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ORIGINAL PAPER

Evaluation of impact of industrial effluents on intertidal sediments of a creek

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Abstract A large amount of material in the form of industrial effluents and urban sewage containing metal contaminants directly enters Dudh creek. Metals on entering the creek tend to settle at the bottom and become part of the sediments. The distribution of metals with depth reflects changes in their supply as well as diagenetic modifications with time. In the present study, an attempt has been made to understand the impact of waste discharged from Tarapur Maharashtra Industrial Development Corporation on Dudh creek. Two cores were collected, one close to the creek mouth and the other in the inner part of the creek. Sediment component, organic carbon and metal (vanadium, copper, nickel, lead, zinc, manganese, iron and aluminium) analyses were carried out on the two cores. The variation in the distribution of sediment components with depth reflects changes in hydrodynamic condition of the creek over the years. Increase in concentration of most of the metals in the upper part of the cores indicates additional input in recent years. The core collected in the inner part of the creek showed higher metal and organic carbon concentration as compared to the downstream core. This was very well supported by distribution of points on an isocon plot. Enrichment factor and index of geoaccumulation were used to find the extent of pollution in sediments of the creek. Correlation and R-mode factor analysis have also been computed to understand the association and source of metal input in sediments of Dudh creek.

Keywords Anthropogenic · Hydrodynamic condition · Isocon plot · Metals · Pollution · Source

Introduction

Creeks are the intertidal regions developed along the coasts and are sites of major port, industrial, urban and recreational activities (Ridgway and Shimmield 2002). As a result, large amounts of contaminants both organic as well as inorganic are being added to the coastal environments (Valette-Silver 1993; Williams et al. 1994; Fianko et al. 2007; Ip et al. 2007). Creeks are low-energy environments and favor deposition of fine-grained sediments along with associated metals and organic matter. In recent years the creeks in western India have been under stress due to enhanced release of material from increasing industrialization and urbanization. In the intertidal region, flocculation occurs due to mixing of freshwater with saline waters, wherein metals from dissolved phase tend to get adsorbed onto suspended clay particles, form a complex with organic compounds or co-precipitate with oxides and hydroxides (Stecko and Bendell-Young, 2000; Liaghati et al. 2003). Due to increase in size of floccules and slackening of flow velocity, metals along with suspended particles settle at the bottom and become part of the sediments. Sondi et al. (1995) have stated that salt-induced flocculation of fine-grained particles was found to be the dominant process that governs the sedimentation pattern of clayey sediments. Further, enrichment of sediments with metals and organic matter of terrestrial origin in the upper estuary is related to salt-induced coagulation of colloidal inorganic and organic

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materials (Sondi et al. 2008). Trace metal enrichment is of major concern because of their toxicity, persistence and the possibility of their entering the food chain.

Creeks are very sensitive to climatic and environmental changes that are recorded effectively in different geochemical phases of sediments. Distribution pattern of particles in sediment cores reflect prevailing hydrodynamic conditions of the past and measurements of metals in sediment cores provide records of historical contamination (Ramesh et al. 2002; Vaalgamma and Conley 2008; Hwang et al. 2009; Ruiz et al. 2009). Earlier studies have shown different levels of pollution or contamination in core samples of the intertidal regions of the east and west coast of India (Achyuthan et al. 2002; Ayyamperumal et al. 2006; Priju and Narayana, 2006; Janaki-Raman et al. 2007; Kwokal et al. 2008; Kumar and Edward 2009; Fernandes et al. 2011).

Kharekuran-Murbe (Dudh) macrotidal creek with a spring and neap tidal range of 5.35 and 2.1 (Swamy et al. 1982), respectively, is located in Thane District of Northern Maharashtra coast (Fig. 1). The freshwater to the creek is supplied by Dudh River. The creek is approximately 23 km long and shows a meandering path from the mouth to the upper limit of tidal influence. The catchment area is underlain by basaltic lava flows that erupted through fissures during the Late Cretaceous Period to the early Eocene Epoch and recent alluvium consisting of sands and clays overly the lava flows (Naik et al. 2007).

Tarapur Maharashtra Industrial Development Corporation (MIDC) with a number of industrial units lies in close proximity to the creek. The wastewater generated from the cities located in the region along with industrial effluent is finally disposed in the creeks (MPCB 2005).

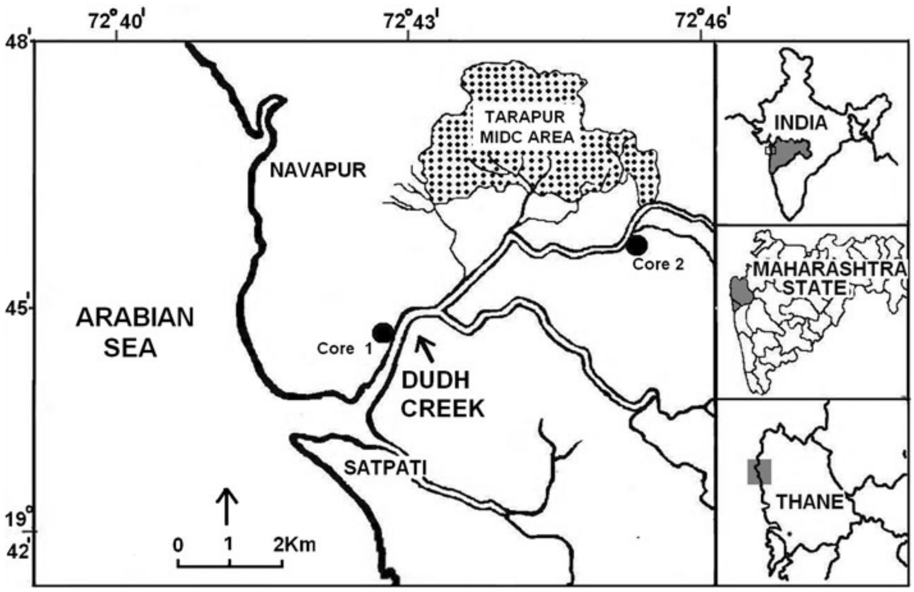
The addition of industrial effluents along with municipal wastes has resulted in the deterioration of water quality of the creek (Naik et al. 2007).

In this study two sediment cores were collected, during field survey carried out from 20th to 29th May 2009, representing the mouth (19°44′ 43.9″N, 72°42′39.6″E) and the inner part (19°46′13.0″N, 72°45′15″E) of Dudh creek. The study was carried out with an objective to understand the variation in distribution of metals in sediments with time and the possible influence of Tarapur MIDC on the creek.

