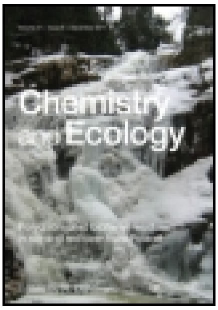

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Heavy metals contamination in mudflat and mangrove sediments (Mumbai, India)

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The focus of this study, carried out on mudflat and mangrove sediments of Ulhas Estuary and Thane Creek in Mumbai, India, documents how sediment analysis in different ecosystems can help in understanding metal behaviour and pollution status of the region. Based on the the geoaccumulation index (I_{geo}), the study shows that the estuarine and creek regions, being recipients of industrial and domestic wastes, display moderate pollution. Ulhas Estuary with higher clay and organic matter contents, exhibits higher amounts of metals than Thane Creek. Furthermore, using correlation and cluster analyses, the creek projects stable subenvironments with similar types of metal associations, with Fe and total organic carbon as the dominant metal carriers. By contrast, in the estuarine subenvironments, the metal associations do not reveal any distinct trend, which may be attributed to the disturbance caused by dredging activities routinely carried out in the region. Factor analysis carried out on I_{geo} data in both regions further helped in identifying polluted metal groups.

Keywords: anthropogenic; estuary; creek; metals; Mumbai; pollution

1. Introduction

Sediment analyses have been found to play an important role in the assessment of metal contamination in aquatic systems [1–3]. They act like a sink for various pollutants like pesticides and heavy metals, and also as a source under changing environmental conditions, releasing metals into the water column. Trace elements are introduced into the environment in a variety of ways, such as atmospheric deposition, erosion of geological materials and through anthropogenic activities [4,5]. In estuarine and coastal regions, when dissolved metals from natural or anthropogenic sources come into contact with saline water they are quickly adsorbed to particulate matter and are removed from the water column to the bottom sediments. Thus, metals from different sources are ultimately concentrated in the sediments [6]. The order of magnitude of contaminant concentrations is higher in sediment than in water and sediments also show less variation over time and space, allowing for a more consistent assessment of spatial and temporal contamination. Furthermore, sediments have a long residence time and are, thus, the preferred monitoring tool [7,8]. The concentration of metals in sediment depends on various factors such as the textural

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characteristics, organic matter content, mineralogical composition and depositional environment of the region [9]. The metals are also dominated by a complex dynamic equilibrium governed by various physical, chemical and biological factors [10]. In addition, the mobility of metals in the environment depends strongly on their chemical form or the bonding types of the element [11].

Mumbai encompasses a narrow strip of coastal water which is very important from an environmental point of view because it supports a vast area of mangrove forest in addition to a wide variety of flora and fauna. Although mangrove and its adjacent ecosystems are of tremendous value to coastal communities and associated species, they are being destroyed at an alarming rate. With the continuing degradation and destruction of mangroves, there is a critical need to understand them better. Also, in recent years, there has been increasing concern regarding pollution levels in these environments. With this in mind, this study aims to determine the distribution of various metals (Fe, Mn, Cu, Pb, Co, Ni, Zn, Cr, Al, Ca and V) in mudflat and mangrove sediments. The aims of the study are to (1) understand the dynamics of geochemical processes that govern the behaviour and fate of metals in estuarine subenvironments, and (2) identify the different factors responsible for the variability of metal concentrations in the sediments.

2. Materials and methods

2.1. *Study area*

The city of Mumbai is an elongated trapezoidal area lying between 18°55′N and 19°20′N latitudes and 72°45′E and 73°00′E longitudes. This mainland has at its northern end the Ulhas River, on the south-eastern end Thane Creek and on the west the Arabian Sea. Ulhas River, ∼–135 km long, rises in the rainy ravines of the Bhor Ghat and reaches the Arabian Sea at Vasai creek [12]. The river is shallow with a sandy basin, because the land run-off carries huge amounts of sediments from its catchment area. Extensive mudflats and mangroves are formed along both estuarine banks. During the dry season, barrages constructed upstream of the estuary and its associated tributaries allow only a limited river discharge to flow. Several industrial complexes located upstream in the Mumbra–Ambarnath segment release wastewater into the estuary either directly or indirectly. The estuarine flushing time varies between 73 and 211 tidal cycles [13] during the dry season (October to May), which suggests that there might be a possibility of contaminant build-up inside the estuary. However, the estuary is well flushed during the monsoon season.

Extending from Ulhas River to the head of Mumbai harbour bay is Thane Creek. The creek is fringed with mangroves along both banks, coupled with heavy industrialisation and urbanisation. Geologically, the Mumbai–Thane region is part of the Deccan trap that was formed by volcanic effusions at the end of the Cretaceous period [14]. The subsurface geology consists of three sedimentary units overlying the acoustic basement, mainly representing the seaward extension of the deccan traps. The top 2.5-3.0m thick sedimentary layer is relatively modern being deposited during the past 600–700 years [15]. The creek is narrow and shallow at the riverine end and broader and deeper towards the sea. It receives ∼ 294 million litres per day (mld) of industrial waste and 145–260 mld of domestic waste within the Thane city limits [16]; this waste includes chemical, textile, pharmaceutical, engineering and major fertiliser complexes [17].

2.2. *Sampling and analyses*

In September 2008, sediment cores were collected from intertidal regions along the south-east and northern part of Mumbai, as shown in Figure 1. The latitudes, longitudes and core lengths (cm) of each sampling site are given in Table 1. Representing the upper portion of the creek and the middle portion of the estuary, a mudflat and a mangrove core were collected from each location,

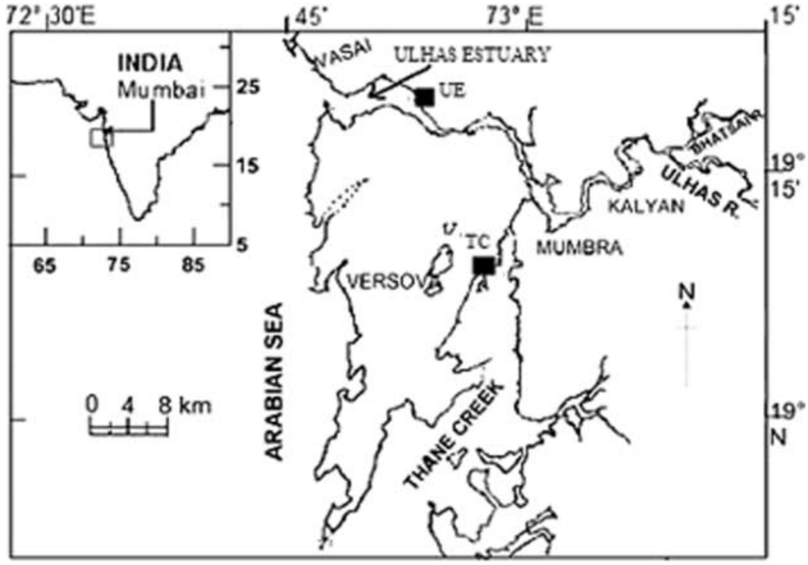

Figure 1. Map showing the sampling locations.

Table 1. Latitudes and longitudes of sampling stations.

Station		Latitude	Longitude	Core length (cm)
Thane creek	Mudflat	19°09′10.5″N	72°58′0.5″E	28
	Mangrove			34
Ulhas estuary	Mudflat	19°19′43.4″N	72°52′43.3″E	28
	Mangrove			58

maintaining a distance of $\sim$ 50 m between the subenvironments. Core samples were collected 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 then retrieved. The core length varied between the sites due to variations in the nature of the substratum. GPS was used to determine the geographical coordinates.

In the laboratory, each core was subsampled at 2cm intervals, transferred to a labelled polyethylene bag, pH values were determined using a pH meter (Thermo Orion 420 A+ model) and the sample was stored at 4 °C until further analysis. For sedimentological and geochemical parameters, the sediment samples were oven-dried at 60 °C. Sediment component analysis was performed using the sieving technique according to Folk [18]. Total organic carbon (TOC) was estimated using chromic acid digestion followed by back-titration with ferrous ammonium sulfate [19]. A standard procedure [20] was used to measure the total phosphorus (TP) and total nitrogen (TN) in the sediment. TP was measured using the ascorbic acid–molybdenum blue method, whereas TN was determined as an azo dye complex. Using a standard calibration curve, the values of phosphorus and nitrogen were calculated by a double-beam UV–Vis spectrophotometer, with absorbance readings taken at 880 and 540 nm, respectively. To determine the presence of metals (Fe, Mn, Cu, Pb, Co, Ni, Zn, Cr, Al, Ca and V), the sediment was digested using an acid mixture of $HF/HNO_3/HClO_4$ (7:3:1) in an open digestion system as described by Jarvis and Jarvis [21]. The samples were then run using a Varian AA-240FS flame atomic absorption spectrometry (AAS) following calibration with suitable Merck elemental standards. A recalibration check was performed at regular intervals. Together with the samples, a certified reference standard from the Canadian National Bureau of Standards (BCSS-1) was digested and run to test the analytical and instrument accuracy of the method. The recoveries were between: 86 and 91% for Fe, Cu, Ni and Al; 87 and 92% for Mn and Co; 80 and 85% for Pb and Zn; 90 and 95% for Cr; and 82 and 90% for V and Ca, with a precision of +6%.

