



Impact of industrial effluents on geochemical association of metals within intertidal sediments of a creek



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ARTICLE INFO

Article history:

Received 14 February 2015

Revised 20 July 2015

Accepted 23 July 2015

Available online 29 July 2015

Keywords:

Speciation
Trace metals
Sediment
Creek
Toxicity

ABSTRACT

Metal speciation studies were carried out on three intertidal core sediments of the industrially impacted Dudh creek located along west coast of India. Metals indicated a drastic increase in the bioavailable fraction towards the surface of the cores, suggesting an increase in anthropogenic metal input in recent years as compared to the past. Also, when compared with Vaitarna estuary and Khonda creek of Thane district, the speciation of metals in Dudh creek sediments was observed to have been highly modified in recent years. High concentrations of metals associated with bioavailable fractions therefore suggested a risk of toxicity to sediment associated biota of Dudh creek.

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1. Introduction

Continuous addition of large amount of industrial and municipal wastes has resulted in very high deposition of trace metal contaminants within sediments of Dudh (Kharekuran-Murbe) creek present along the west coast of India (Volvoikar and Nayak, 2013a). Though Dudh (Kharekuran-Murbe) creek is small in terms of size and the catchment area, the extent of its level of pollution is very high as compared to other contaminated estuaries and creeks present along the coast of India (Dessai and Nayak, 2009; Fernandes et al., 2011; Volvoikar and Nayak, 2013b, 2014; Pande and Nayak, 2013a,b; Fernandes et al., 2014) as well as other anthropogenically impacted coastal regions of the world (Hornberger et al., 1999; Ong Che, 1999; Mortimer and Rae, 2000; Cobelo-García and Prego, 2004; Sharmin et al., 2010; Passos et al., 2011). Tarapur Maharashtra Industrial Development Corporation (MIDC) with around 1182 industrial units is located in the catchment area of Dudh creek (MPCB, 2005). Amongst these, dye and dye intermediates, iron and steel, pesticides, drugs and pharmaceuticals are categorized as highly polluting industries of Tarapur MIDC (MPCB, 2010). The industrial effluents and the domestic wastewater generated in this region is finally disposed

off in nearby creeks and ultimately in adjacent coastal region. Dudh creek is therefore one of the best examples to study the impact of human interference on natural environment. These highly polluted sediments have a high potential of toxicity of associated biota and affect the surrounding environment. Information on influence of industrial pollution on biota of Dudh creek is unavailable. However, benthic ecosystem of adjacent coastal waters receiving effluents discharged from Tarapur MIDC through Dudh and other creeks of the region has been adversely influenced, as a result of their interaction with and response to organic pollution (Sivaraj et al., 2014).

In addition to organic pollution, study of impact of trace metal pollution on sediment geochemistry is also of major concern. Since, following the change in physico-chemical conditions, these deposited sediments tend to act as major secondary metal pollution source to overlying water column even after periods of a few years (Williamson et al., 1996; Volvoikar and Nayak, 2013c). Metal pollution studies therefore give information on present status of environmental health, as well as are also useful in predicting the future consequences. Impact of the pollution on the environment is however related to the availability of heavy metals, i.e. to the reversibility of the process by which metals are incorporated to the solid matrix (Alvarez et al., 2011). Bioavailability or bioaccumulation of metal contaminants is in turn mainly dependent on the partitioning behavior or binding strength of the contaminant to sediment (Eggleton and Thomas, 2004). It is thus the physico-chemical forms of the trace metals and not the

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total trace metal content in sediments that determine their potential bioavailability and remobilization (Ibhadon et al., 2004).

Earlier studies carried out on intertidal sediments of Dudh creek however have reported only the total trace metal concentration. The information on metal speciation/geochemical partitioning within these highly anthropogenically impacted sediments still remains unavailable. Knowledge of geochemical partitioning of metals in sediments is of great importance in risk assessment (Burton et al., 2006). It is necessary to identify and quantify the forms in which a metal is present in sediments to gain a more precise understanding of the potential and actual impacts of elevated concentrations (Liu and Shen, 2014). Speciation study is also important to evaluate processes of downstream transport, deposition and release under changing environmental conditions (Li et al., 2000; Krupadam et al., 2006). Thus the present study has been carried out with an objective of investigating the influence of anthropogenic discharges on the geochemistry of creek sediments.

The major mechanisms of metal accumulation in sediments lead to the existence of five major metal geochemical forms: (1) exchangeable (2) bound to carbonate phase (3) bound to Fe–Mn oxides (4) bound to organic/sulphide phase and (5) residual metal phase (Li et al., 2001). A large part of metals introduced by human activity are known to be present in the exchangeable and carbonate fractions. The metals associated with these two fractions are therefore the most mobile forms. Reducible (Fe–Mn oxide) and oxidizable (organic/sulphide) phases act as sink of metals. Metal content bound to these fractions can be mobilized with increasing reducing or oxidizing conditions in the environment. While metals in the residual fraction, strongly bound to solid matter, originate mainly from natural sources (Filgueiras et al., 2002; Trujillo-Cárdenas et al., 2010). Thus speciation of metals i.e. the concentration of metals (Fe, Mn, Cu, Zn, Ni and Pb) in the five sedimentary fractions have been studied.

1.1. Study area

Dudh creek, also known as Kharekuran–Murbe creek is located in Thane District of Maharashtra state (Fig. 1). The creek is approximately 23 km long and shows a meandering path from the mouth to the upper limit of tidal influence. It is a macrotidal creek with a spring tidal range of 5.35 and neap tidal range of 2.1 (Swamy et al., 1982). It receives freshwater from Dudh River. 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 overlying the lava flows (Naik et al., 2007).

2. Materials and methods

Three intertidal sediment cores were collected from Dudh creek during field survey carried out from 20th to 29th May 2009. Cores were collected with the help of hand operated PVC corer. Core S22 of length 30 cm (19° 46' 13.0" N, 72° 45' 15" E), core S13 of length 16 cm (19° 45' 41.7" N; 72° 43' 28.7" E) and core S12 of length 56 cm (19° 44' 43.9" N, 72° 42' 39.6" E) were collected respectively from the inner portion, middle portion and closer to the mouth of the creek. Sampling stations were located with hand held GPS. Immediately after the extraction, sediment cores were sectioned at 2 cm interval with the help of a plastic knife. The sub-samples were then sealed in clean plastic bags, labeled and stored in ice box. In the laboratory sediment sub samples were then oven dried at 60 °C. The dried sub samples were further finely powdered and homogenized using agate mortar and pestle. The powdered sediment sub samples were then used to carry out speciation study, for which a modified sequential extraction procedure (Dessai and Nayak, 2009) proposed by Tessier et al. (1979) was used. The procedure involves five steps wherein metals associated with different sedimentary fractions/phases are separated using successively aggressive reagents [MgCl₂ (exchangeable), NaOAc (carbonates), NH₂OH·HCl (Fe/Mn oxides), H₂O₂ (organic/sulphidic) and HF–HNO₃–HClO₄ (residual)].