Materials and methods

The two sediment cores representing the mouth and inner part of the creek and having lengths of 56 and 30 cm, respectively, were collected from the intertidal region of Dudh creek with the help of a handheld PVC corer. Sampling was carried out during low tide. The cores were subsampled at 2 cm intervals with the help of a plastic knife to avoid contamination. The sub-samples were then placed in labeled plastic bags, sealed and kept in the ice box. In the laboratory, the sub-samples were dried in an oven at 60 °C. Part of the sample was homogenized with the help of agate mortar and pestle and was used for organic carbon and metal analysis. Sediment granulometric components (sand:silt:clay) were analyzed by wet sieving and pipette method following Folk (1968). The organic carbon was estimated using the method given by Gaudette et al. (1974). This method utilizes exothermic heating and oxidation of the sediment with $K_2Cr_2O_7$ and concentrated H_2SO_4. Excess dichromate is titrated with 0.5 N $Fe(NH_4)_2SO_46H_2O$ solution to a sharp one drop end point. For total

Fig. 1 Location of core samples collected from Kharekuran-Murbe (Dudh) creek, Maharashtra



decomposition of sediments, 0.3 g of finely powdered sediment sample was digested in open Teflon beaker. 10 ml of 7:3:1 acid mixture of HF, HNO_3 and $HClO_4$ was added to sample, kept overnight and later dried on hot plate (at 70 °C). Again 5 ml of the above acid mixture was added to the beaker and dried for 1 h in order to ensure complete digestion of the sediment. To this 2 ml of concentrated HCl was added and dried completely. To the dried sample 10 ml of 1:1 HNO_3 was added and warmed for few minutes. The solution was then made to 100 ml using Milli Q water and was then stored in pre-cleaned plastic bottle. The solutions obtained for all the sediment samples were then aspirated into the flame of atomic absorption spectrophotometer (Varian AA240FS) for the analyses of metals viz. vanadium (V), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), manganese (Mn), iron (Fe) and aluminium (Al). Care was taken to avoid contamination at every step for all the parameters studied. All the reagents used for this study were of analytical grade. Reagent blanks without sample and certified reference standard from the Canadian National Bureau of Standards (BCSS-1) were also treated following the above-mentioned procedure and analyzed along with the sample solutions. Reagent blanks indicated absence of contamination for all the metals studied. The accuracy of the analytical procedure was assessed using certified standard reference material (BCSS-1). Accuracy was ±5 % for Mn and V, ±6 % for Fe, Cu, Ni and Al, ±9 % for Zn and Pb. The atomic absorption spectrophotometer (AA240FS) was standardized by calibration curve method before analyzing the samples for metal concentration. The calibration standards of different concentrations were prepared for all the metals from the stock solutions (1,000 mg/l). Reproducibility of the instrument was checked by analyzing duplicate random samples. The precision obtained for the metals is as follows: Fe 2.19 %, Mn 3.04 %, Al 3.24 %, V 2.33 %, Cu 2.75 %, Ni 2.89 %, Pb 2.26 % and Zn 3.67 % of the standard deviation (%SD).

Statistical correlation and R-mode factor analyses were carried out on sediment components, organic carbon and metals of the two cores by using the software STATISTICA (StatSoft 1999). Enrichment factor (EF) and index of geoaccumulation (I_{geo}) were computed to understand the enrichment of metal concentrations and the degree of pollution in sediments of the creek.

Enrichment factor (EF) proposed by Simex and Helz (1981) was calculated using the average metal concentration of the earth's crust (Wedepohl 1995) according to the following equation (Dai et al. 2007).

$$\text{Enrichment factor} = (C_{sample}/Al_{sample})/(C_{crust}/Al_{crust})$$

where, C_{sample} and C_{crust} is the concentration of the element in the sample and in the continental crust, respectively.

Table 1 EF showing seven levels of contamination (Chen et al. 2007)

EF	Level of contamination
<1	No enrichment
<3	Minor enrichment
3–5	Moderate enrichment
5–10	Moderately severe enrichment
10–25	Severe enrichment
25–50	Very severe enrichment
>50	Extremely severe enrichment

Table 2 I_{geo} class showing sediment quality (Müller 1969)

I_{geo}	I_{geo} classes	Sediment quality
<0	0	Unpolluted
0–<1	1	Unpolluted and moderately polluted
1–2	2	Moderately polluted
2–3	3	Moderately to highly polluted
3–4	4	Highly polluted
4–5	5	Highly to very highly polluted
>5	6	Very highly polluted

Al_{sample} and Al_{crust} represent concentration of Al in the sample and in the continental crust, respectively. In this study, Al is used as a normalizer, because, trace element concentrations can be normalized to an element which is conservative with respect to chemical weathering and which has no significant anthropogenic source and Al fulfills this requirement (Wang et al. 2008). EF is divided into seven classes of contamination (Chen et al. 2007) as shown in Table 1. Geoaccumulation index as proposed by Müller (1969) was calculated as:

$$I_{geo} = \log_2 C_n/1.5\,B_n$$

where, C_n is the concentration of the studied element and B_n is the geochemical background value taken from global average shale for element '*n*' and factor 1.5 is used to compensate for lithogenic variations in background data. I_{geo} is divided into seven classes and are shown in Table 2.

Results and discussion

Sediment components and organic carbon

In the core collected from the mouth of the creek (Core 1) the percentage of sand varies from 11.3 to 85.8 % (avg. 32.6 %), that of silt varies from 6.64 to 38.6 % (avg. 30.7 %) and of clay from 7.6 to 58 % (avg. 36.7 %). The organic carbon value varies from 0.24 to 1.73 % (avg.

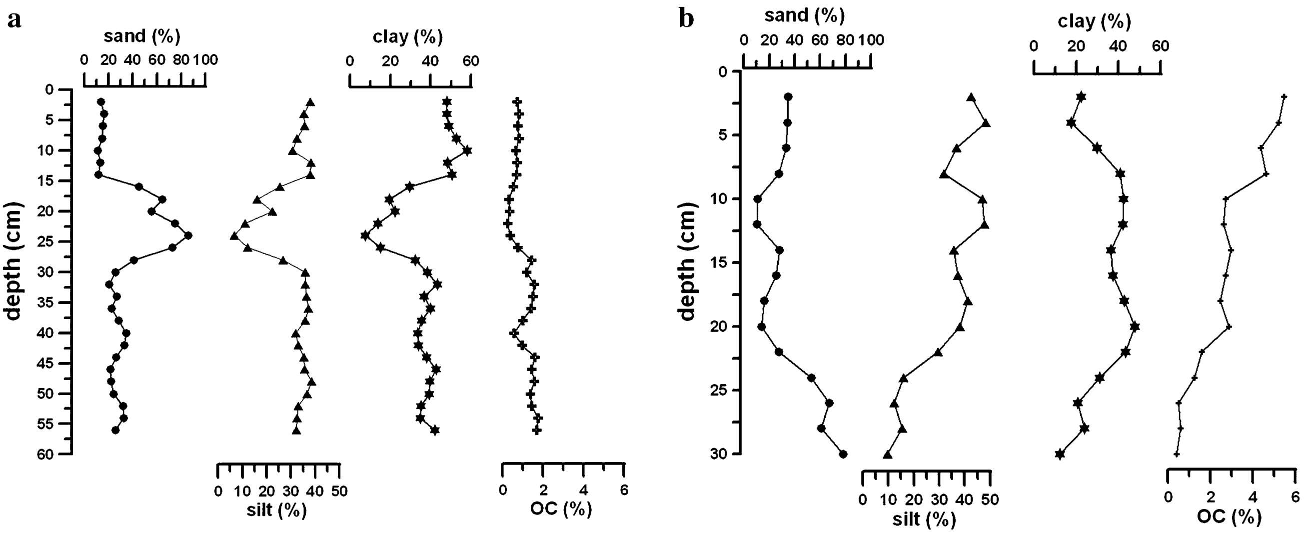


Fig. 2 Depth distribution of sediment components and organic carbon **a** core collected towards the mouth **b** core collected towards the inner portion of the creek