2.3. *Statistical analysis*

Statistical procedures are used to make inferences about the important pathways of elemental deposition [22]. Pearson's correlation coefficient matrix and cluster analysis were employed to study the interrelationship among the chemical elements, organic matter and the sediment components. Factor analysis was also carried out to identify relatively homogeneous groups of metals with similar properties. Prior to the analysis, the data were standardised to produce a normal distribution of all variables, because the studied parameters had different magnitudes and scales of measurements, which would have given more weight to certain variables if not taken into account. All statistical analyses were carried out using the software package STATISTICA 6.0.

3. Results and discussion

The range and average of textural parameters (sand, silt and clay) as well as other sediment parameters such as pH, organic matter (TOC, TP, TN) of the four sediment cores are presented in Table 2.

3.1. *Ulhas Estuary*

The downcore profiles of pH, sediment components along with organic matter are shown in Figure 2. pH shows an overall decreasing trend from the bottom to the surface in the mudflat core, whereas in the mangrove core an initial decrease is followed by an increase in the upper portion of the core. Organic matter, TP and TN in each core show similar increasing and decreasing trends. TOC fluctuates prominently in the mudflat core, whereas in the mangrove core a gradual decrease in TOC is observed from the bottom to the surface. The sediments in the area are found to be composed mainly of clayey silt. The percentage of sand fluctuates, whereas silt and clay show more constant trends along the length of the mudflat core with slight variation at the bottom. For the mangrove core, the sand component exhibits a constant trend, whereas silt and clay show minor fluctuations at the bottom and surface.

Plots of the concentrations of selected metals with depth are shown in Figure 3. In the mudflat core, and based on the vertical distribution patterns, Fe, Mn, Cu, Al, Ca and V increase from the

Table 2. Sediment components and organic matter for mudflat and mangrove regions of Ulhas Estuary and Thane Creek.

	Ulhas Estuary				Thane Creek			
	Mudflat		Mangrove		Mudflat		Mangrove	
Variables	Range	Average	Range	Average	Range	Average	Range	Average
pH	7.28–8.10	7.72	6.98–7.95	7.43	7.44–8.19	7.77	7.42–8.11	7.77
TOC (%)	0.69–1.43	0.87	0.25–1.84	0.89	0.76–2.35	1.65	1.34–1.89	1.67
TP ($mg \cdot g^{-1}$)	0.30–1.52	0.41	0.31–0.61	0.43	0.24–0.40	0.33	0.2–0.99	0.56
TN ($mg \cdot g^{-1}$)	0.18–1.48	0.80	0.33–0.87	0.54	0.35–0.82	0.53	0.26–0.60	0.47
C/N	5–21	12	5–30	17	17–50	32.21	18–34	26
Sand (%)	0.33–2.99	1.88	0.05 – 2.13	0.34	0.25–2.52	1.16	0.96–5.96	1.94
Silt (%)	25–43	30	15–54	27	25–44	33.48	19.92–54	33.91
Clay (%)	55–73	68	46–85	73	55–74	65	44–79	64

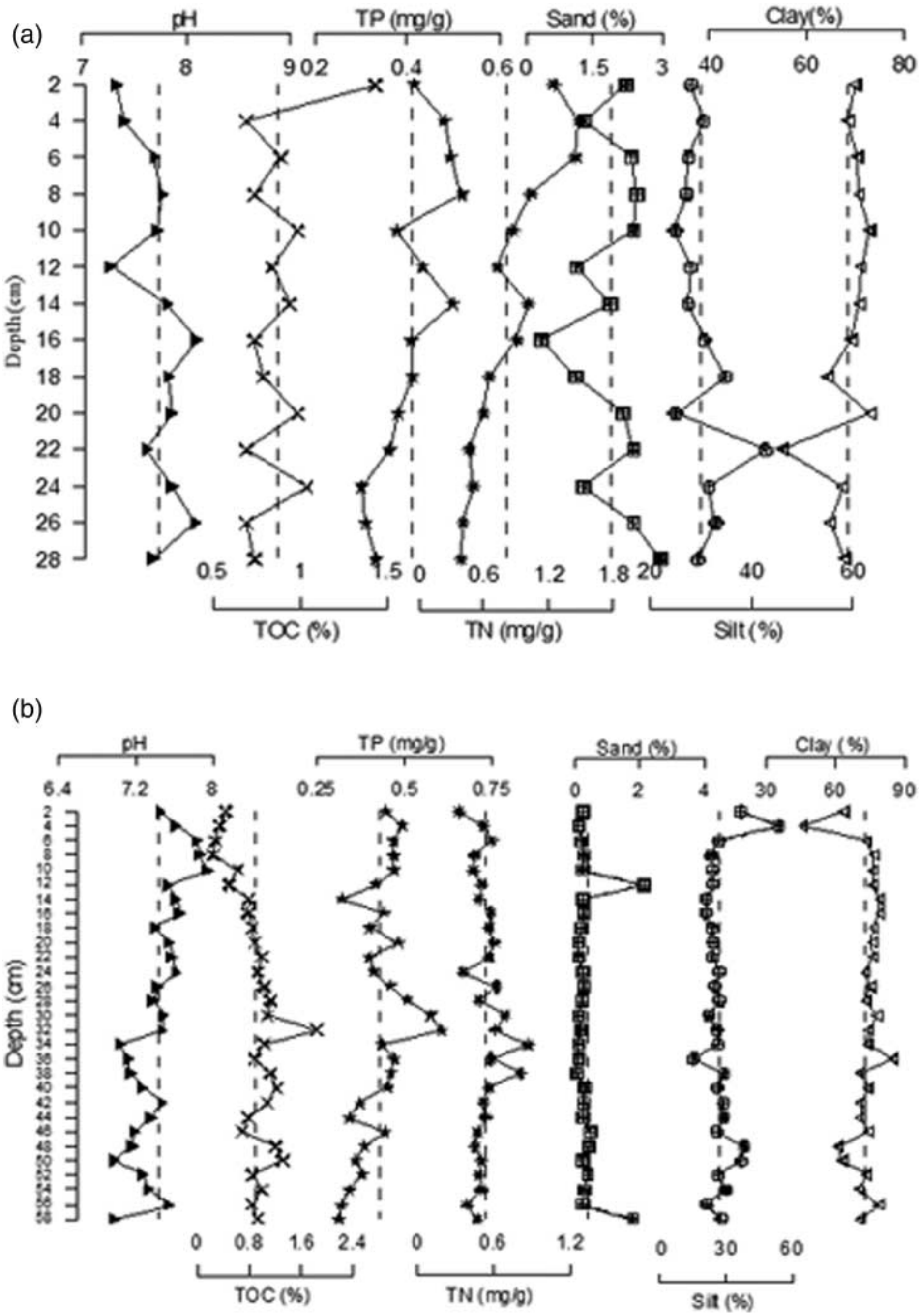

Figure 2. Downcore variations in pH, TP, TN, TOC and sediment components with vertical average lines in Ulhas mudflat core (a) and mangrove core (b).

bottom to the surface, whereas the remaining elements, after an initial decrease at the bottom, increase in the upper few cm of the core. In the mangrove core, after an initial decrease at the bottom, Fe, Mn and V increase, whereas Cu, Zn, Cr and Ca increase from the bottom to the surface. Pb along with Al is constant, with minor fluctuations in the middle portion of the core. Co and Ni decrease at the bottom, then exhibit fluctuating increases and decreases throughout the core.