The separated solutions obtained during sequential extraction procedure were aspirated into the flame atomic absorption spectrophotometer (AAS) (Varian AA240FS) for the analyses of the metals viz. iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), nickel (Ni) and lead (Pb). Care was taken to avoid contamination at every step. Reagent blanks without sample were 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). Recovery was above 95% for all the studied metals. 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

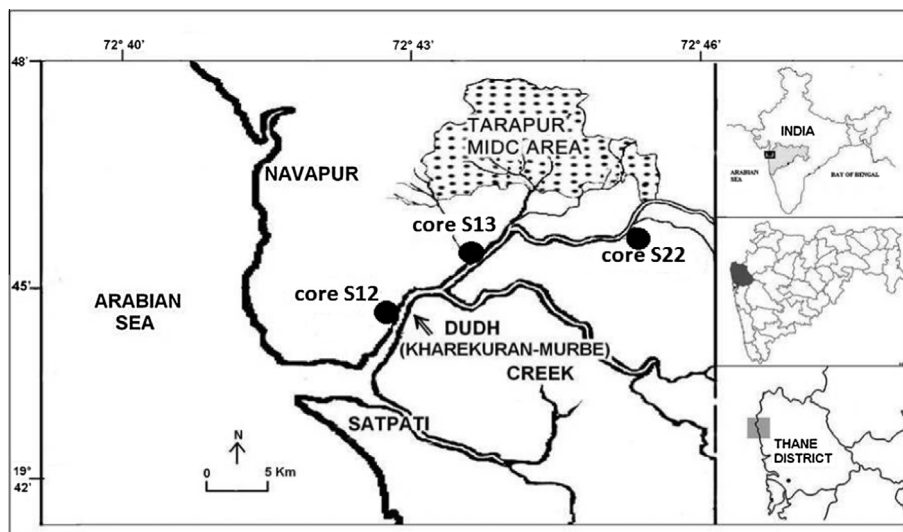


Fig. 1. Map showing locations of the sediment cores sample collection in Dudh creek.

solutions (1000 mg/l). The recovery of metals from sequential extraction procedure was also good and was calculated as: (sum of metal concentration in the five fractions/total metal concentration obtained after total acid digestion) \times 100.

3. Results and discussion

3.1. Metal speciation in Dudh creek

In core collected from the inner portion of the creek (core S22), Fe and Mn show their highest association with the residual fraction (F5). Wherein Fe varies from 42,069 ppm to 64,356 ppm (avg. 50,563 ppm) and account for 46.3% to 90.3% (avg. 71%), while Mn ranges from 168 ppm to 427 ppm (avg. 244 ppm) and account for 22.3% to 58% (avg. 44%) when recomputed taking all five fractions to hundred (Table 1). However other sedimentary fractions namely Fe–Mn oxide (F3) as well as exchangeable (F1) and carbonate (F2) fractions also significantly control the distribution of Mn in this core. Highest association of Fe with the residual fraction (F5) can thus be directly attributed to its high abundance in the earth's crust (Yuan et al., 2004; Jain et al., 2008). It also suggests relatively low mobility of this element (Caplat et al., 2005) as compared to Mn, as metals associated with this fraction cannot be remobilized under the conditions normally encountered in nature (Izquierdo et al., 1997).

Amongst the studied trace metals, Cu is mainly found to be associated with organic/sulphide fraction (F4) in this core (Table 1). While, major concentration of Zn and Ni is found to be associated with Fe–Mn oxide fraction (F3). In addition Zn and Ni also show significant higher association with carbonate and organic/sulphide fractions respectively. While Pb shows its highest association with residual fraction (F5). It also shows significant higher association with Fe–Mn oxide (F3) and organic/sulphide (F4) fractions as well. Thus, following residual fraction, oxidizable (organic/sulphide) and reducible (Fe–Mn oxide) fractions significantly control the distribution of metals in this core.

The sampling location of core S22 is in close proximity of a sewage outfall and thus receives large continuous amount of organic as well as inorganic industrial and domestic waste material. Earlier studies carried out on contaminated sediments elsewhere, have also reported association of Cu with organic matter and sulphides (Tokalioğlu et al., 2000), the latter perhaps being in the form of cuprous sulphide when found in anoxic conditions and in the presence of sulphur compounds (Alagarsamy, 2009). Study carried out by Jones and Turki (1997) on the contaminated sediments of Tees estuary, North-east England also indicated oxidizable fraction to be the dominant Cu host. In addition, trace metal contaminants also get adsorbed onto or occluded within the hydrogenous and

Table 2

Average concentration of metals in bioavailable fractions (F1 + F2 + F3 + F4) of cores collected from Dudh creek.

Ppm	Core S12 (Mangrove)	Core S13 (Mangrove)	Core S22 (Mudflat)
Fe	5920	7225	22,711
Mn	370	751	335
Cu	42	74	549
Zn	27	54	893
Ni	32	65	165
Pb	17	28	68

biogenic phases which coat natural particles (Chapman et al., 1998; Turner, 2000). The most significant of which is hydrous iron and manganese oxides, characterized by high adsorptive capacities and low degrees of crystallinity, the latter effect is caused by successive cycles of dissolution-precipitation and facilitates the non-stoichiometric incorporation of metals into the oxides (Chao, 1984). The solubility and mobility of Cu in this core is therefore mainly controlled by organic matter mineralization (Caplat et al., 2005) and that of Zn, Ni and Pb by redox conditions. Intertidal sediments of inner portion of Dudh creek therefore act as a large sink of heavy metals, which upon change in redox conditions, have a potential to act as their source as well. While the portion of Zn associated with carbonate fraction is readily available. Thus, amongst the studied trace metals Zn is considered to be most labile metal and having highest mobility. These metal contaminated sediments therefore pose a very high risk of toxicity to associated biota.