0.99 %). From the distribution pattern of sediment components (Fig. 2a), the core can be divided into three sections, the lower (56 to 30 cm), middle (30 to 14 cm) and the upper (14 cm to surface) sections. In the lower section of the core, fluctuating trend is observed with not much variation in sand percentage which is compensated by finer sediment fractions. In the middle section of the core, sand percentage increases drastically from 30 to 24 cm. Further up, sand concentration decreases up to 14 cm. The variation in sand percentage is compensated by silt and clay. In the upper section, sand percentage is relatively low and is almost constant. The clay percentage is high in this section, with a slight decrease at 12 cm depth, followed by an increase up to 10 cm; where clay concentration is highest. Further up, a gradual decrease in clay up to the surface is seen which is compensated by silt. Organic carbon value is relatively higher in the lower section as compared to the middle and upper sections.

In the core collected from the inner part of the creek (Core 2) the abundance of sand varies from 10.3 to 78.0 % (avg. 34.7 %), of silt from 9.74 to 48.3 % (avg. 32.7 %) and of clay from 11.02 to 47.7 % (avg. 32.7 %). The organic carbon varies from 0.38 to 5.45 % (avg. 2.68 %). An overall decreasing trend of sand percentage is observed from the bottom up to 10 cm of the core, above 10 cm almost constant trend (Fig. 2b) is observed. Silt and organic carbon show an overall increasing trend. The clay is more in the middle of the core and decreases towards the bottom and top of the core. Further, from the distribution pattern of sediment components with depth, the core can be divided into two sections, viz. a lower section from bottom to 20 cm and the upper section from 20 cm to the surface. In the lower section, sand decreases and is compensated by silt and clay. Above this, in the upper section of the core, sand shows gradual increasing trend with slightly lower values between 12 and 10 cm. Silt and clay largely compensate for the variation in sand percentage at all depths except near the surface of the core between 8 cm to surface wherein increase in silt percentage up to 4 cm depth followed by subsequent decrease at the surface is compensated by clay. Organic carbon shows an overall increasing trend with a peak at 8 cm depth.

In the core collected near the creek mouth, the high sand content in the middle section reflects a higher hydrodynamic energy as the grain size of sediment reflects prevailing hydrodynamic condition (Dolch and Hass 2008). Waves and tides associated with currents must have facilitated deposition of coarser sediment fraction carrying away finer sediment component (Siraswar and Nayak 2011). Further, abrupt change in sand percentage suggests a transition from a relatively high-energy depositional environment to lower-energy environment (Fox et al. 1999). Higher organic carbon values in the lower section are associated with higher values of finer sediments. Distribution of organic carbon matches with silt between 44 and 36 cm. Also in the middle section of the core, variation in organic carbon matches the variation in silt and clay showing decrease up to 24 cm followed by an increase, thus reflecting the incorporation of organic matter to the finest fractions of sediments by adsorption phenomena (Keil et al. 1994). In the upper section, the organic carbon is almost constant with slightly increasing trend except near the surface where slight decrease is noted. Variation of organic carbon agrees very well with share of finer fractions between 28 and 8 cm indicating a close relationship. The higher values of organic carbon associated

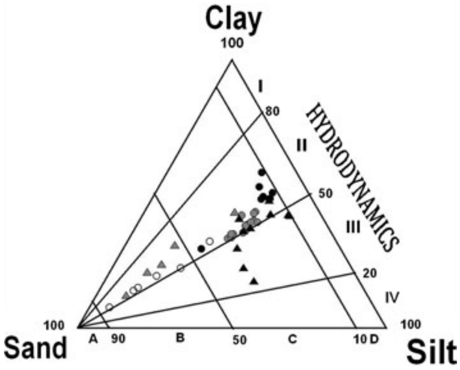


Fig. 3 Ternary diagram showing deposition of sand:silt:clay under varying hydrodynamic conditions after Pejrup (1988). *Circles* represent core collected towards the mouth and *triangles*, core collected from the inner portion of the creek. The *black color* represents the upper section, *empty symbols* represent middle and *grey color* is used to represent lower section of the cores

with finer sediment component, namely silt in the upper section of the core collected from inner portion of the creek indicates enhanced supply of organic material from the overlying water column in recent years (Badr et al. 2009) probably through polluted waters.

An attempt has been made to understand the hydrodynamic conditions in which sediments have been deposited over a period of time within the creek using ternary diagram proposed by Pejrup (1988). Diagram (Fig. 3) is divided into four sections (I–IV) reflecting increasingly violent hydrodynamic conditions. Each section is further divided into four classes (A–D) according to their sand content. Thus, the triangle has been divided into 16 groups each having a different number and a letter providing the groups with unique characteristics. The majority of sediment components of Dudh creek fall in group II (B and C) indicating deposition of sediments under quiet hydrodynamic conditions, except for the surface sediments of core collected from the inner portion of the creek which fall in group III (C) indicating deposition of sediments under relatively higher (violent) hydrodynamic conditions in recent years. Thus the ternary diagram helped in understanding a change from calm to relatively violent hydrodynamic conditions of Dudh creek with time. The spatial distribution of sediment components in the creek also revealed relatively higher average percentage of sand and silt and lower average percentage of clay in the core collected from the inner part of the creek as compared to the core collected from the mouth. Creek with just 23 km length and with Deccan basalts as the main geological formation in the catchment area, large variation in natural sediment input and mineralogy is not expected. However, around 2,000 mm rainfall received between June and September every year may bring mixed size sediment material and allow deposition of coarser sediments in the inner portion of the creek. The wide range of sediment components at two locations therefore indicate differences in hydrodynamics of depositional environments (He et al. 2006) and type of material retained at these locations.

The correlation between sediment components, organic carbon and metals in both cores are presented in Tables 3, 4. In core collected towards the mouth, silt shows significant positive correlation with clay and organic carbon, indicating association of organic matter by fine sediment fraction, while in core collected from the inner portion of the creek, silt shows significant relationship only with organic carbon.

