative. At both the sites, Pb is the most abundant metal in this fraction. However, in core TC, it is associated with only TP (Fig. 5D1). A similar observation has been noticed in the correlation analysis. On the other hand, in core UE, the three components of OM (TP, TN, TOC) are found to associate with Pb (Fig. 5D2). This difference may be due to selective adsorption onto some components of the OM (Reyes-Solís et al., 2009). Some types of OM have fewer sites per unit surface (e.g. lignins) while others have many (fulvic materials). The intensity of complexation is also found to vary progressively with the metal concentration, with high-intensity sites being filled first, followed by sites of lower intensity (Luoma and Rainbow, 2008).

(e) *Residual Fraction (F5)*, named inert phase, corresponds to that part of the metal, which cannot be mobilized. In Fig. 5E1–2, at both the sites, the finer sediment components are found to act

as metal carriers. In this study, more than 90% of total Fe and total Cu are present in the residual fraction (Supplement Figs. S1g and S2g), indicating that they are mainly of lithogenic origin as seen in similar studies carried out in the Pearl River Estuary and East China Sea (Yuan et al., 2004). Also, appreciable amounts of Cu, Co and Zn are seen in this fraction. Therefore, from the extraction data and the positive correlations seen between Zn and Cu with Al and Fe in core TC; Cu with Al and Co with Fe in core UE, we can infer that these elements are mainly contained in the F5 fraction (silicates such as biotite and chlorite). Thus, the anthropogenic influence of these metals in the sediments seems to be minor.

The Individual Contamination Factor (ICF) and the Global Contamination Factor (GCF) have been calculated from the fractionation data (Ikem et al., 2003; Abdallah, 2012) as per the following equations:

$$ICF_{\text{metal}} = \frac{C_{\text{nonresistant}}}{C_{\text{resistant}}}$$

$$GCF = \sum_{i=1}^n Cfi$$

Further, the Risk Assessment Code (RAC) has been used to assess environmental risks and estimate the possible damage to benthic organisms caused by the contaminated sediments (Ghrefat and Yusuf, 2006). The ICF, GCF and RAC (Table 4) reveal low risk to the aquatic biota, except of Mn in the creek sediments.

The study carried out on sediment cores of intertidal regions along Mumbai coast, showed significant role of organic matter and grain size as metal carriers. Based on the total metal contents and the various sediment quality guidelines employed, Ulhas estuary displayed greater metal contamination as compared to Thane creek. However, the speciation results indicated higher percentage of metals in the residual fraction of both the sites, suggesting low risk to the aquatic biota of the region, except of Mn in sediments of Thane creek. This study is the first, in relation to chemical fractionation of metals in sediments of Mumbai, and provides baseline information for further study in the region.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.marpolbul.2013.11.013>.

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