Further, in order to understand the risk of metals to the sediment dwelling organisms and consequently to the human population, the data of metals in the bioavailable fractions (F1 + F2 + F3 + F4) is compared with the sediment quality values (SQV) using SQUIRT (Screening Quick Reference Table). SQUIRT was developed by NOAA for screening purposes. The guideline values were categorized by Buchman (1999) into five classes (Tables 3 and 4) namely TEL, ERL, PEL, ERM and AET. The probability of toxicity of metals to sediment dwelling organisms is known to increase from TEL to AET. In this core, metals namely, Mn, Cu, Zn and Ni (Table 2) show values above AET (Tables 3 and 4), thus suggesting very high bioavailability and risk of toxicity of these metals to sediment dwelling organisms. While risk of toxicity of Pb, is relatively lower as its value fall above ERL. Fe concentration is much lower than AET, thus is not harmful to the organisms at this location.

In core collected from the middle portion of Dudh creek (core S13), highest concentration of Fe is found to be associated with residual fraction (F5) and that of Mn with Fe–Mn oxide fraction (F3) (Table 5). Fe in residual fraction varies from 39,789 ppm to

Table 1
Range and average of metal concentration in five fractions.

Core S22	F1	F2	F3	F4	F5
Fe	2.58–29.1(9.93) 0.004–0.032 (0.013)	15.51–1584 (219.2) 0.02–1.74 (0.28)	6241–52,948 (20,711) 9.4–50 (26)	180–5211 (1771) 0.3–4.8 (2.3)	42,069–64,356 (50,563) 46.3–90.3 (71)
Mn	6.88–163 (58.7) 0.9–24.0 (11.1)	16.0–135 (68.3) 5.3–18.3 (10.9)	63.3–331 (178) 18–42 (29)	4.8–54 (31) 1.3–6.5 (5.1)	168–427 (244) 22.3–58 (44)
Cu	0.82–18.5 (7.7) 0.4–1.8 (1.1)	10.9–216 (78) 5.7–17.6 (9.4)	22–179 (58) 2.3–18 (9.5)	10–891 (405) 7.4–65 (46)	94–353 (190) 15.7–67.4 (34)
Zn	0.13–421 (113) 0.08–20.8 (6.7)	7.2–1068 (211) 5.2–39 (16)	34–1155 (486) 32–62 (49)	6–182 (83) 2.7–13 (9.2)	56–174 (91) 2.7–53 (19)
Ni	6.5–22 (11) 2.4–8.5 (4.7)	5.6–49 (15) 2.7–13 (5.9)	9.9–205 (104) 10–56 (39)	4.6–63 (36) 4.8–19 (14)	65–100 (83) 18–71 (37)
Pb	5.7–20 (8.8) 4.6–12 (8)	4.1–18.8 (8.1) 4.3–11 (7.2)	8.2–80.2 (30.5) 12–42 (25)	6.2–49 (20.6) 9–25 (18)	32–73 (45) 29–56 (42)

Values on top represent concentration in ppm and values below in bold represent percentage.

Table 3
Screening Quick Reference Table (SQUIRT) for metals in marine sediments (Buchman, 1999).

Elements	TEL	ERL	PEL	ERM	AET
Fe	–	–	–	–	22% (Neanthes)
Mn	–	–	–	–	260 ppm (Neanthes)
Cu	18.7	34	108	270	390 ppm (Microtox and Oyster Larvae)
Zn	124	150	271	410	410 ppm (Infaunal community)
Co	–	–	–	–	10 ppm (Neanthes)
Ni	15.9	20.9	42.8	51.6	110 ppm (Echinoderm Larvae)
Pb	30.2	46.7	112	218	400 ppm (Bivalve)

Table 4
Sediment guidelines and terms used in SQUIRT.

Sediment guidelines	
Threshold Effect Level (TEL)	Maximum concentration at which no toxic effects are observed
Effects Range Low (ERL)	10th percentile values in effects or toxicity may begin to be observed in sensitive species
Probable Effects Level (PEL)	Lower limit of concentrations at which toxic effects are observed
Effects Range Median (ERM)	50th percentile value in effects
Apparent Effects Threshold (AET)	Concentration above which adverse biological impacts are observed

45,258 ppm (avg. 42,791 ppm) and account for 81.6% to 88% (avg. 85.6%) of the total, thus suggesting its origin mainly from lithogenic sources. Followed by residual fraction Fe is mainly associated with Fe–Mn oxide fraction, indicating its precipitation as Fe–Mn oxy-hydroxides as well. While Fe–Mn oxide bound (F3) Mn varies from 178 ppm to 775 ppm (avg. 383 ppm) attaining 25.5% to 52.5% (avg. 36.8%) of the total. Unlike Fe, Mn exhibits lower association with residual fraction and higher association with other sedimentary fractions, namely Fe–Mn oxide (F3) and carbonate (F2) (Table 5), thus indicating its mainly anthropogenic/non lithogenic origin. The result also suggests higher mobility of Mn in this core.

Similarly, unlike in core S22, highest concentration of all the studied trace metals (Cu, Zn, Ni and Pb) is found to be associated with residual fraction (F5) in this core (i.e. core S13). However, in addition to that of residual fraction, other sedimentary fractions also seem to significantly control the distribution of metals in this core. Thus following residual bound fraction Cu is mainly associated with organic/sulphide (F4) fraction, while Zn and Ni are mainly associated with Fe–Mn oxide (F3) fraction (Table 5) similar to that observed in core S22. Zn and Ni thus exhibit relatively higher mobility than that of Cu in this core as well. However, following residual bound fraction Pb is mainly associated with

exchangeable (F1 = avg. 16.6%) and carbonate (F2 = avg. 14.6%) fractions in this core; thus seem to have higher mobility as compared to the other metals. Sediments of middle portion of Dudh creek therefore act as a sink of Cu, Zn and Ni, and also have a potential to act as their source upon changes in redox conditions similar to that observed in core S22. While high concentration of Pb that is associated with exchangeable and carbonate fractions is readily available. It is important to note here that in core S22, Pb did not show higher association with exchangeable (F1 = avg. 8%) and carbonate (F2 = avg. 7.2%) fractions. Instead, after residual fraction, Pb was mainly associated with Fe–Mn oxide (F3 = avg. 25%) and organic/sulphide (F4 = avg. 18%) fractions, suggesting difference in processes governing its distribution at the two locations.

When compared with sediment quality values (Tables 2–4), only one metal i.e. Mn indicates values above AET, suggesting its high bioavailability and risk of toxicity to sediment dwelling organisms. Followed by risk of toxicity of Ni wherein its average value in bioavailable fraction falls above ERM. While risk of toxicity of Cu in this core is relatively lower as its value fall above ERL. Fe concentration is much lower than AET and that of Pb and Zn is much below TEL, thus are not harmful to the organisms.