Fe, Mn and Al

In the core collected towards the mouth Fe varies from 7.31 to 10.8 % (avg 8.96 %) while Mn ranges from 1038 to 2144 ppm (avg. 1546 ppm). The concentration of Fe and

Table 3 Correlation between sand, silt, clay, organic carbon and metals in core collected towards the mouth of the creek

	Sand (%)	Silt (%)	Clay (%)	OC (%)	V (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Mn (ppm)	Fe (%)	Al (%)
Sand (%)	1.00											
Silt (%)	−0.95	1.00										
Clay (%)	−0.97	0.85	1.00									
OC (%)	−0.46	**0.**57	0.34	1.00								
V(ppm)	0.43	−0.52	−0.34	−0.51	1.00							
Cu(ppm)	0.21	−0.44	−0.03	−0.63	**0.**65	1.00						
Ni(ppm)	−0.25	−0.01	0.42	−0.46	0.32	0.79	1.00					
Pb(ppm)	−0.21	0.14	0.24	0.08	0.21	0.31	0.25	1.00				
Zn(ppm)	0.17	−0.27	−0.09	−0.47	0.28	0.59	0.28	0.03	1.00			
Mn(ppm)	0.41	−0.50	−0.32	−0.72	0.55	0.72	0.37	0.10	0.80	1.00		
Fe (%)	0.25	−0.45	−0.08	−0.77	0.58	0.89	0.68	0.25	0.65	**0.**77	1.00	
Al (%)	−0.23	0.13	0.28	0.12	0.30	0.29	0.22	0.40	0.42	0.23	0.23	1.00

* Values in bold are significant at $p < 0.05$, $N = 28$ (Casewise deletion of missing data)

Table 4 Correlation between sand, silt, clay, organic carbon and metals in core collected from the inner part of the creek

	Sand (%)	Silt (%)	Clay (%)	OC (%)	V (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Mn (ppm)	Fe (%)	Al (%)
Sand (%)	1.00											
Silt (%)	−0.89	1.00										
Clay (%)	−0.83	0.48	1.00									
OC (%)	−0.54	0.76	0.11	1.00								
V(ppm)	−0.44	0.64	0.06	0.82	1.00							
Cu(ppm)	−0.60	0.72	0.27	0.90	0.91	1.00						
Ni(ppm)	−0.80	0.80	0.56	0.72	0.45	0.71	1.00					
Pb(ppm)	0.67	−0.69	−0.43	−0.63	−0.63	−0.69	−0.64	1.00				
Zn(ppm)	−0.38	0.63	−0.04	0.94	0.82	0.86	0.55	−0.65	1.00			
Mn(ppm)	0.33	−0.51	−0.02	−0.86	−0.59	−0.63	−0.52	0.39	−0.77	1.00		
Fe (%)	0.26	−0.01	−0.49	0.19	−0.06	−0.07	0.05	0.24	0.12	−0.28	1.00	
Al (%)	−0.64	0.35	0.79	−0.01	0.20	0.26	0.39	−0.41	−0.14	0.19	−0.40	1.00

* Values in bold are significant at $p < 0.05$, $N = 15$ (Casewise deletion of missing data)

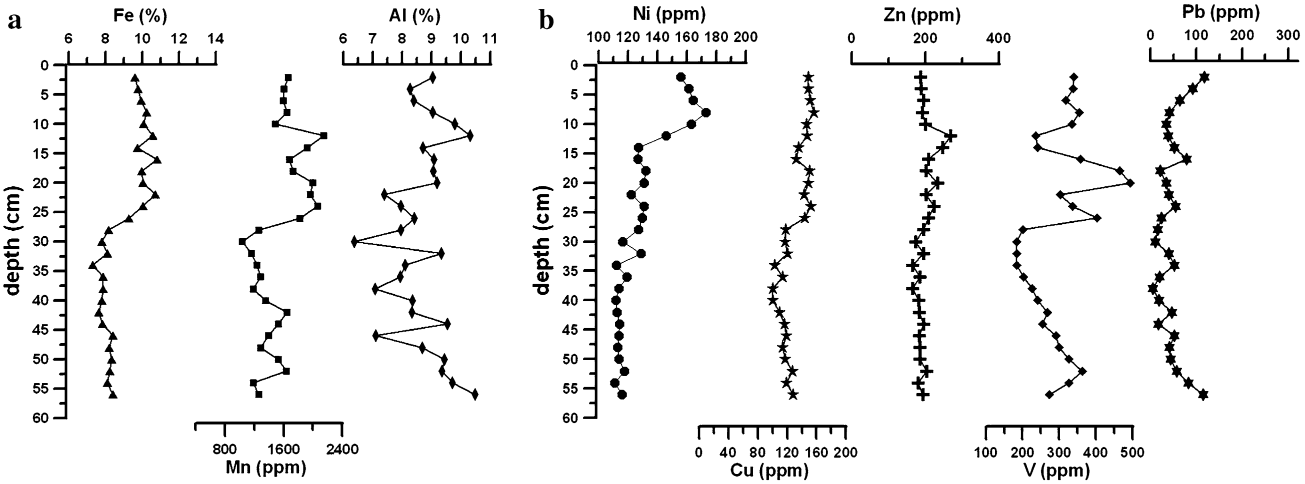


Fig. 4 Depth distribution of metals **a** Fe, Mn and Al **b** Ni, Cu, Zn, V and Pb in core collected towards the mouth

Mn is low in the lower section of the core as compared to middle and upper sections (Fig. 4a). In the lower section Fe is observed to show an overall decreasing trend. Mn also decreases in this section with fluctuating trend. In the middle section, a sudden and large increase in Fe concentration up to 22 cm is observed. Above this Fe concentration decreases up to 14 cm. The Fe concentration is high in this section. Mn concentration varies the same way as Fe in this section and shows a sudden increase up to the depth of 24 cm which further decreases. In the upper section of the core, Fe shows a gradual decrease towards the surface, while Mn shows similar distribution pattern as that of Fe up to the depth of 10 cm with the highest value at 12 cm, above which Mn concentration is almost constant.

In the core collected from the inner portion of the creek, Fe varies from 8.55 to 13.1 % (avg. 10.2 %) and Mn ranges from 748 to 2,347 ppm (avg. 1616 ppm). In the lower section of the core (Fig. 5a) Fe shows slightly increasing trend with the same point-to-point variation as that of clay and silt from bottom to 22 cm, while Mn decreases in this section and has an opposite trend to that of Fe. A similar decrease has also been noted for sand in this section, thus, indicating the difference in association of the two metals with sediment components. Further in the upper section, Fe shows a decreasing trend up to the depth of 16 cm followed by a fluctuating trend up to 6 cm and then increase towards the surface with the highest value at 4 cm depth. The sudden increase in Fe concentration may be due to the recent addition of wastes from industries present in the catchment area making their way directly or indirectly to the creek (Bhagure and Mirgane 2010). The Mn shows an increasing trend from 20 to 12 cm depth, with the highest concentration at 12 cm depth. Above this Mn decreases drastically up to 8 cm followed by a gradual decrease up to