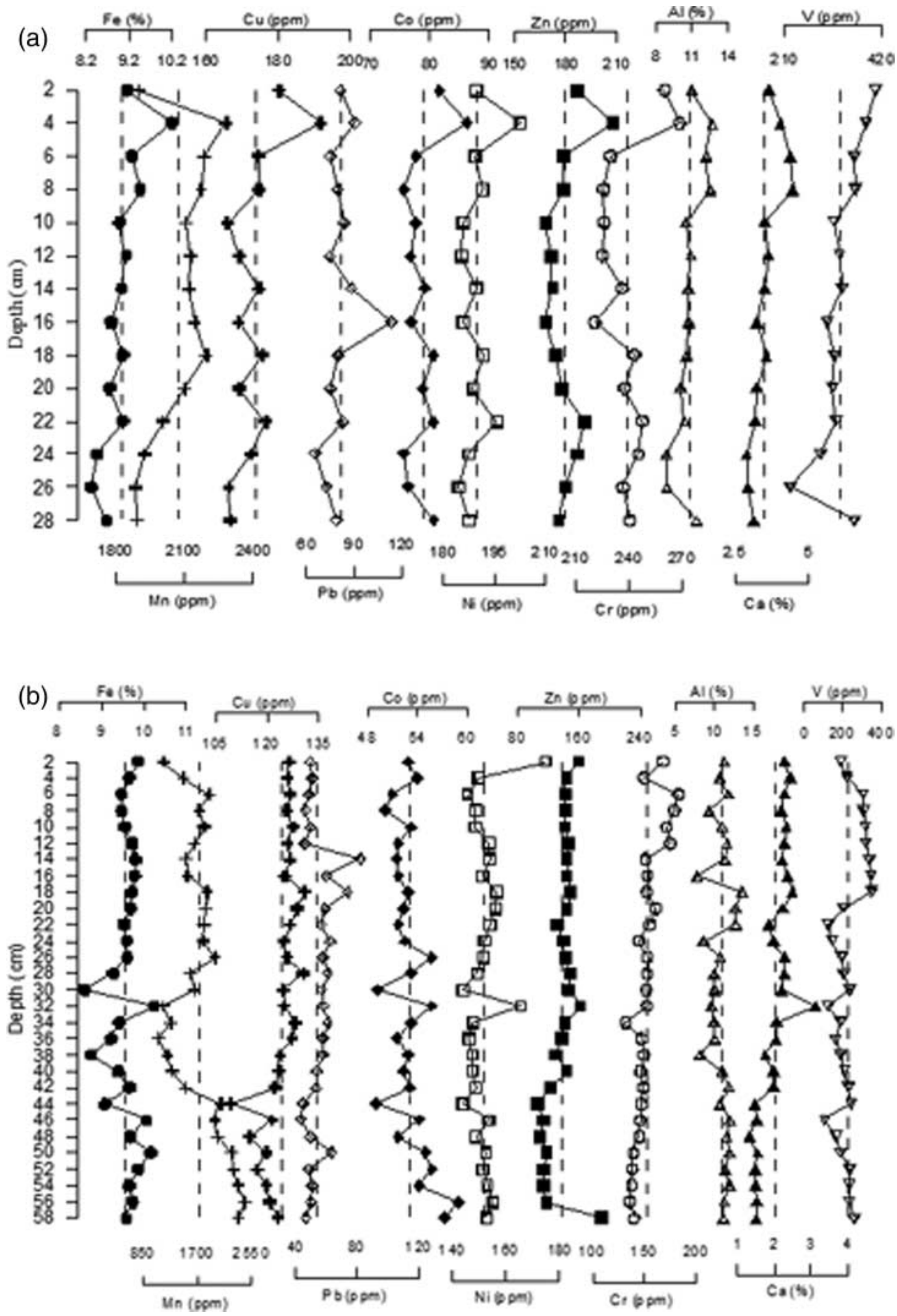

Figure 3. Downcore variation in metals with vertical average lines in Ulhas mudflat core (a) and mangrove core (b).

3.2. *Thane Creek*

Figure 4 shows the vertical distribution patterns of pH, sediment components and organic matter for Thane region. In both the cores, pH exhibits opposing trends, i.e. in the mudflat core it shows

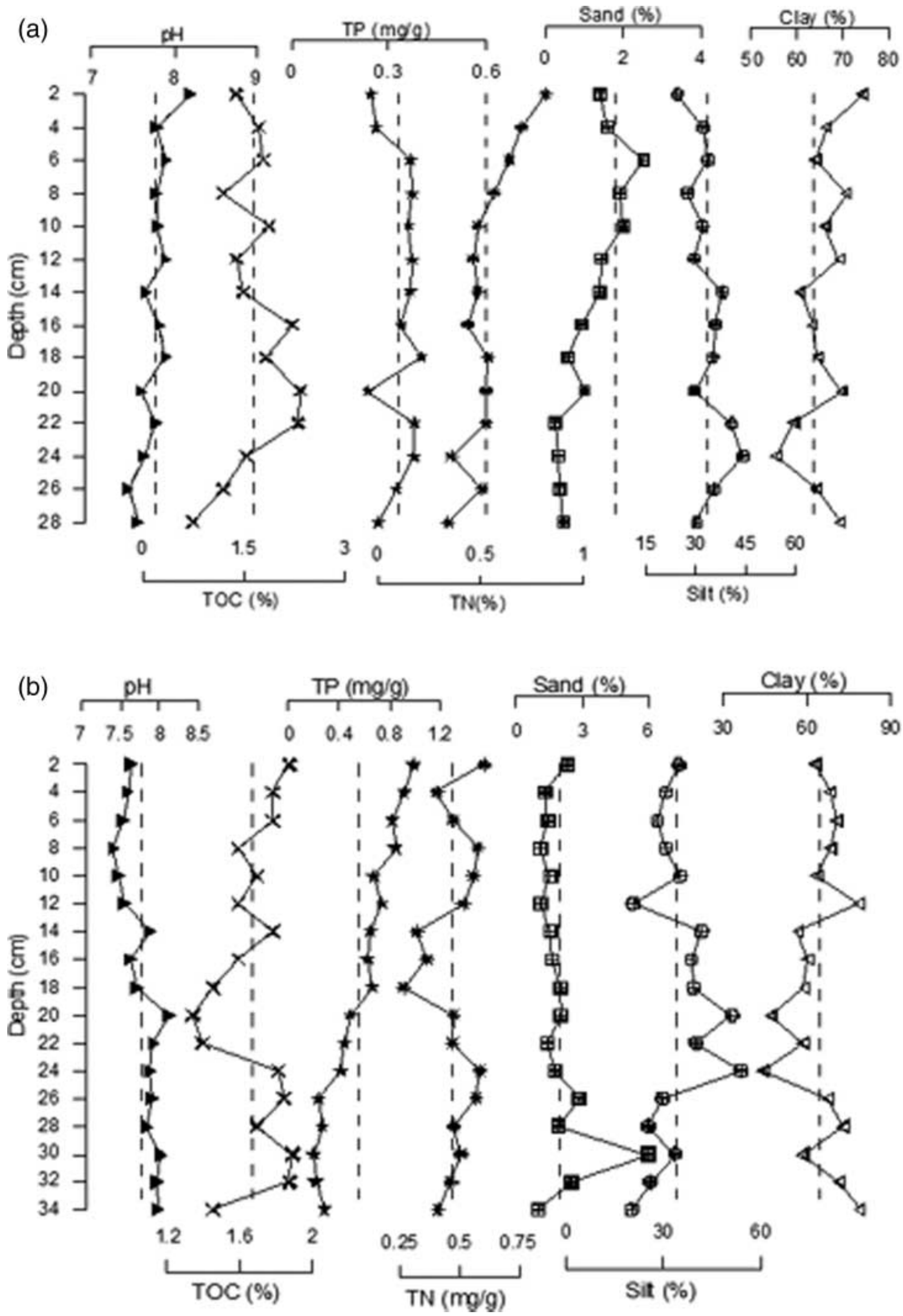

Figure 4. Downcore variations in pH, TP, TN, TOC and sediment components with vertical average lines in Thane mudflat core (a) and mangrove core (b).

an increase, whereas in the mangrove core a decrease is seen from the bottom to surface. An increase in TOC from the bottom to 20 cm depth is followed by a decrease towards the surface in the mudflat core, whereas in the mangrove core, TOC is found to increase at the surface after a decrease at the bottom. In the mudflat core, TP initially increases from the bottom to 22 cm depth, then decreases towards the surface, whereas TN increases gradually from the bottom to the surface. In the mangrove core, TP shows a uniform increase from the bottom to the surface, whereas TN fluctuates with increases and decreases along the length of the core. In the sediment components, the silt and clay fractions show alternate increases and decreases trends from the bottom to the surface in both the cores. Sand exhibits an increase from the bottom to 6 cm depth, followed by a decrease to the surface in the mudflat core, whereas a more stable trend with an increased peak at the bottom is seen in the mangrove core.

The distribution trends of the metals studied are shown in Figure 5. In the mudflat core, Fe and Mn show alternate increases and decreases from the bottom to the surface. Cu shows an overall decrease, whereas Pb increases gradually from the bottom to surface. However, Co shows a decrease from the bottom to the surface, Ni, Zn and Cr exhibit an increase, whereas V does not show any appreciable change in its concentration over the entire length of the core, except in the middle portion where an increase is observed. Al and Ca show similar increasing and decreasing trends from the bottom to 14 cm depth, whereas above 14 cm to the surface the opposite trend is seen for both elements. In the mangrove core, Fe, Mn and Ca show an overall increase, Cu and Pb exhibit similar increases and decreases, whereas Co, Ni and Al show a general decrease from the bottom to the surface of the core. After an initial decrease at the bottom, Zn increases towards the surface, whereas Cr increases from the bottom to 28 cm and then decreases to the surface. V increases from the bottom to 12 cm, whereas above 12 cm a decrease is observed.