Whereas, in core collected towards the mouth of the creek (core S12), Fe, Mn and all the studied trace metals indicate their highest association with residual fraction (F5). The result therefore suggests main lithogenic origin for all the studied metals in this core. Fe in residual fraction varies from 40,718 ppm to 63,004 ppm (avg. 51,701 ppm) and account for 83% to 94% (avg. 90%) of the total (Table 6). Mn varies from 228 ppm to 617 ppm (avg. 352 ppm) and account for 29% to 72% (avg. 50.4%) of the total. Following residual bound fraction, Mn distribution is largely controlled by Fe–Mn oxide fraction. Thus Mn is considered to be more labile as compared to Fe in this core, similar to that observed for cores S22 and S13. Fe–Mn oxide (for Cu = avg. 12.6%, Zn = 21% and Ni = 12.4%) and organic/sulphide (for Cu = avg. 12%) fractions are found to play a significant role in metal distribution in this core as well, similar to that observed in cores S22 and S13. Relatively higher concentration of Pb in exchangeable (avg. 16%) and carbonate (avg. 11%) fractions similar to that observed in core S13, suggests, its relatively higher mobility as compared to other metals in this core. Sediment deposited towards the mouth of the creek can therefore be considered to act as sink of Cu, Zn and Ni, while Pb seems to be readily available.

Similar to core S13, only one metal i.e. Mn indicates values above AET (Tables 2–4) in this core, suggesting its very high bioavailability and risk of toxicity to sediment dwelling organisms. Risk of toxicity of Cu and Ni is relatively lower as their values fall above ERL. Similar to cores S22 and S13, Fe concentration in core 12 is much lower than AET. Pb and Zn concentration is also much below TEL, thus these metals are not harmful to the organisms at

Table 5
Range and average of metal concentration in five fractions.

Core S13	F1	F2	F3	F4	F5
Fe	4.7–18.5 (9.8) 0.009–0.04 (0.02)	10.6–80.3 (28.1) 0.02–0.15 (0.06)	5715–8253 (6494) 11.2–16 (13)	92.3–2110 (693) 0.18–4.3 (1.4)	39,789–45,258 (42,791) 81.6–88 (85.6)
Mn	4.4–21.7 (8.9) 0.4–1.9 (0.9)	163–494 (305) 23.4–43.2 (29.6)	178–775 (383) 25.5–52.5 (36.8)	21.4–88.8 (54.7) 3.1–7.9 (5.2)	210–332 (254) 17.7–47.5 (27.5)
Cu	0.3–2.8 (1.7) 0.2–2.5 (1.4)	4.3–17 (9.0) 5–6.7 (6.0)	12.8–27.8 (17.3) 8.6–16 (12.5)	10.4–148 (45.7) 12.5–54.1 (25.1)	53.2–91.4 (73.8) 28.7–65.5 (55.1)
Zn	0.04–1.17 (0.44) 0.06–0.8 (0.4)	2.5–20 (7.5) 3.4–14.1 (6.9)	19.2–64.7 (38.4) 26.7–51.2 (37.5)	2.2–17.5 (7.7) 3–16.1 (7.3)	38–53.7 (44) 27–67 (48)
Ni	5.9–8.2 (7.5) 4.6–8.2 (6.1)	5–25 (11.2) 5.2–14.2 (8.2)	19.3–60 (36.2) 20.1–34.1 (27.4)	2.2–29 (9.9) 2.3–16 (6.9)	58–68 (62.6) 32.2–64 (51.4)
Pb	7.5–11.5 (9) 7.1–20.6 (16.6)	5.9–10.9 (7.9) 6.3–19.8 (14.6)	2.3–18.4 (5.9) 4.6–17.4 (9.3)	1–25 (5.4) 1.7–24 (7.4)	25.1–47.8 (29.7) 45.2–61.4 (52.2)

Values on top represent concentration in ppm and values below in bold represent percentage.

Table 6
Range and average of metal concentration in five fractions.

Core S12	F1	F2	F3	F4	F5
Fe	6–13 (9) 0.009–0.024 (0.016)	2.6–31 (8.6) 0.004–0.046 (0.015)	2888–5959 (4494) 5.3–10 (7.8)	89–5648 (1409) 0.1–10 (2.6)	40,718–63,004 (51,701) 83–94 (90)
Mn	5.3–18.7 (11.8) 1.1–2.4 (1.7)	40.2–115 (70) 5.9–17 (9.9)	94–467 (231) 12.3–50 (30)	16–120 (58) 1.8–14 (7.7)	228–617 (352) 29–72 (50.4)
Cu	0.3–3.8 (2) 0.2–2.8 (1.5)	5–11 (7.3) 4–7.3 (5.5)	11–26 (16.8) 8–17 (12.6)	4.1–30 (16) 3–22 (12)	62–109 (91) 58–76 (68)
Zn	0.2–0.9 (0.5) 0.3–1.16 (0.5)	0.9–6.0 (2.5) 1–5.8 (2.7)	6.7–41 (19.5) 7.9–38 (21)	1–8 (4.4) 1.2–10 (5.1)	42–83 (62) 50.1–89.5 (71)
Ni	5.1–9.6 (8.2) 5–10.2 (8.4)	1.7–5.7 (3.2) 1.8–4.8 (3.2)	6.3–23 (12.5) 6.3–19.4 (12.4)	3–12 (7.8) 3–12 (7.9)	53–80 (67) 58–80 (68.1)
Pb	5.1–7.9 (6.3) 12.1–18 (16)	3–5.9 (4.6) 7.8–13.5 (11)	0.08–6.1 (2.6) 0.2–13.7 (6.2)	1.2–5.1 (3.5) 3–13 (8.4)	21–28 (24) 48.8–68.6 (58.6)

Values on top represent concentration in ppm and values below in bold represent percentage.