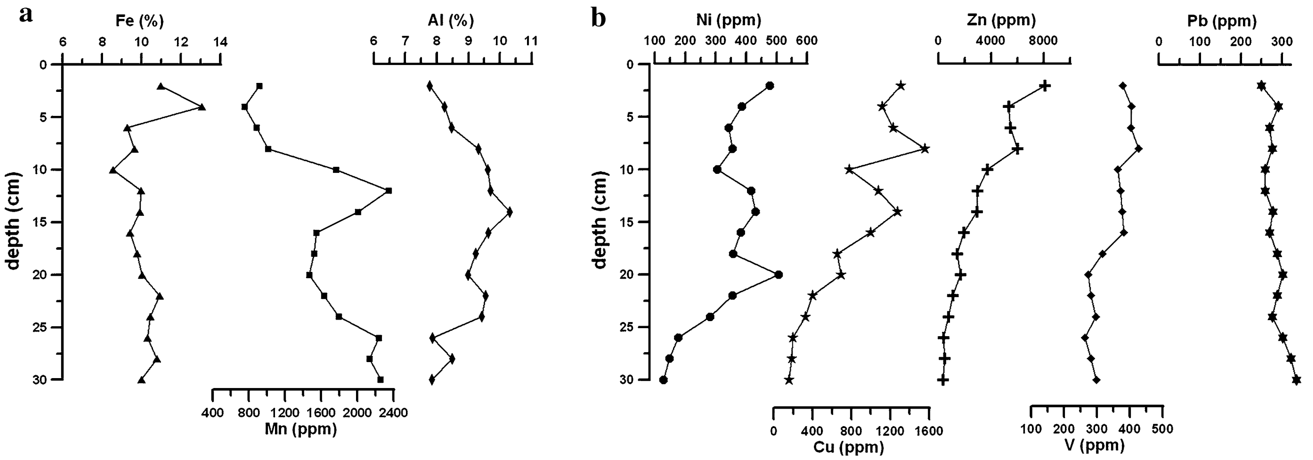


Fig. 5 Depth distribution of metals **a** Fe, Mn and Al **b** Ni, Cu, Zn, V and Pb in core collected from the inner portion of the creek

4 cm. Mn variation matches clay in the upper section between 14 cm up to the surface of the core, while Fe concentration shows a slight similarity to silt.

Low concentration of Fe and Mn in the lower section, sudden increase in the middle section and maintaining higher values in the upper section in the core collected near mouth indicates early diagenetic process. The distribution pattern of Fe and Mn has been used to understand their post-depositional behavior by Singh and Nayak (2009) earlier. The sudden increase in redox sensitive elements namely in Fe and Mn above 30 cm depth indicates changing redox condition from anoxic to oxic, wherein there is migration of Fe^{2+} and Mn^{2+} species which are produced as a result of Fe–Mn oxyhydroxide dissolution in the partly reduced sediment layer below 30 cm and reprecipitation near the oxic-suboxic interface (Sundararajan and Natesan 2010). Further, a similar point-to-point variation of Fe and Mn is observed between 56 and 52 cm in the lower section, 30–24 cm in the middle section and 14 cm to the surface in the upper section of the core. This is also supported by strong positive correlation between Fe and Mn (Table 3) indicating strong association of the geochemical matrix between the two elements (Jonathan et al. 2010). From the overall distribution pattern, sudden increase in concentration of Fe and Mn in the middle section of the core is the result of formation of insoluble oxyhydroxides in the oxic sediment layer (Fernandes and Nayak 2009) of muddy sand. This is also supported by the significant positive correlation of Mn with sand (Table 3).

A peak value of Mn at 12 cm along with slight increase in Fe concentration at this depth in the core collected from the inner portion of the creek probably indicates precipitation of Fe and Mn-oxides in the oxic sediments (Caetano et al. 2009). However, Fe and Mn show negatively correlation (Table 4) between themselves and also, no significant correlation of Fe and Mn with sediment components indicating difference in processes of deposition. Differences in Fe and Mn distribution pattern and their associations, in the inner core could be due to difference in hydrodynamics, elemental behavior with respect to physico-chemical conditions and source of supply.

Al indicates terrigenous input and is the major component in the clay lattice. In the core collected towards the mouth of the creek, Al varies from 6.38 to 10.5 % (average 8.66 %). A large fluctuating trend is seen (Fig. 4a) along the length of the core with relatively higher values towards the bottom and top of the core. In the lower section of the core Al shows an overall decreasing trend with peaks of high and low values in between. Distribution of Al agrees with that of organic carbon between 38 and 30 cm. In the middle section of the core, an overall increasing trend is noted. In the upper section of the core, Al concentration is higher at 12 cm followed by a gradual decrease up to 4 cm. In the core collected from the inner portion of the creek, Al varies from 7.78 to 10.3 % with an average value of 8.96 %. Al is observed to have higher concentration in the middle and lower portion of the core (Fig. 5a). The variation in Al concentration in the upper and bottom part of the core agrees with the distribution pattern of clay. In the lower section of the core, Al shows an increasing trend similar to that of finer sediment components and organic carbon, except at 20 cm where Al concentration decreases. In the upper section of the core, Al increases up to 14 cm followed by a decrease up to the surface.

Correlation coefficient indicated no significant relationship of Al with any of the sediment components for the core collected towards the mouth of the creek (Table 3). In the core collected towards the inner portion of the creek, Al exhibited significant positive correlation with clay size fraction (Table 4) indicating its natural source. The association of Al with fine-grained sediments suggests that they are detrital minerals dominated by phyllosilicates (Buckley and Cranston 1991; Jonathan et al. 2004). No significant relationship of Al with Fe, Mn and organic carbon indicates that they are derived from different sources.

Trace metals

In core collected towards the mouth of the creek, the concentration of metals varied from 183 to 493 ppm (avg. 297 ppm) for V, 110–173 ppm (avg. 128 ppm) for Ni, 100–156 ppm (avg. 129 ppm) for Cu, 165–268 (avg. 197 ppm) for Zn, 4.67–116 ppm (avg. 46.6 ppm) for Pb. In general V, Cu and to some extent Zn concentrations are lower in the lower section of the core as compared to the middle and upper sections (Fig. 4b). Ni concentration is high in the upper section as compared to the lower and the middle, while, Pb concentration is high towards the bottom and top of the core. The lower section of the core shows an overall decreasing trend of V. Similarly, Cu and Pb also show a decreasing trend with fluctuations and agree with Fe and Mn. As compared to these, not much variation in Zn and Ni concentration is observed. In addition, Zn also shows similar point-to-point distribution pattern as that of Al in this section between 50 and 30 cm. In the middle section of the core, V, Cu and Zn show drastic increase agreeing with sand, Fe and Mn distribution. The increased concentration of metals in the coarser fractions may be attributed to inputs from the anthropogenic sources such as industrial wastes. A gradual increasing trend is noted for Ni with a slightly lower value at 22 cm depth. Decrease in concentration at this depth is also observed for Cu, Zn and V. Pb shows a fluctuating trend in this section. In the upper section of the core, Ni, Cu and to some extent V increases up to 8 cm followed by a decrease towards the surface. Zn concentration is the highest at 12 cm and coincides with Mn peak at this depth. This is followed by a sudden decrease at 10 cm depth above which a gradual decrease up to the surface is observed for Zn and agrees well with Al except at the surface. Pb shows decrease up to 10 cm followed by an increase up to the surface. The higher concentration of metals in the middle and upper sections of the core, similar to that of Fe and Mn, indicates precipitation of Fe–Mn oxyhydroxides and co-precipitation of metals in the top sections of the core that were in contact with oxygenated bottom waters (Selvaraj et al. 2010). This is also supported by significant positive correlation of metals namely V, Cu, Ni and Zn with Fe and Mn (Table 3). No major influence of sediment components on the distribution of metals is evident except for V and Mn which shows significant positive correlation with sand and Ni with that of clay. Thus oxides of Fe and Mn can be considered as the most important component in influencing processes of metal transport and distribution (Thomas and Bendell-Young 1999) in this core except for Pb which seems not influenced by diagenetic processes.