3.3. *Comparison between intra- and intersites*

When the distributions of the different sediment parameters are analysed at each site, in Ulhas Estuary, both subenvironments show mixed behaviour with respect to the accumulation of metals and organic matter, as well as in the distribution of sediment components. Here, the mudflat region is found to be dominated by higher values of TN, sand and silt among the sediment components, along with all the metals studied except Fe and Al which are found to be higher in the mangrove area. In the case of Thane Creek, overall higher concentrations of all the studied geochemical parameters except TN, clay, Mn and Ca are noted in the mangrove core compared with the mudflat core. According to Clark *et al.* [23], mangrove roots create a baffle that promotes the accumulation of fine grained organic matter-rich sediments which act as a sink for trace metals. Further, due to the decomposition of organic matter and depletion of oxygen, the sediments become anoxic and the metals present are converted to sulfides and become fixed in the sediments in a highly insoluble form [24]. It is interesting to note that the distribution pattern of TP in the mangrove sediments of Thane Creek is almost identical to that of Fe and Mn, whereas no such relationship is seen in its mudflat core. The behaviour of TP must be controlled by Fe [25,26] and also Mn in this region, possibly due to the process of diagenesis.

When both the sites are compared, Thane mudflat and mangrove regions are found to have comparatively higher amounts of organic matter, except for the low TOC in mudflat core, compared with the corresponding Ulhas mangrove and mudflat cores. The source of organic matter to the creek must be of terrestrial origin, as seen from the high C/N ratio (Table 2). In recent years due to faster industrialisation, there has been a rapid growth of residential areas around the creek ensuing a high disposal rate of domestic waste in the creek. In addition, at the confluence of Thane Creek and Ulhas River, the basin of the creek is narrow (Figure 1) and the geomorphology is such that during low tides the water from the creek is prevented from being disposed of effectively in the Ulhas River. This contributes to a reduction in the overall flushing capacity of the creek, thereby increasing the accumulation time and rate of discharge of wastes into the creek. Furthermore, in Thane Creek, although the amount of organic matter is comparatively high, metal loads are quite low. This observation implies that the creek might be acting like a passive link and not an active

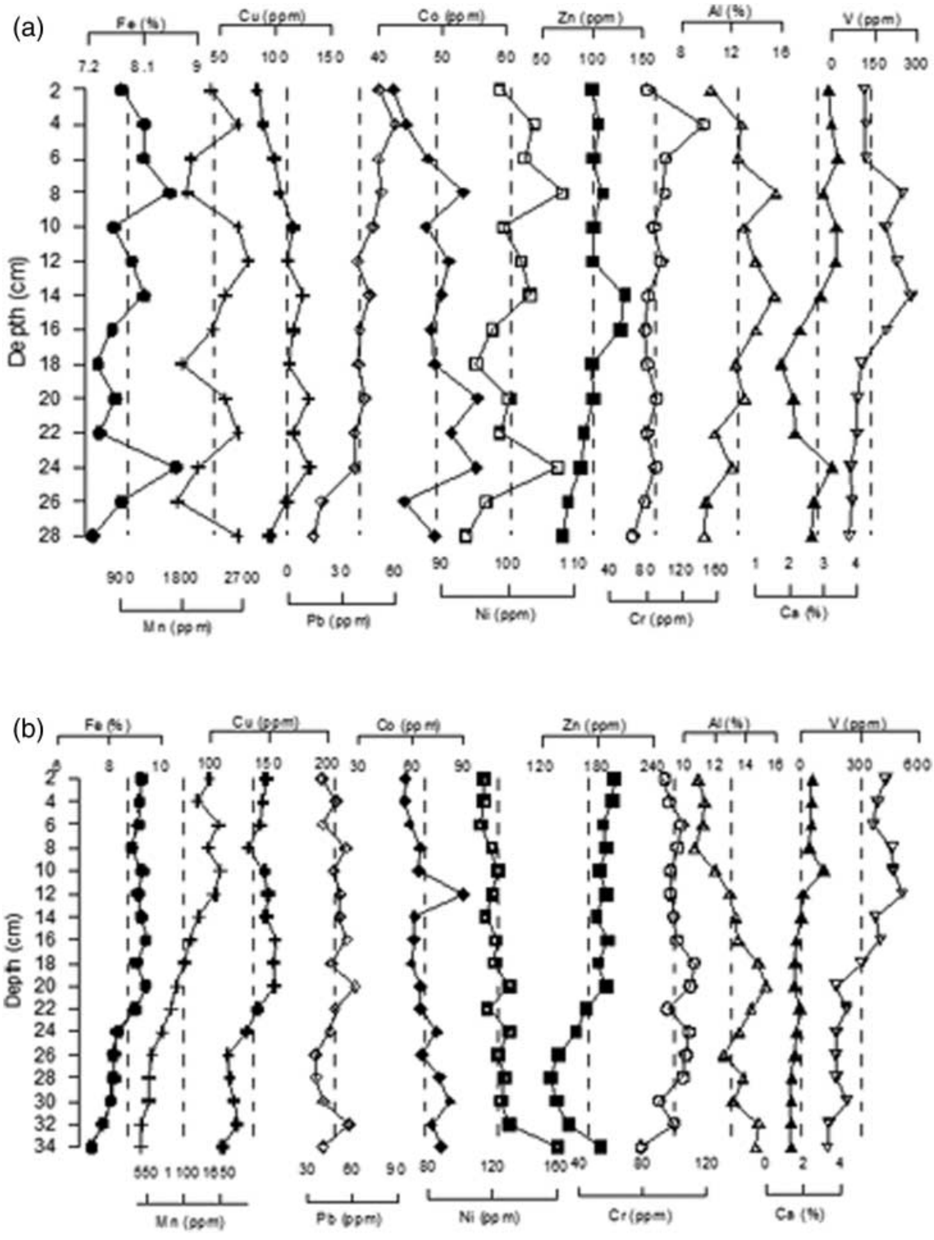

Figure 5. Downcore variation in metals with vertical average lines in Thane mudflat core (a) and mangrove core (b).

trap for metals, as previously suggested by Sharma *et al.* [27]. By contrast, in Ulhas Estuary, a relatively higher concentration of metals and lower concentrations of organic matter are seen in both the mudflat and the mangrove. The low levels of organic matter might be the result of marine sedimentation and mixing processes at the sediment–water interface, where rates of delivery and rates of degradation by microbial-mediated processes can be high [28]. The observed overall elevated concentrations of the elements at this zone may be attributed to multiple factors like particle-size sorting via flocculation and resuspension. Fouling of sediments by frequent dredging activities which are routinely carried out in the estuary to maintain the navigation channel, along with coagulations due to the mixing of salt- and freshwater leading to greater sedimentation in the upper littoral zones, might be one of the potential factors. In light of the above, it may be inferred that the rate of sedimentation in Ulhas Estuary must be relatively high. A previous study carried out by Ram *et al.* [29], reported a higher sedimentation rate of 2.9 $cm \cdot year^{-1}$ in a sediment core collected offshore of Ulhas Estuary compared with 1.46 $cm \cdot year^{-1}$ obtained for Thane Creek [27]. The high sedimentation rate might have resulted in the high metal concentrations observed in Ulhas Estuary.

Further, it is seen that in Ulhas mudflat and Thane mangrove, the cores show a decrease in pH from the bottom to the surface. The gradual accumulation of detritus from the overlying water column, coupled with the slow decomposition of organic matter results in anoxic conditions, which might have resulted in the production of organic acids [30]. In the case of metals, the percentage of Fe is higher in mangrove sediments at both the sites than in mudflat sediments. Ramanathan *et al.* [31], reported a high concentration of Fe in mangrove sediments and this was accounted for by textural and mineralogical characteristics of the mangrove sediments. Similar observations were also made by Ray *et al.* [32] and Marchand *et al.* [33]. All the metals studied are found to be higher in the estuary than in the creek, indicating the estuary to be more vulnerable in terms of metal accumulation, possibly due to the higher clay percentage. Clays have high specific surface area and can directly trap heavy metals; they may also act as a substrate for organic matter flocculation [34] which in turn adsorbs metals. Also, the horizontal salinity gradient between the eastern and western segments of the creek is not high [35], suggesting good mixing across the bay. The salinity in the creek region is higher than in the Ulhas Estuary [36]. Physical mixing of fluvial and marine particulates leads to a continous decrease in trace element concentrations in the particulate matter with increasing salinity [37]. The concentration of Mn is high in all the studied cores, except for the Thane mangrove core. The relative low concentration of Mn might be due to diagenetic Mn reduction and its subsequent diffusion into the overlying waters [38]. The distribution patterns of Ca show similar trends in all the studied cores, i.e. Ca dissolution is seen in all four cores, resulting in higher concentrations in the upper sediments, rapidly decreasing to low constant values at depth, indicating a higher marine influence in recent years. However, in the Thane mudflat core the Ca concentration is found to increase below 18 cm depth. This may be because with the burial and continued reduction of sulfate ions, alkalinity tends to increase with depth allowing $CaCO_3$ to reprecipitate [39].