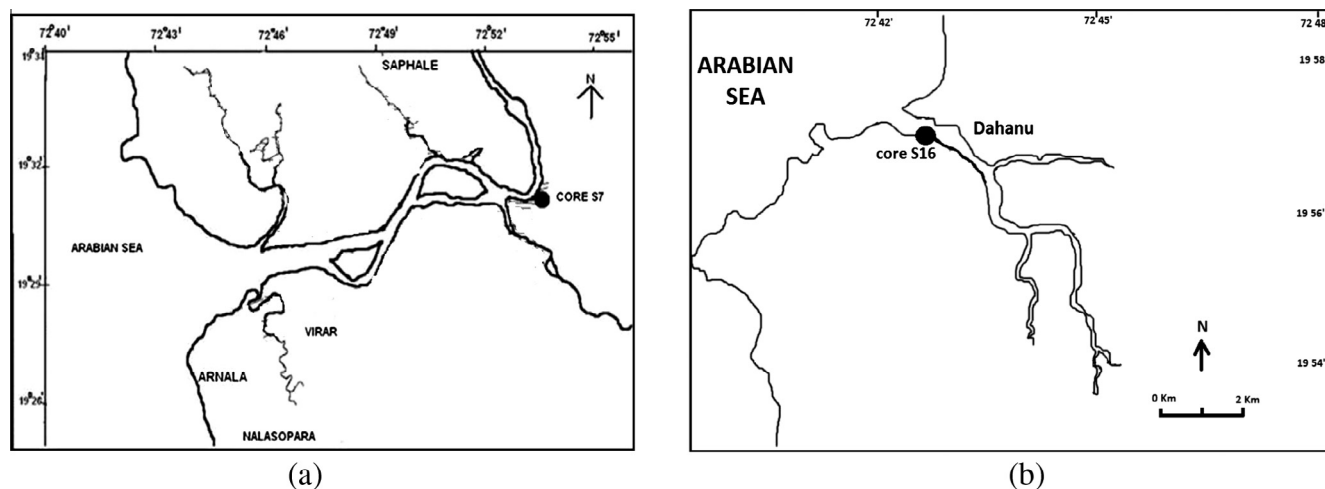


Fig. 2. Map showing locations of the sediment cores sample collection in (a) Vaitarna estuary, (b) Khonda creek.

this location as well. In addition, the magnitude of metal enrichment in bioavailable fraction is noted to show a decrease from inner portion of the creek to closer to the mouth i.e. metal concentration in bioavailable fraction follows the order: core S22 > core S13 > core S12 for all the studied metals except Mn.

Thus, in addition to some similarities, concentration and association of trace metals at the three locations show a large difference. Relatively higher concentration of Pb in exchangeable and carbonate fractions noted in cores S12 and S13 and that in Fe–Mn oxide and organic/sulphide fractions in core S22 can be explained by the difference in stability of this metal under varying physico-chemical conditions. Core S22 as explained earlier, due to its proximity to sewage outfall, as well as being the least flushed part of the creek is assumed to have lower dissolved oxygen concentration. Thus under anoxic or low oxygen conditions metals tend to readily form stable metal sulphide complexes which ultimately get deposited within the sediment column. Further downstream the physico-chemical conditions tend to change. Here tidal flushing seems to play a major role in distribution and dilution of metals. Tidal flushing is highest near the mouth and decreases further upstream. The influence of this process on metal distribution within Dudh creek is clearly evident from the observed concentrations of metals in bioavailable (i.e. exchangeable, carbonate, Fe–Mn oxide and organic/sulphide) and residual fractions (Tables 1, 5 and 6). Wherein, a significant decrease in bioavailable metal concentration and an increase in residual metal concentration from inner portion to closer to the mouth of the creek have been observed.

Table 7

Concentration of metals in bioavailable fractions (F1 + F2 + F3 + F4) in surface sediments of cores collected from Dudh creek, Vaitarna estuary and Khonda creek.

Ppm	Dudh creek			Vaitarna estuary	Khonda creek
	Core S12	Core S13	Core S22	Core S7	Core S16
Fe	5781	6199	48,874	8114	5861
Mn	641	574	164	670	689
Cu	35	48	1038	59	28
Zn	47	37	2673	24	18
Ni	42	44	303	29	28
Pb	22	22	137	23	26

Lead sulphides are not stable under such well flushed oxygenated conditions. Thus probably show its lower association with organic/sulphide fraction and tend to show its higher association with exchangeable and carbonate fractions in the downstream region.

3.1.1. Comparison of speciation of metals in Dudh creek sediment with nearby Vaitarna estuary and Khonda creek

The seriousness of metal contamination within Dudh creek sediments can be further better understood by comparing the results with other less industrially impacted wetlands of the region. Thus metal speciation within surface samples of Dudh creek sediments have been compared with intertidal sediments of nearby Vaitarna estuary (Fig. 2a) and Khonda creek (Fig. 2b).

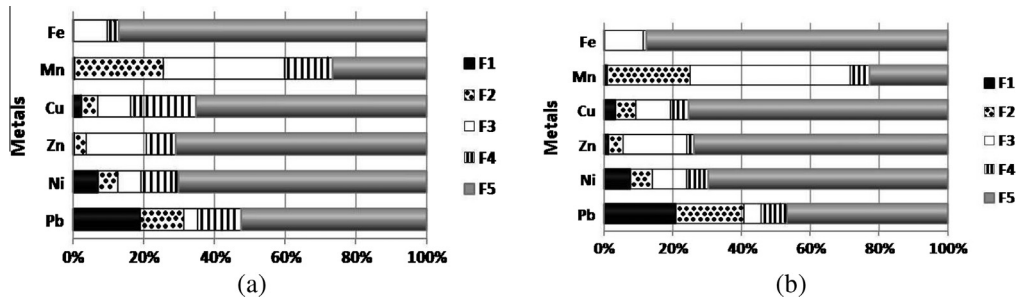


Fig. 3. Fractionation of metals in surface sample of (a) core S7 and (b) core S16.