In the core collected from the inner portion of the creek, concentration of metals varied from 262 to 426 ppm (avg. 341 ppm) for V, 128–506 ppm (avg. 336 ppm) for Ni, 155–1,555 ppm (avg. 795 ppm) for Cu, 346–8,101 ppm (avg. 2,835 ppm) for Zn and 249–335 ppm (avg. 284 ppm) for Pb. In general V, Ni, Cu and Zn show increasing trend and Pb shows an overall decreasing trend from bottom to the top of the core (Fig. 5b). In the lower section of the core, overall slightly decreasing trend of V is noted with its minimum concentration at 26 cm, while Ni, Cu and Zn show an increasing trend agreeing with the distribution pattern of finer sediment components and organic carbon. In the upper section of the core, V shows a fluctuating trend. Ni, Cu and Zn show the same variation patterns as that of organic carbon at all depths between 20 cm up to the surface. Pb distribution matches that of Fe and show same point-to-point variation pattern from 20 cm up to surface of the core. No similarity of Pb with Mn distribution pattern was observed. The observed differences in association of Pb with Fe and Mn may be the result of the important role played by Fe oxide recycling in the precipitation of Pb as compared to Mn, cycling of which is less important (Ruiz-Fernández et al. 2009).

Correlation values indicate significant positive association of Pb with sand. Although metals are usually associated with finer fractions they have also been shown to accumulate on the surface of coarser materials like sand (Kljakovic-Gašpic et al. 2009). V, Cu, Ni, Zn along with organic carbon show significant positive correlation with finer sediment fractions (Table 4). Finer-grained fractions and their associated sediment phases have a higher proportion of trace elements more often greater than the coarse-grained sediments which are connected with larger surface area of smaller particles (Mikulic et al. 2008). Also, the strong correlation between these elements and organic carbon underlines an association in the form of organo-metallic complexes (Zourarah et al. 2009). No significant correlation of metals with Al is evident. Weaker correlation of metals with Al which is a geochemical proxy suggest that factors other than particle size contribute significantly to the variations of these elements (Zhang et al. 2007). Fe and Mn are also observed to have no influence on the distribution of metals in this core indicating absence of diagenetic enrichment. Thus correlation analyses strongly support anthropogenic addition of metals to this part of the creek. Within the Tarapur MIDC area 1,182 industries are present and include chemical, pharmaceutical, engineering, steel, textile, glass, rubber, tiles, marble, packaging, paper, plastic, food, decorative plywood, wood and others. These industries use raw materials such as inorganic and organic compounds, dyes, pigments, bulk drugs, oils, alloy and non alloy steel sheets, ferrous and non-ferrous materials, metallic powder, aluminium alloys, scrap and annealed wire, stainless steel and steel wire rods, color and chemicals, asbestos, chemical solvents like zinc oxide, raw rubber, cement chips, plastic, sugar, etc. Amongst these, dye and dye intermediates, iron and steel, pesticides, drugs and pharmaceuticals are categorized as highly polluting industries at Tarapur (MPCB 2010). According to MPCB report (2005) the wastewater generated from the cities located in the Thane region along with industrial effluent is finally disposed off in the nearby creeks. Elevated concentrations and the increase of metals from the bottom to the top of the core in the present study indicate addition of metals from industrial effluents, the magnitude of which has increased in recent years.

Distribution of metals varies largely in the two cores. The core collected towards the mouth has lower average concentration of most of the metals as compared to the core collected from the inner portion of the creek. This may be because of the influence of tidal flushing which is higher towards the mouth as compared to the inner portion of the creek where tidal flushing is probably not effective in removal of finer sediments, organic matter and associated metals. Variations in parameters between locations can be well depicted using an "isocon" plot (Cundy et al. 1997). An isocon is a straight line through the origin. The slope of the isocon defines the mass change in the alteration, and the deviation of a data point from the isocon defines the concentration change for the corresponding component (Grant 1986). From the distribution of the average data points it is observed that sediment components, organic carbon, Fe, Mn, Al, and V lie close to the straight line (Fig. 6), thus indicating little or no variation in their composition and therefore are said to be of natural origin or less affected by anthropogenic processes in both the cores. The trace metals mainly Zn, Ni, Cu and Pb, lie away from the line and lie towards the core collected from the inner portion of the creek, thus indicating elevated concentrations of metals originating from anthropogenic sources in the inner portion of the creek as compared to the sediments towards the mouth. It is also evident that anthropogenic addition of Zn is highest in comparison with other metals.

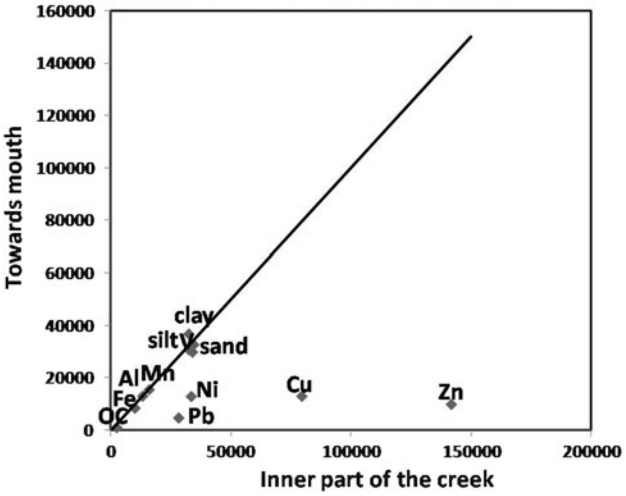


Fig. 6 Isocon plot. Each element has been multiplied by the same number in both the cores to ensure that it plots on the same scale. Also to separate the closely spaced average data points, sand, silt, clay, organic carbon, Al and Fe are multiplied by 1000, Ni, Cu, V, Pb by 100, Zn and Mn by 50

Factor analysis

In order to understand the source of metal input in sediments of Dudh creek, R-mode factor analysis has been performed. The factor loadings are presented in Table 5a, b for both cores. For core collected towards the mouth, three factors could be extracted (Fig. 7a) contributing to about 81 % of the total variance with Eigenvalue >1. From the figure, two groups can be identified for all the three factors and named as positively and negatively loaded. For the first factor, finer sediment components and organic carbon are observed to be positively loaded, thus indicating association of organic matter with fine-grained sediments. All the studied metals along with sand are negatively loaded out of which Fe, Mn, V and Cu loadings are significant. They are thus opposite in behavior to those of the first group and indicate adsorption of metals, especially V and Cu onto Fe–Mn oxyhydroxide precipitate. In the second factor, significant positive loading of sand and negative loading of clay indicate differences in their geochemical behavior. Factor 3 is less significant as compared to factor 1 and 2 and does not represent any major associations. Thus it is clear that in the core collected towards the mouth, sediment components and organic carbon does not play a major role in metal distribution. Even Fe–Mn oxyhydroxides are not effective enough in controlling the distribution of most of the metals, except for V and Cu.