A comparison of metal concentraions from this study with Indian river/estuary and some world river/estuary values is given in Table 3, and reveals that the average concentrations of most metals in the Ulhas Estuary (Fe, Mn, Cu, Pb, Co, Ni, Zn and Cr) are several magnitudes higher than the average for world and Indian water bodies, except for Manori Creek which exhibits higher values for some elements. Average values of Mn in Mahanadi River and Ulhas Estuary and V in Godavari River and Ulhas Estuary are comparable.

3.4. *Correlation coefficients*

To discover metal associations with different carrier phases in the sediment of the study site, correlation analysis was carried out. In the case of Ulhas Estuary, when the correlations between the different variables are studied, it is observed that in the mudflat core (Table 4), TN exhibits strong correlations with TP, clay and almost all the metals. In an environment rich in organic matter it is possible to experience both the deposition and remobilisation of trace metals, through sulfide formation, adsorption, redox-sensitive metals, formation of organic complexes and biological degradation [40]. Sediment components associate negatively or show weaker correlations with all the studied variables. Strong correlations are seen between Fe and Mn and also towards all the metals, which suggest that they may be acting as a controlling factor in the precipitation and

Table 3. Comparison of metal concentrations in the study area with sediment from world and Indian water bodies.

Location	Fe (%)	Mn (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Co (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	V (mg/kg)	Ref
Ribeira Bay (Brazil)	4.08	469	14	–	–	45	113	72	87	[57]
Haraz River (Caspian Sea basin)	1.5	–	31.38	27	13	44	81.5	22.38	–	[58]
Saros Gulf (Aegean Sea)	1.33–4.04	351–4718	11.9–42.4	3.9–48.2	–	46.5–152	48.7–117	18.8–216	–	[59]
Mahanadi river (India)	5.6	2020	57	60	–	9	125	15	–	[60]
Godavari river (India)	6	1060	73	13	50	52	53	126	310	[61]
Manori creek (India)	12	1020	167	95	40	65	221	203	259	[62]
Hugli estuary (India)	–	502	19	29	14	27	80	50	–	[63]
Thane Creek	7.83	2290	110	41	49	101	100	90	141	This study
Ulhas Estuary	9.02	2077	173	82	79	190	180	239	331	This study

redistribution of the other elements. All the studied elements show a high degree of correlation with each other, indicating their identical behaviour during transport in the estuarine environment. In the mangrove core (Table 4), pH correlates with Cr, Ca and V, and TP correlates with Cu, Cr and Ca, whereas TOC and TN show weak or negative correlations with all the variables studied. Sediment component correlations are also very weak. Therefore, the textural characteristics of the sediments are not found to play a significant role in the distribution of metals and nutrients in the estuary. There are good associations of Fe with Co, Ni and Al, and Mn with Co and Al. Interelemental associations are found to be very weak which suggests that the metals might come from varied sources. The above variations in metals with respect to carrier phase (clay, organic carbon, silt and Fe) are indicative of a basic shift in the geochemical properties on moving from the mudflat to the mangrove region.

In the Thane mudflat core (Table 5), pH correlates well with Pb, whereas sand is found to show associations with almost all the metals except for Cu and Co, and to a lesser extent with Mn. This indicates that the finer grain size effect does not exclusively control the distribution of metals. This might be because, depending on the different environmental conditions, there could be shifts in preferences of metals onto adsorption sites (e.g. organic matter, Fe-Mn oxides etc.) before sedimentation. TOC correlates with silt, Cu, Pb and Zn, TP correlates with silt, Cu, Al and V, whereas TN correlates well with Pb and to a lesser extent with Cr. The grain size distribution and organic matter content are two critical factors that influence metal distribution in sediments [41,42]. The redox-sensitive element, Fe, is found to correlate well with all the metals, whereas Mn exhibits weak or negative associations with all the metals which suggest that Mn oxide may be only a minor host phase for these elements in the creek environment. When interelemental associations are seen, all the metals except for Cr and Ca show good correlations with each other which indicates that they might be discharged from the same source or have similar post-depositional activities. When the correlation matrix for the mangrove core is seen (Table 5), pH is found to associate well with Ni and Al, whereas TP associates well with most of the elements except Co, Ni and Al with which it shows negative correlations. TOC, along with TN, shows negative or poor associations with almost all the studied elements indicating that TOC and TN are not acting as metal concentrators in these sediments. Among the sediment components, sand and clay show weaker or negative associations with all the studied variables, whereas silt shows good

Table 4. Correlation coefficient matrix for metals in sediments from the Ulhas Estuary.

	pH	TOC	TP	TN	Sand	Silt	Clay	Fe	Mn	Cu	Pb	Co	Ni	Zn	Cr	Al	Ca
Mudflat ($n = 14$)																	
TOC	−0.32	1.00															
TP	−0.31	−0.01	1.00														
TN	−0.42	0.25	**0.81**	1.00													
Sand	−0.10	0.09	−0.11	−0.18	1.00												
Silt	0.09	−0.42	−0.36	−0.37	−0.10	1.00											
Clay	−0.07	0.41	0.38	0.40	−0.05	**−0.99**	1.00										
Fe	**−0.61**	−0.10	**0.77**	**0.78**	−0.11	−0.09	0.11	1.00									
Mn	−0.11	−0.32	**0.75**	**0.59**	−0.43	−0.20	0.27	**0.72**	1.00								
Cu	−0.50	0.04	0.50	**0.66**	−0.19	0.21	−0.19	**0.82**	0.42	1.00							
Pb	0.18	−0.24	0.33	0.35	−0.47	0.04	0.03	0.27	0.41	0.15	1.00						
Co	**−0.54**	0.03	0.18	0.35	0.04	0.21	−0.22	**0.62**	0.21	**0.74**	0.22	1.00					
Ni	−0.37	−0.23	0.38	0.43	−0.02	0.36	−0.36	**0.77**	0.43	**0.90**	0.16	**0.78**	1.00				
Zn	−0.42	−0.05	0.02	0.25	0.05	0.38	−0.39	0.53	0.03	**0.81**	−0.15	**0.65**	**0.82**	1.00			
Cr	−0.44	0.24	−0.09	0.17	0.07	0.31	−0.33	0.38	−0.15	**0.76**	−0.13	**0.81**	**0.72**	**0.85**	1.00		
Al	−0.48	−0.18	**0.79**	**0.73**	0.11	−0.26	0.24	**0.85**	**0.62**	**0.54**	0.31	0.44	0.52	0.23	0.08	1.00	
Ca	−0.39	0.00	**0.89**	**0.81**	0.08	−0.37	0.36	**0.79**	**0.68**	0.48	0.08	0.16	0.37	0.12	−0.06	**0.86**	1.00
V	**−0.72**	0.33	**0.62**	**0.68**	0.17	−0.27	0.24	**0.74**	0.31	**0.62**	0.15	**0.62**	0.51	0.33	0.39	**0.81**	**0.65**
Mangrove ($n = 29$)																	
TOC	**−0.51**	1.00															
TP	0.26	0.13	1.00														
TN	−0.31	0.24	0.28	1.00													
Sand	−0.09	−0.20	−0.23	−0.16	1.00												
Silt	−0.15	−0.09	−0.02	−0.15	−0.13	1.00											
Clay	0.15	0.11	0.04	0.16	0.04	**−1.00**	1.00										
Fe	0.01	0.07	−0.21	**−0.50**	0.13	0.17	−0.19	1.00									
Mn	−0.23	0.01	**−0.65**	−0.31	0.22	0.00	−0.02	0.19	1.00								
Cu	0.34	−0.17	**0.47**	0.17	−0.04	−0.26	0.26	−0.03	**−0.45**	1.00							
Pb	−0.02	0.32	−0.01	0.21	−0.33	−0.20	0.23	0.05	−0.27	**0.46**	1.00						
Co	−0.29	0.29	−0.26	−0.22	0.09	0.12	−0.13	**0.54**	**0.56**	−0.05	−0.03	1.00					
Ni	0.04	0.06	0.04	**−0.41**	0.05	0.13	−0.14	**0.61**	−0.05	0.22	0.11	**0.38**	1.00				
Zn	0.13	−0.04	0.35	0.02	0.26	−0.11	0.09	−0.01	−0.20	**0.65**	0.19	0.08	0.34	1.00			
Cr	**0.71**	**−0.57**	**0.40**	−0.15	0.21	−0.14	0.12	−0.05	**−0.41**	**0.42**	−0.19	**−0.46**	0.11	0.31	1.00		
Al	−0.07	−0.10	**−0.38**	−0.19	0.13	0.08	−0.09	0.37	0.32	−0.03	−0.01	0.13	0.21	−0.18	0.02	1.00	
Ca	**0.51**	−0.02	**0.70**	0.11	−0.06	−0.11	0.12	0.10	**−0.65**	**0.71**	0.34	−0.14	0.32	**0.61**	**0.53**	−0.21	1.00
V	**0.47**	**−0.51**	−0.22	−0.03	0.27	−0.22	0.20	−0.07	0.09	0.18	0.16	−0.23	−0.17	0.20	**0.42**	0.05	0.22

Note: Entries given in bold are significant at $p < 0.05$.