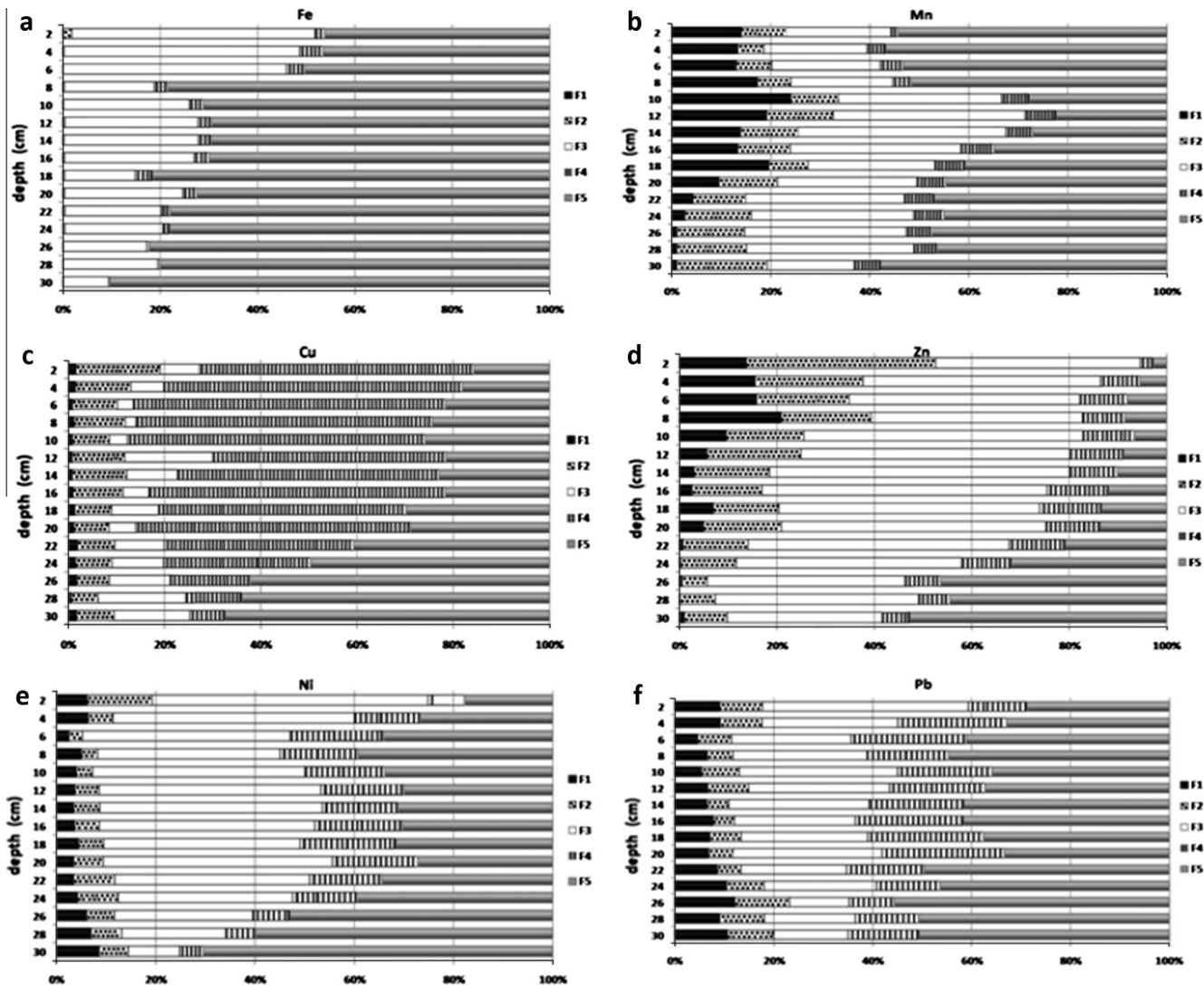


Fig. 4. Vertical distribution of (a) Fe, (b) Mn, (c) Cu, (d) Zn, (e) Ni and (f) Pb associated with different fractions in core S22.

Surface sediments act as diffusion barrier for solutes migrating upwards from reducing zones of sediment and exchange readily with suspended sediments and water. Organisms feeding on suspension matter and also epibenthic organisms are exposed directly to metals in the environment of the sediment-water interface (Luoma and Bryan, 1981). Thus, the result of speciation analysis

of metals on the surface sediment sample of core S7 collected from Vaitarna estuary and core S16 collected from Khonda creek have been compared with that of Dudh creek (Table 7). The result of speciation analysis indicated all the studied metals except Mn to be mainly associated with residual fraction at the two locations (Fig. 3a and b). Thus, indicating lithogenic as the main source of

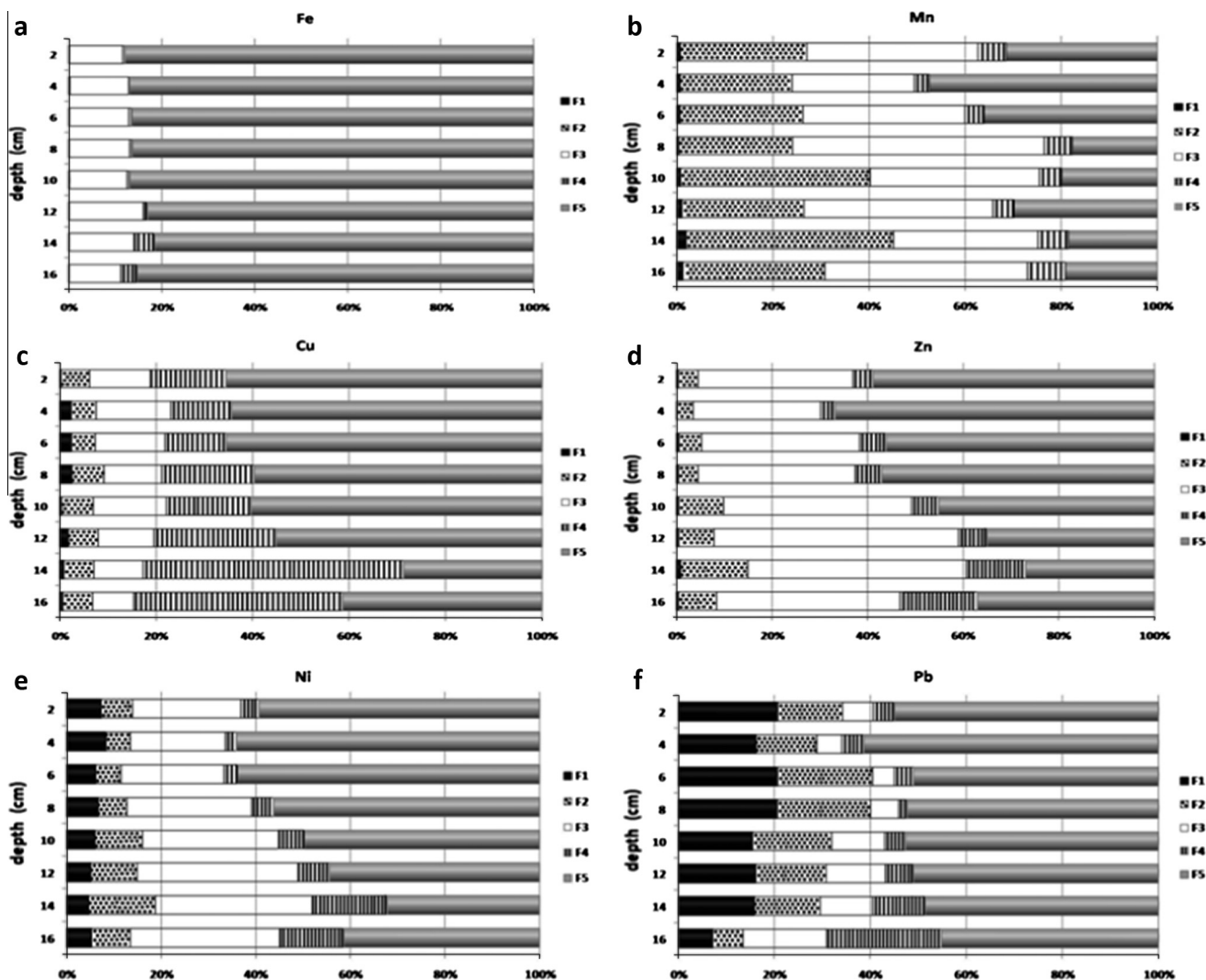


Fig. 5. Vertical distribution of (a) Fe, (b) Mn, (c) Cu, (d) Zn, (e) Ni and (f) Pb associated with different fractions in core S13.

metals in Vaitarna estuary and Khonda creek unlike Dudh creek which showed non-lithogenic origin for most of the studied metals especially in the inner portion of the creek.