For core collected from the inner portion of the creek, two factors could be extracted (Fig. 7b) accounting for 78 % of the total variance with Eigenvalue >1. In the first factor sand and Pb are significantly positively loaded. This group also includes Mn with lower loadings and minor loadings of Fe indicating little influence of Fe–Mn oxyhydroxides on the distribution of Pb. This also indicates that Pb is from different source when compared to other trace metals. Silt, organic carbon, V, Cu, Ni and Zn are significantly negatively loaded indicating association of metals with one of the finer sediment components, i.e. silt and organic carbon and has associations that are different from the first group. Factor 2 shows significant positive loadings of clay and Al of lithogenic origin and having no association with trace metals. Factor analysis thus supports different sources including anthropogenic input of metals to the creek, the main source of which can be industrial effluents from Tarapur MIDC area which are continuously being drained into the Dudh creek due to which the creek is almost perpetually full of leaked effluents (Naik et al. 2007). However, Pb may be from vehicular source.

Table 5 Factor loadings for (a) mouth **b)**the inner part of the creek

	Factor 1	Factor 2	Factor 3
(a) Core collected towards the mouth			
Sand	−0.57	0.79[a]	0.16
Silt	0.72[a]	−0.62	−0.09
Clay	0.42	−0.87[a]	−0.21
OC	0.82[a]	−0.09	0.39
V	−0.73[a]	−0.00	0.30
Cu	−0.87[a]	−0.38	−0.07
Ni	−0.51	−0.66	−0.37
Pb	−0.13	−0.51	0.53
Zn	−0.68	−0.23	0.05
Mn	−0.88[a]	−0.07	0.00
Fe	−0.89[a]	−0.30	−0.15
Al	−0.20	−0.56	0.65
Expl.Var	5.34	3.08	1.2
Prp.Totl	0.45	0.26	0.1
	Factor 1	Factor 2	
(b) Core collected from the inner part of the creek			
Sand	0.81[a]	−0.50	
Silt	−0.89[a]	0.11	
Clay	−0.46	0.82[a]	
OC	−0.91[a]	−0.41	
V	−0.81[a]	−0.27	
Cu	−0.92[a]	−0.15	
Ni	−0.84[a]	0.15	
Pb	0.81[a]	−0.16	
Zn	−0.81[a]	−0.49	
Mn	0.68	0.51	
Fe	0.07	−0.63	
Al	−0.36	0.81[a]	
Expl.Var	6.64	2.81	
Prp.Totl	0.55	0.23	

Extraction: Principal components ([a]Marked loadings are >0.7)

Pollution level in Dudh creek

The average values of EF and I_{geo} of the studied metals in both the cores revealed that the sediments of Dudh creek are severely enriched and extremely polluted with Zn, Cu, Ni, Pb followed by V. Fe and Mn also show minor enrichment (Table 6a, b). Spatial variation in the degree of pollution is also clearly evident within the creek and is observed to be of major concern especially towards the inner portion where the level of trace metal enrichment is many folds higher than the core collected towards the mouth. Less concentration of metals near the mouth may be due to good tidal flushing especially during ebb tide, dragging most of the contaminants towards the sea before it can settle in the creek. Also, from the depth variation of EF (Fig. 8a, b) and I_{geo} (Fig. 9a, b) an increase in magnitude of enrichment is seen for most of the metals from bottom to top of the core and thus has resulted in extreme deterioration of sediment quality of the creek in recent years, due to the release of waste from MIDC.

If an EF value is between 0.5 and 1.5, it suggests that the trace metals may be entirely from crustal materials or natural weathering processes Zhang and Liu (2002) and if an EF is greater than 1.5, it suggests that a significant portion of trace metal is delivered from non-crustal or natural weathering processes, the trace metals are provided by other sources (Feng et al. 2004). Higher values obtained in the present case strongly support anthropogenic source.

Conclusion

The sudden and large increase in sand percentage in the middle and lower sections of core collected towards the mouth and core collected towards the inner portion of the creek, respectively, indicate deposition of sediment under high hydrodynamic energy conditions at these depths. The

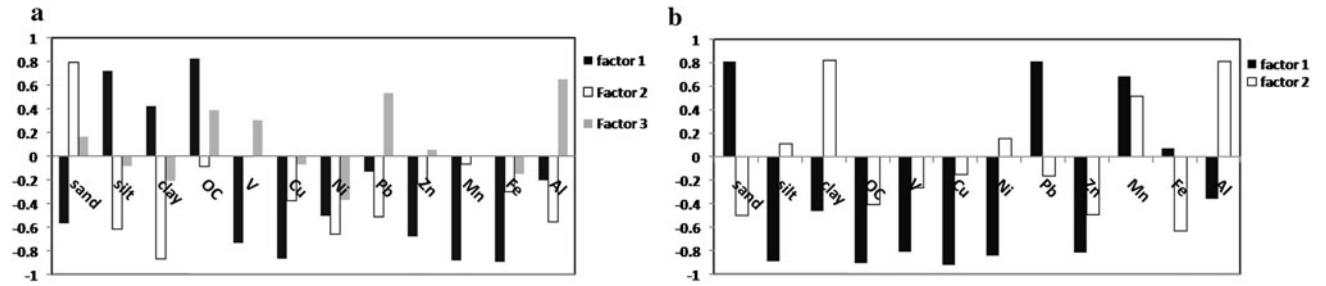


Fig. 7 R-mode factor analysis for **a** core collected towards the mouth **b** core collected from the inner portion of the creek

Table 6 Average values of EF and I_{geo} in core collected (a) towards the mouth (b) Average values of EF and I_{geo} in core collected from the inner part of the creek

Metal	Avg EF	Level	Avg I_{geo} value	Sediment quality
(a) Average values of EF and I_{geo} in core collected towards the mouth				
V	5	Moderate enrichment	2.4	Moderately to highly polluted
Cu	8.2	Moderately severe	2.1	Moderately to highly polluted
Ni	6.2	Moderately severe	1.5	Moderately polluted
Pb	2.4	Minor enrichment	1.5	Moderately polluted
Zn	3.4	Moderate enrichment	1.6	Moderately polluted
Mn	2.6	Minor enrichment	1.9	Moderately polluted
Fe	2.6	Minor enrichment	1.5	Moderately polluted
(b) Average values of EF and I_{geo} in core collected from the inner part of the creek				
V	5.6	Moderately severe	3.3	Highly polluted
Cu	47.8	Very severe	4.4	Highly to very highly polluted
Ni	15.6	Severe	2.8	Moderately to highly polluted
Pb	15	Severe	4.4	Highly to very highly polluted
Zn	48	Very severe	4.9	Highly to very highly polluted
Mn	2.7	Minor enrichment	1.9	Moderately polluted
Fe	2.9	Minor enrichment	1.7	Moderately polluted