Table 5. Correlation coefficient matrix of metals in sediments of Thane Creek.

	pH	TOC	TP	TN	Sand	Silt	Clay	Fe	Mn	Cu	Pb	Co	Ni	Zn	Cr	Al	Ca
Mudflat ($n = 14$)																	
pH	1.00																
TOC	0.16	1.00															
TP	0.04	0.04	1.00														
TN	**0.66**	0.13	−0.34	1.00													
Sand	0.46	0.01	0.03	0.49	1.00												
Silt	−0.43	0.30	**0.54**	−0.50	−0.49	1.00											
Clay	0.39	−0.32	**−0.58**	0.47	0.38	**−0.99**	1.00										
Fe	−0.02	−0.22	0.22	0.08	0.38	0.14	−0.20	1.00									
Mn	−0.01	−0.03	−0.34	−0.22	0.04	−0.18	0.18	−0.26	1.00								
Cu	−0.49	0.45	0.36	**−0.64**	−0.34	**0.62**	**−0.61**	0.10	−0.10	1.00							
Pb	**0.61**	0.39	0.01	**0.67**	**0.72**	−0.23	0.15	0.46	−0.06	−0.18	1.00						
Co	−0.36	0.23	0.23	**−0.57**	−0.18	0.30	−0.29	0.26	0.09	**0.72**	−0.07	1.00					
Ni	0.06	−0.02	0.22	0.13	0.44	0.12	−0.19	**0.95**	−0.10	0.13	**0.60**	0.37	1.00				
Zn	0.33	0.41	0.18	0.20	0.46	0.01	−0.08	0.28	−0.02	0.21	**0.65**	0.06	0.37	1.00			
Cr	0.16	0.16	−0.13	0.47	0.50	−0.12	0.05	0.52	0.04	−0.26	**0.71**	−0.10	**0.60**	0.25	1.00		
Al	0.07	0.18	0.33	−0.07	0.53	−0.05	−0.02	0.50	−0.02	0.35	**0.55**	0.40	**0.59**	**0.81**	0.34	1.00	
Ca	0.22	−0.41	0.05	0.21	**0.62**	−0.18	0.10	**0.62**	0.17	−0.33	0.33	−0.24	**0.57**	0.01	0.42	0.14	1.00
V	0.23	−0.04	0.36	0.01	**0.56**	−0.21	0.14	0.33	0.11	0.12	0.44	0.09	0.41	**0.77**	0.14	**0.87**	0.28
Mangrove ($n = 17$)																	
TOC	−0.11	1.00															
TP	**−0.79**	−0.02	1.00														
TN	−0.15	0.16	0.23	1.00													
Sand	0.44	0.42	−0.44	0.16	1.00												
Silt	0.27	−0.16	0.05	−0.04	0.08	1.00											
Clay	−0.33	0.08	0.03	−0.01	−0.24	**−0.99**	1.00										
Fe	**−0.52**	−0.22	**0.78**	−0.12	−0.32	0.42	−0.35	1.00									
Mn	**−0.82**	−0.02	**0.85**	0.06	−0.41	0.05	0.01	**0.80**	1.00								
Cu	−0.42	−0.30	**0.72**	−0.30	−0.33	0.45	−0.39	**0.94**	**0.72**	1.00							
Pb	−0.04	−0.39	0.21	−0.23	−0.28	0.33	−0.28	0.41	0.21	**0.54**	1.00						
Co	0.00	−0.07	**−0.49**	0.23	0.22	−0.40	0.38	**−0.49**	−0.34	−0.42	0.05	1.00					
Ni	**0.52**	−0.29	**−0.61**	−0.05	−0.02	−0.19	0.19	**−0.73**	**−0.59**	**−0.58**	−0.08	0.42	1.00				
Zn	−0.45	−0.43	**0.72**	−0.19	**−0.62**	−0.02	0.12	0.48	**0.57**	**0.57**	0.36	−0.31	0.03	1.00			
Cr	−0.06	−0.04	0.06	−0.05	−0.07	**0.50**	−0.47	0.35	0.08	0.32	0.16	−0.25	−0.40	−0.31	1.00		
Al	**0.77**	**−0.49**	**−0.68**	−0.47	0.10	0.24	−0.24	−0.34	**−0.63**	−0.12	0.26	0.31	**0.56**	−0.24	0.10	1.00	
Ca	**−0.79**	0.17	**0.78**	0.34	−0.35	−0.03	0.08	**0.60**	**0.90**	0.46	0.01	−0.40	**−0.52**	0.47	−0.08	**−0.78**	1.00
V	**−0.86**	0.00	**0.73**	0.06	−0.34	−0.19	0.24	**0.59**	**0.87**	**0.51**	0.27	0.00	−0.48	0.47	−0.06	**−0.64**	**0.77**

Note: Entries given in bold are significant at $p < 0.05$.

associations with Fe, Cr and Cu. Good associations are seen for Fe and Mn with Pb, Zn, Cr, Ca and V. Fe–Mn complexes seem to have a strong bearing on the dispersal patterns of other metals in this sedimentary environment and this may be due to their geochemical affinity [43]. In the case of interelemental correlations, Cu seems to be correlated with almost all the metals compared with the other elements. These observations suggest that the mangrove sediments might have the same origin or sources of metals and/or may be influenced by the same factors and processes.

When the correlation results are analysed together for both the studied environments, pH is found to influence the distribution of some metals in both cores of Thane Creek and only the mangrove core of Ulhas Estuary, whereas it exhibits no significance in the Ulhas mudflat core. The association of pH with metals might be due to the changes in the fresh/saline water interaction. The pH value in estuarine sediments is an important factor that regulates the concentration of dissolved metals in water and sediment [44,45]. In the case of organic matter, TP is found to correlate well with all the metals at both the sites compared with TOC and TN. Marine sediments may contain phosphorus either incorporated into organic material or as phosphate ions bound to various sediment components like aluminosilicate minerals and iron and manganese oxides [46]. Significant correlations between Fe and Mn in both the study sites imply its origin from detrital mineral and anthropogenic inputs and incorporation into sediment in the form of iron oxide and hydrous manganese. Fe, Cr and Al show good associations with each other in the mudflat cores of both sites. Chen *et al.* [47] have reported that Cr is similar to Fe and Al in terms of ionic size and geochemical properties, which could account for the good correlations observed. Another important fact observed in the correlation analysis is weaker associations between the metals and the finer sediment fractions, namely silt and clay. This implies that the concentrations of metals in sediments cannot be interpreted simply with a change in grain size. Other physicochemical processes may be involved. The weak or negative correlations of most of the studied metals with Al in both mangrove sites, suggests that they might have come from a source independent of aluminium silicates or that they are not significantly adsorbed by aluminium silicates. Ca must have a marine origin, because biogenic carbonates (especially carbonate shells) are found to constitute an important sediment fraction in the region (Thane Creek). In Thane mudflat and mangrove regions, good interelemental correlations are observed, indicating that the metals were deposited without much geochemical change moving from the mudflat to mangrove region. However, in Ulhas Estuary, only the mudflat core shows such associations. Different processes like biological effects and external inputs operating in the mangrove and adjacent estuarine mudflat sediments may have resulted in the nonsignificant correlations observed among most of the metals studied.