3.2. Change in metal speciation with depth: anthropogenic and diagenetic influence

Variation in metal speciation along the length of the core helps in understanding the processes controlling metal distribution over a period of time. It also determines the fate of the deposited metals within the sedimentary column. Cores with maximum length of 56 cm collected from Dudh creek will represent not more than forty-five years of sediment accumulation. Since, rate of sedimentation within coastal region including mudflats of Maharashtra have been found to vary between 0.24 – 2.72 cm/yr (Fernandes, 2012; Sharma et al., 1994).

The depth-wise distribution pattern of Fe in Fe–Mn oxide fraction (F3) of core S22 collected from inner portion of the creek shows an increase, while Fe in residual fraction shows a decrease from bottom to surface (Fig. 4a). Thus suggesting decrease in addition of Fe of lithogenic origin in recent years as compared to the past. Higher association of Fe with reducible fraction (F3) above 8 cm depth further suggest, the oxidation and re-precipitation of

Fe released as Fe^{2+} from Fe–Mn oxyhydroxides dissolved under reducing conditions in lower levels. Similarly, Mn in exchangeable fraction shows a notable increase from bottom to surface of the core (Fig. 4b), thus suggesting a gradual increase in anthropogenic Mn loading in recent years. Between 16 cm and 10 cm depths it shows least association with residual fraction (F5); and large increase in exchangeable (F1) and Fe–Mn oxide (F3) fractions. Thus, similar to that of Fe, depth-wise distribution pattern of Mn also seems to represent influence of post depositional changes on its speciation at this depth. Mn association with sulphide fraction is the least as it prefers to escape from the deeper anoxic layers to near surface oxic layers and form Mn oxyhydroxides (Zwolsman et al., 1993; Lacerda et al., 1997).

The depth-wise distribution pattern also indicate residual fraction bound Cu to show a large decrease and that associated with organic/sulphide fraction to exhibit a large increase from bottom to surface of the core (Fig. 4c). The upper 22 cm of the core therefore reflects non-lithogenic as the main source of Cu in this part of the creek. Similar to that of Cu, the depth-wise distribution pattern of Zn also indicates a gradual decrease in residual bound fraction and an increase in exchangeable, carbonate and Fe–Mn oxide bound fractions from bottom to surface of the core (Fig. 4d). Residual bound Zn is noted to be very low above 24 cm depth

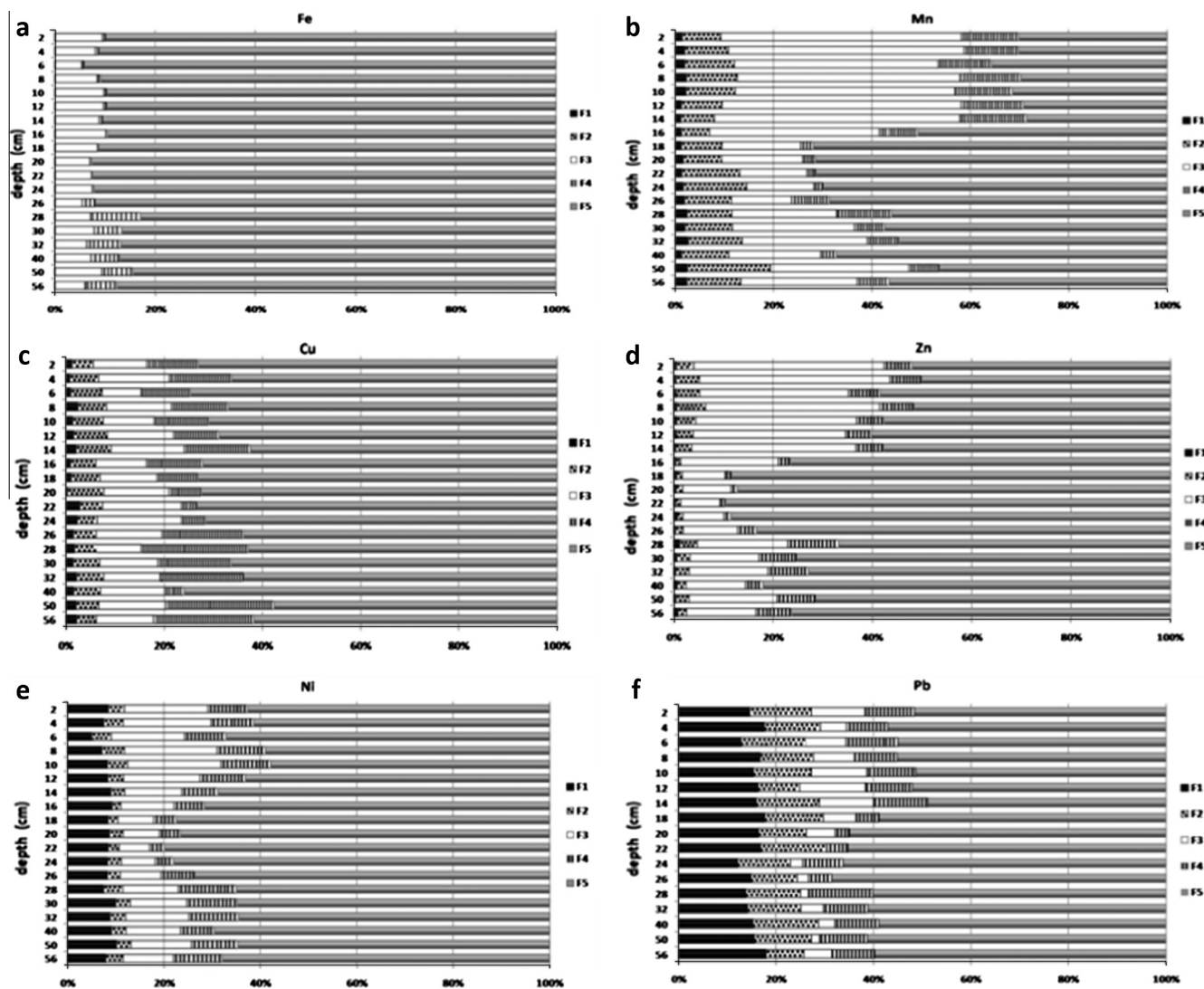


Fig. 6. Vertical distribution of (a) Fe, (b) Mn, (c) Cu, (d) Zn, (e) Ni and (f) Pb associated with different fractions in core S12.