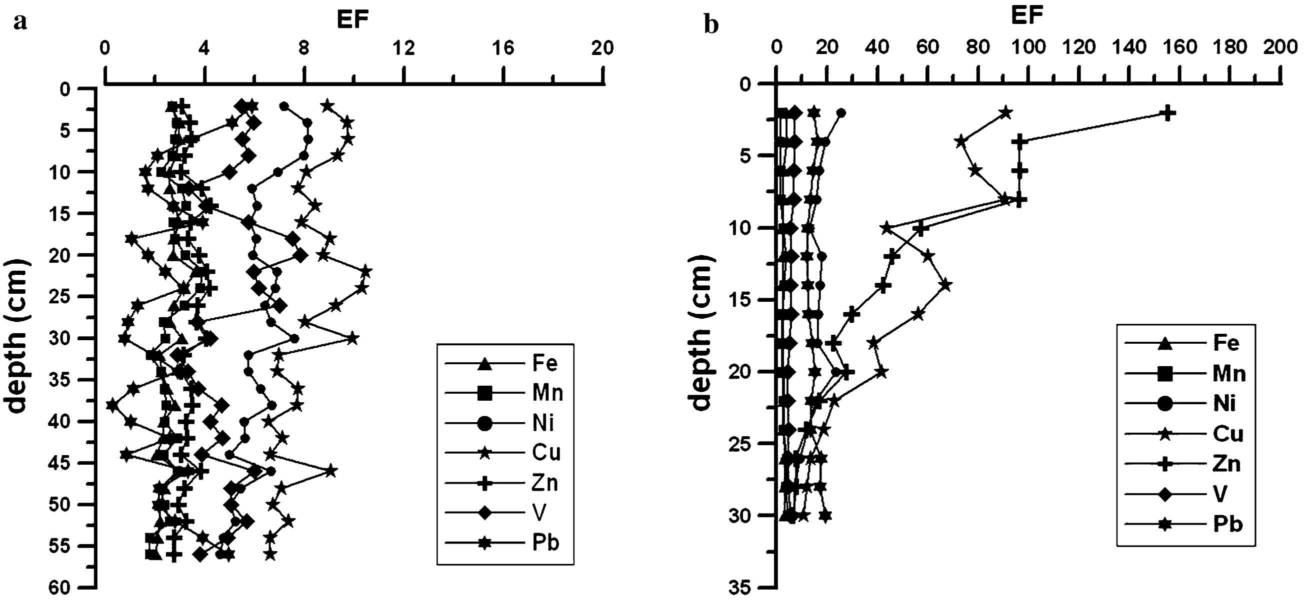


Fig. 8 Depth distribution of enrichment factor for **a** core collected towards the mouth **b** core collected from the inner portion of the creek

increased concentration of Fe and Mn along with other metals in the middle and upper sections of the core collected towards the mouth pointed towards anthropogenic addition in recent years. Correlation analyses helped in understanding strong association between elements (V, Cu, Ni, and Zn), silt and organic carbon which is probably in the form of organometallic complexes in the core collected from the inner portion of the creek. Sediment components and organic carbon were found to have negligible or minor influence on metal distribution in core collected towards the mouth.

The observed elevated concentrations of metals and organic carbon towards the inner portion of the creek has been attributed to less effective tidal flushing as compared to the mouth. Isocon plot has helped to depict variations in parameters between sites. From the distribution of average data points, sediment components, organic carbon, Fe, Mn, Al and V were found to be of natural origin or are less affected by anthropogenic processes in both the cores, while Zn, Ni, Cu and Pb had elevated concentrations originating from anthropogenic sources towards the inner

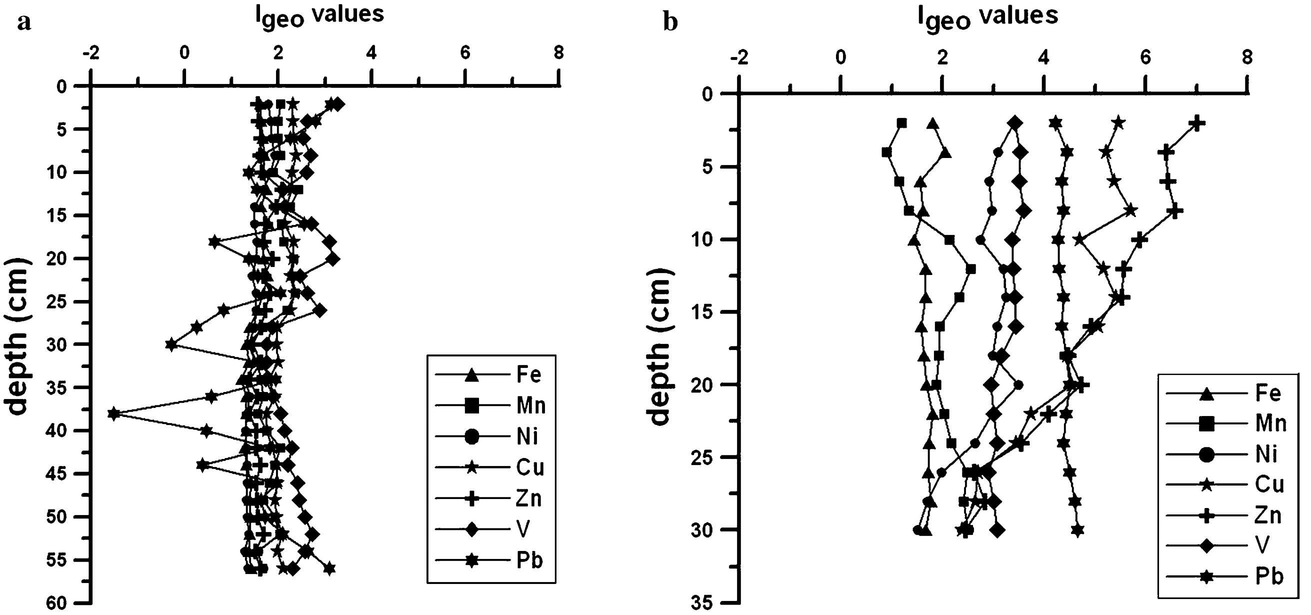


Fig. 9 Depth distribution of values of index of geoaccumulation (I_{geo}) for **a** core collected towards the mouth **b** core collected from the inner portion

portion of the creek as compared to the mouth. Factor analysis also pointed towards anthropogenic input of metals to the creek as the main source from the nearby industries. EF and I_{geo} helped to study the level of pollution in the sediments of Dudh creek. The creek is found to be severely enriched with Zn, Cu, Ni, Pb followed by V, while Fe and Mn showed minor enrichment. The sediment quality of Dudh creek has deteriorated especially in recent years by the addition of waste from Tarapur MIDC.

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