3.5. *Cluster analysis*

In an attempt to further clarify the main controlling factors that determine the distribution of metals in the estuarine and creek systems, cluster analysis was carried out on the entire data set using complete linkage and Eucledian distance. The main purpose of the technique was to reduce the data set and obtain possible relationships between the variables in the samples collected along the Mumbai coast. Cluster analysis examines the distances between the samples in a data set and this is represented as a two-dimensional plot called a dendrogram. Dendogram plots of the two study sites are presented in Figure 6. In Ulhas Estuary, the mudflat and mangrove cores show the formation of three distinct clusters, while in Thane Creek each subenvironment shows two clusters. The dendogram plots are found to mirror the observations seen in correlation analysis. However, the metal associations with the different sediment phases vary at each site. In the case of Ulhas mudflat, silt along with Fe–Mn are found to be the dominant metal carriers, whereas in the mangrove core, Fe–Mn, organic matter and pH are found to contribute significantly to the metal distributions (Figure 6a,b). The presence of organic matter as a metal carrier in the mangrove

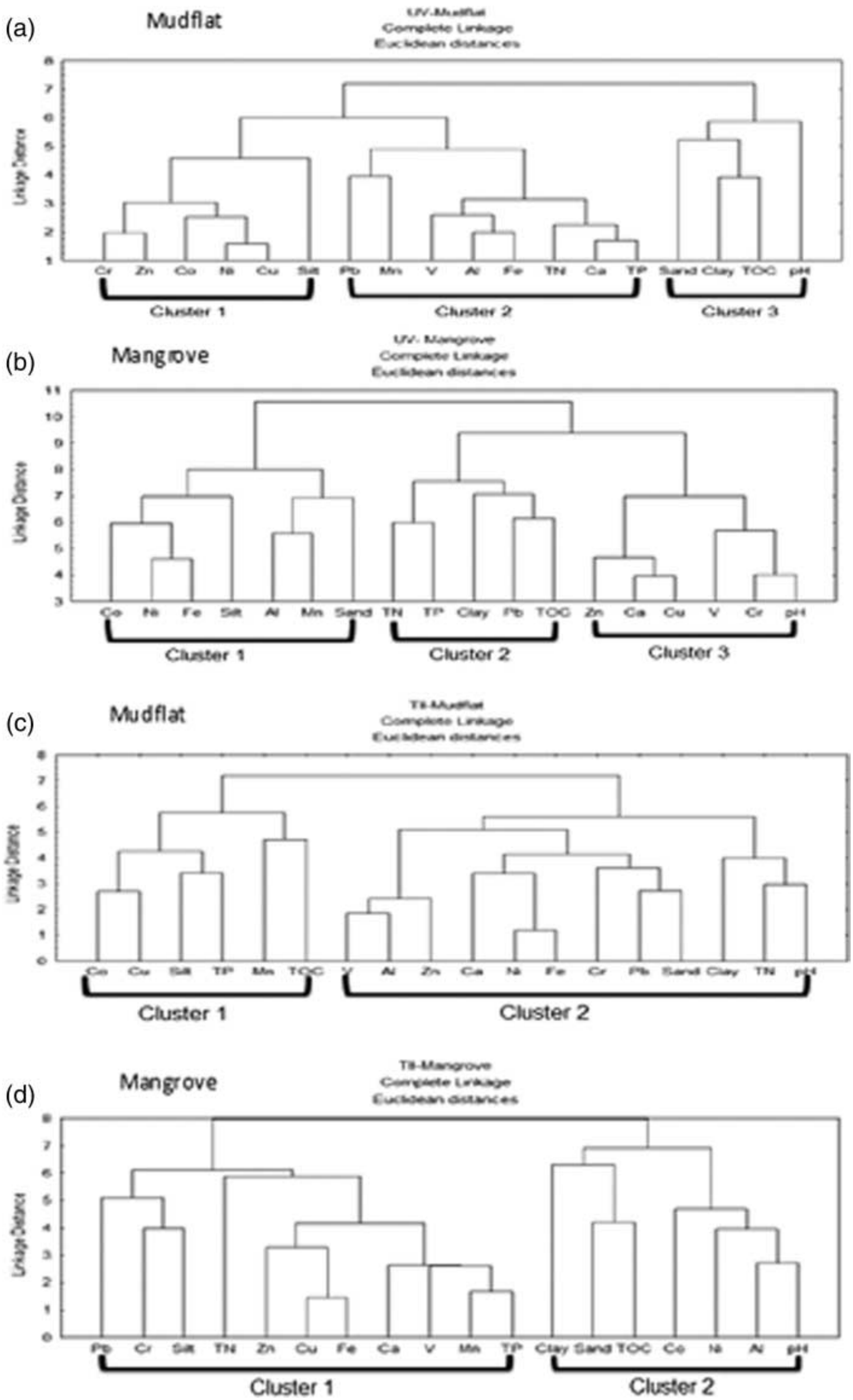

Figure 6. Cluster analysis for Ulhas Estuary (a, b) and Thane Creek (c, d).

core suggests that the metals might have been transported to the mangrove region as organic debris. Further, a change in pH and a reduction in organic matter might be facilitating in trapping metals in the mangrove region. In Thane Creek, Fe–Mn and TOC are observed to be the dominant metal carriers in the mudflat and mangrove regions, respectively (Figure 6c,d). The association of metals with sand in the mudflat core suggests that the metals are preferably attached to the coarser grains and are deposited as coatings. The dwindling vegetation along the banks of the creek due to extensive development, which includes surface quarrying for construction materials, provides a large amount of lithogenic flux into Thane Creek [48]. In general, differences in the area, volume and water retention time of the estuary and creek basins might account for the observed differences in associations among the different variables studied.

On the whole, adsorption and/or coprecipitation with Fe–Mn (hydro-) oxides and organic matter are found to be the main controlling factors responsible for the observed geochemical behaviour of trace metals in the mudflat and mangrove environments at both sites. In the case of Thane Creek, from the cluster plots, the overall distribution and association of metals with the carrier phase are the same in both subenvironments. It can, therefore, be concluded that sediments from the mudflat and mangrove regions have similar chemical characteristics. However, in Ulhas Estuary, different metal associations are observed between the mudflat and mangrove environments. As already mentioned, the Ulhas Estuary is frequently dredged to maintain the navigation channel. The dredging might have resulted in resuspension and sediment mixing, resulting in organic matter diagenesis or remobilisation of Fe–Mn oxides. Resuspension of sediment causes its oxidation, leading to the mobilisation of metals into the water body [49]. These phenomena might have produced the associations of metals with the carrier phases observed in the mudflat region. However, in the Ulhas mangrove, the metal associations with the carrier phase are found to be similar to that of the Thane mangrove. This indicates that sediment deposition must be undisturbed in this region and hence portrays the general processes of metal associations that occur in a mangrove environment. We can summarise that dredging activities in Ulhas Estuary might have masked the actual interpretation of the process of metal association and deposition in the mudflat region.

3.6. *Geoaccumulation index (I_{geo})*

To better estimate the extent of metal load of anthropogenic input in sediments of the study sites, the geoaccumulation index (I_{geo}) was computed. I_{geo} was originally introduced by Muller [50], to determine and define metal contamination in sediments, by comparing current concentrations with the background levels. It can be calculated by the following equation:

$$I_{geo} = \log_2[Cn/(1.5Bn)]$$

where, Cn is the measured concentration of the examined metal 'n' in the sediment, Bn is the geochemical background concentration of the metal 'n', and a factor of 1.5 is used because of possible variations in background values for a given metal in the environment, as well as very small anthropogenic influences. Analysis of our data by simple linear regression resulted in the appearance of frequent statistical outliers. Consequently, we chose to use metal background values. Normally, it is more appropriate to use the background data of the study region than data for average shale to assess the contamination levels of metal. Because of the unavailability of previous heavy metal concentrations in the studied area, these values could not be used as pre-industrial values. Therefore, this study used the mean element concentration given by Turekian and Wedepohl [51] for Indian region background data in line with Bhonsle and Sahu [12] who used the same background values to assess the pollution status of the Mumbai region. Muller [50], described seven classes of geoaccumulation index: unpolluted ($0 \leq I_{geo}$), unpolluted to moderately polluted

Table 6. I_{geo} values for Ulhas and Thane cores.

Stations		I_{geo} class	Elements
Ulhas	Mudflat	1	Fe, Ni, Zn, Cr, V
		2	Mn, Cu, Pb, Co
	Mangrove	1	Fe, Cu, Pb, Co, Ni, Zn, Cr, V
		2	Mn
Thane	Mudflat	1	Fe, Cu, Pb, Co, Ni, Zn, Cr, V
		2	Mn
	Mangrove	1	Fe, Mn, Pb, Ni, Zn, Cr
		2	Cu, Co, V

($0 \leq I_{geo} \leq 1$), moderately polluted ($1 \leq I_{geo} \leq 2$), moderate to strongly polluted ($2 \leq I_{geo} \leq 3$), strongly polluted ($3 \leq I_{geo} \leq 4$), strongly to extremely polluted ($4 \leq I_{geo} \leq 5$) and extremely polluted ($I_{geo} \geq 5$).

In this study, the computed I_{geo} values (Table 6) indicate that the sediments of the Ulhas mudflat core exhibit moderate pollution with respect to Mn, Cu, Pb and Co and are unpolluted to moderately polluted with respect to the remaining elements. The mangrove core is moderately polluted with Mn, and unpolluted to moderately polluted with respect to the remaining elements. A large number of industries and major towns in the basin of Ulhas River discharge wastewater into the estuary [52]. Also, rivers flowing along urban areas bring pollutants downstream, which are incorporated into the sediments of the intertidal regions. This process must have resulted in increased accumulation and higher concentrations of metals in the mangrove and mudflat sediments. In the Thane mudflat core, all the elements except for Mn fall within the unpolluted to moderately polluted class. Mn falls within the moderately polluted class. In the mangrove core, Cu, Co and V fall within the moderately polluted class, whereas the remaining elements fall within unpolluted to moderately polluted class (Table 6). Municipal along with industrial wastewater, fertilisers and herbicides discharged into coastal zones might be important sources of contamination in the region. The potential anthropogenic contributors of Cu are the use of antifouling paints on boats [53], industrial effluent discharge and the input of untreated domestic sewage, because Cu has a preferential association with organic matter [54]. Thus, the two water bodies are found to be different in terms of pollution load of metals. The main reason for the considerable differences between the sites might be, due to the different kinds of pollutant arising from the different industrial and human activities along the Mumbai coast. This may also be due to the dissimilarity in hydrodynamic conditions, sediment texture, organic matter composition and depositional environment between the two sites.

3.7. *Factor analysis*

In order to understand the nature and behaviour of metals in terms of geoaccumulation distribution at the different sites, factor analysis was carried out on the I_{geo} data. Factor analysis is a technique commonly used to analyse geochemical matrices by creating one or more factors, each representing a cluster of interrelated variables within the data set [55]. The identification of metal groups and their interrelations is important for source evaluation [56]. Three factors with eigen values >1 were obtained for all the cores, excluding the Ulhas mudflat core. The loadings between principal factors and metals, as well as the positions of metals in the coordinates of the principal factors, are given in Table 7 and Figure 7, respectively. The maximum amount of total variance observed in the first component at both sites indicates correlations with most of the observed variables. Three metal groups were identified at both sites. The metals in each group are considered to have similar features during transport or to have originated from identical sources (natural or anthropogenic).

Table 7. Factor loadings after a normalised varimax rotation for the three first principal components using I_{geo} values.

	Ulhas						Thane					
	Mudflat			Mangrove			Mudflat			Mangrove		
Variables	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Eigen values	5.19	1.93	0.77	2.67	2.21	1.30	3.81	1.82	1.47	5.24	1.35	1.06
Variance %	57.65	21.49	8.52	29.69	24.63	14.52	42.31	20.19	16.31	58.21	15.00	11.78
Fe	**0.80**	0.54	0.05	−0.11	**0.87**	−0.03	**0.93**	0.17	−0.01	**0.85**	0.26	0.40
Mn	−0.13	**0.88**	0.25	**−0.78**	0.22	0.03	−0.33	0.03	0.53	**0.93**	0.02	0.29
Cu	0.40	**0.89**	0.11	**0.82**	0.14	0.33	−0.06	**0.92**	0.08	**0.73**	0.19	0.59
Pb	−0.01	0.23	**0.96**	0.66	−0.02	−0.26	0.60	−0.10	0.67	0.05	0.11	**0.94**
Co	**0.84**	0.26	0.30	−0.16	**0.76**	−0.32	0.17	**0.91**	0.01	−0.67	−0.19	−0.02
Ni	**0.79**	0.51	0.13	0.29	**0.81**	0.02	**0.91**	0.25	0.21	**−0.81**	−0.40	0.11
Zn	**0.91**	0.13	−0.20	**0.70**	0.22	0.42	0.32	0.10	**0.85**	0.63	−0.37	0.59
Cr	**0.98**	−0.05	−0.08	0.19	−0.08	**0.87**	**0.76**	−0.25	0.29	0.15	**0.94**	0.11
V	0.37	0.66	0.09	−0.09	−0.14	**0.70**	0.24	0.05	**0.84**	**0.86**	−0.16	0.19

Note: Entries in bold are significant at $p < 0.05$.

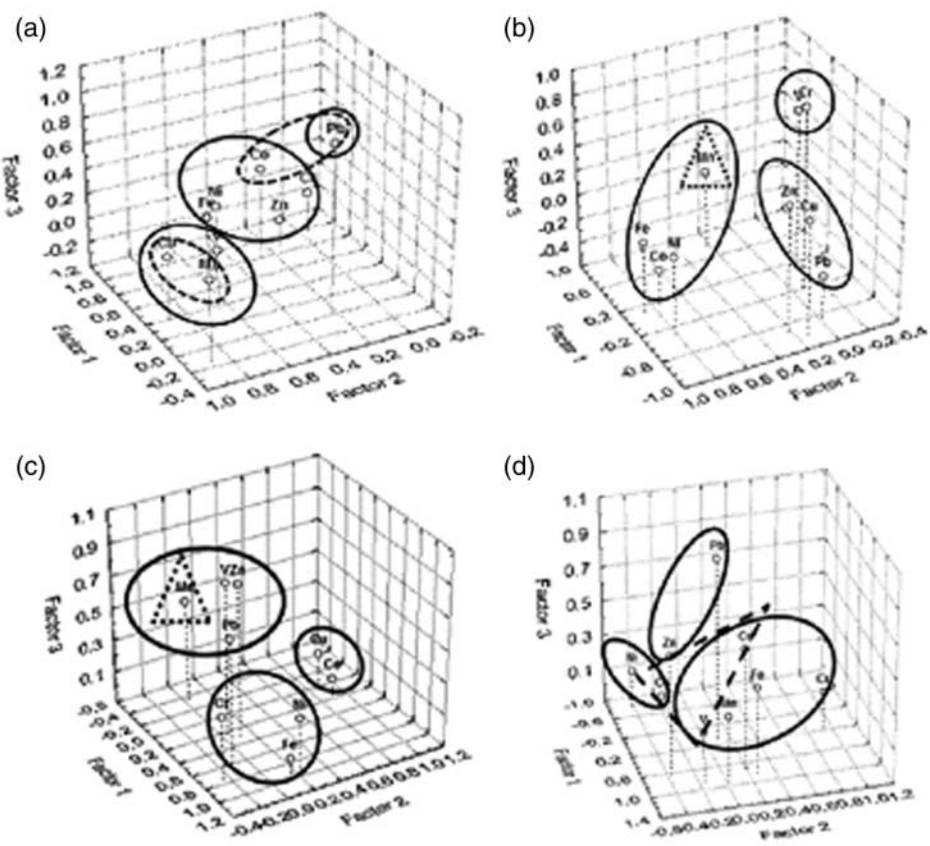

Figure 7

Figure 7. Variations in the coordinates of principal factors (Factor 1 vs. 2 vs. 3) for Ulhas Estuary (a, b) and Thane Creek (c, d).

It is evident from the plots (Figure 7a,b) for the Ulhas Estuary that Mn in the mangrove region is placed differently from the other metals. Similarly, in Thane Creek, Mn in the mudflat region and Cu, Co and V in the mangrove region are farther away from the other metals (Figure 7c,d). The above metals are found to fall within the polluted class for the respective sites (Table 6). However, in the Ulhas mudflat distinct separation of polluted class of metals (Mn, Cu, Pb, Co) is not observed, confirming the complicated behaviour of these pollutants in the region. This may be because the disturbance caused by dredging alters the true pattern of metal associations. The metal groups formed in factor analysis agree well with the observations seen in correlation and cluster analyses. The factor analysis results also confirm the I_{geo} analysis results. This clearly proves that the respective metal carriers seen in correlation and cluster analyses are acting as carriers for the metal deposition at the respective sites, except for the Ulhas mudflat region. Here, sediment disturbance and/or changes in sediment chemistry causes the resuspension of sediment-associated trace metals. This is a serious environmental concern in terms of toxic effects on the aquatic life, as the trace metals accumulated in sediments might be released into the water column and become available to the benthic fauna. This study therefore highlights the need to monitor the Ulhas Estuary, on account of the potential contamination threat by metals through possible remobilisation into the water phase in response to changes in physicochemical conditions.

4. Conclusion

A study carried out on intertidal regions of the Ulhas Estuary and Thane Creek along the Mumbai coast showed different distribution patterns of metals. From the correlation matrix, Fe–Mn oxides and organic matter were found to contribute largely to the metal distribution process. The results indicated that metals in the sediments of both sites were greatly influenced by anthropogenic sources that included the use of fertilisers and herbicides, municipal sewage and industrial effluents. The interelement relationship revealed identical sources of elements in the sediments of the study area, especially in the Thane region. I_{geo} values showed that both regions were moderately polluted by some of the metals. The observation suggested an enhanced rate of human activities coupled with the direct discharge of untreated sewage and effluents from the multifarious industries situated in the upper stretch of the creek and estuary, had resulted in an increase of metal in the coastal region. In addition, there was a risk of secondary water pollution in Ulhas Estuary due to routine dredging which released metals by sediment disturbance and/or changes in sediment chemistry. Factor analysis performed on I_{geo} data helped in identification of the polluted metal groups.

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