and almost negligible at the surface, thus suggesting surface sediment to represent exclusively anthropogenically added metal load from industrial waste/effluents. Similar to that of Zn, Ni also indicates a decrease in residual bound fraction and an increase mainly in Fe–Mn oxide bound fraction from bottom to surface of the core (Fig. 4e). Ni in organic/sulphide fraction also indicates an increase towards surface i.e. up to 4 cm depth. Despite of its overall highest association with residual fraction, Pb exhibits a decrease in residual fraction and an increase in Fe–Mn oxide and organic/sulphide fractions from bottom to surface of the core similar to other studied metals (Fig. 4f). Thus non-lithogenic source is found to be the main source of Pb especially within upper 20 cm i.e. in recent years as compared to the past. The result therefore indicates metal speciation in core S22 to have been completely modified by increased addition of bioavailable metal load in recent years from anthropogenic activities.

While in core S13 collected from middle portion of the creek, the depth-wise distribution pattern of Fe and Mn associated with different sedimentary fractions does not show significant trend unlike in core S22 (Fig. 5a and b). However, the depth-wise distribution patterns of Cu, Zn, Ni and Pb in residual fraction show an increasing trend from bottom to surface of the core (Fig. 5c–f). The noted result is therefore contrasting to that observed for core

S22. Cu associated with organic/sulphide fraction indicates a decrease from bottom to surface, thus suggesting decrease in mobility of Cu towards surface of the core. Large percentage of Cu in oxidizable phase suggests complexation by organic matter in the oxic/suboxic zone above 10 cm depth and incorporation in sulphides in the anoxic zone (Rubio et al., 2010) probably below 12 cm depth. Similarly, Fe–Mn oxide (F3), organic/sulphide (F4) and carbonate bound (F2) Zn exhibit a decreasing trend from bottom to surface of the core. Fe–Mn oxide (F3), organic/sulphide (F4) and carbonate (F2) bound Ni also show a decrease from bottom to surface. However exchangeable fraction bound Ni shows slight increase towards the surface. Fe–Mn oxide (F3) and organic/sulphide (F4) bound Pb also indicates a decrease towards the surface of the core. The result in general therefore suggests increase in lithogenic metal input in surface sediments at this location. However, in exchangeable (F1) and carbonate (F2) fractions, Pb shows an increasing trend towards surface. Similarly exchangeable fraction bound Ni had also shown slight increase towards surface. Thus suggesting increased anthropogenic input of Pb and to some extent Ni in recent years as well at this location.

Sediment core S13 collected from the middle portion of the creek therefore seems to receive relatively higher proportion of metals of lithogenic origin towards surface of the core as compared

to the past. Metal (Pb) concentration of anthropogenic origin also shows a simultaneous large increase towards surface. Deposition of lithogenic material/sedimentary particles received from construction activities being carried out in near vicinity probably explains the increased deposition of residual bound metals towards surface of the core, while large amount of industrial waste/effluents continues to enter the creek environment from the upstream region.

In core S12 collected towards the mouth of the creek, major association of Fe with residual fraction all along the length of the core (Fig. 6a) indicates less influence of anthropogenic activities on Fe distribution. Fe distribution also seems to be less affected by post depositional changes, as the signatures of migration and re-precipitation of Fe in Fe–Mn oxide fraction are not very clear or prominent within the sediment column. Contrastingly, Mn shows large increase in Fe–Mn oxide fraction above 18 cm depth, where corresponding decrease in residual bound Mn is observed (Fig. 6b). The result therefore strongly suggests migration of soluble Mn^{2+} ions from the reducing subsurface layers and subsequent precipitation and enrichment of MnO_2 upon re-oxidation in the oxygenated surface layer (Sirinawin and Sompongchaiyakul, 2005). Mn in exchangeable and carbonate bound fractions however does not show much variation from bottom to surface of the core. Thus similar to that observed in core S22 and unlike in core S13, Mn in Core S12 shows signatures of early diagenetic reactions.

The depth-wise distribution pattern of Cu associated with different sedimentary fractions does not show any significant variation pattern or specific trend in this core (Fig. 6c). The speciation of Cu, therefore, seems to have not been modified much by post depositional or anthropogenic changes. While, the depth-wise distribution pattern of Zn associated with Fe–Mn oxide fraction shows sudden increase above 16 cm depth (Fig. 6d). Similarly, Fe–Mn oxide bound Ni (above 16 cm depth) as well as Pb (above 14 cm depth) also show an increasing trend (Fig. 6e and f). This increase in trace metal concentration (Zn, Ni and Pb) in Fe–Mn oxide fraction similar to that observed for Mn, suggests their mobilization and re-precipitation with Fe–Mn oxides within oxic surface sediment. Exchangeable and carbonate bound Ni and Pb however does not show much variation from bottom to surface of the core (Fig. 6e and f). Additionally, increase in metal concentration in non residual fractions (Mn, Zn and Pb) above 14 cm depth suggests increase in non lithogenic/anthropogenic input in recent years as compared to the past. Trace metals therefore seem to have mainly lithogenic origin in the past or towards bottom of the core. While their distribution seem to have been largely controlled by post depositional processes in recently deposited sediments towards mouth of the creek.

Thus metal speciation in Dudh creek show spatial and temporal variation in anthropogenic influence. Processes controlling metal distribution also seem to change from inner portion to closer to the mouth of the creek as well as over a period of time. Anthropogenic inputs control the distribution of metals towards inner portion while diagenetic processes/redox reactions control the distribution of metals towards the mouth. The middle portion however shows signatures of sediment dumping.

4. Conclusion

Non-lithogenic source was found to be the main source of metals in core S22 collected from inner portion of the creek especially within upper 22 centimeters. Metal speciation in core S22 therefore have been completely modified by anthropogenic activities in recent years. While Fe–Mn oxide largely controlled the metal distribution in core collected closer to the mouth of the creek.

The magnitude of metal enrichment in bioavailable fraction also showed a spatial variation i.e. a decrease from inner portion of the creek to closer to the mouth.

Acknowledgments

One of the authors (Dr. Samida P. Volvoikar) wishes to thank the University Grants Commission (UGC) for granting fellowship under the “Research Fellowships in Sciences for Meritorious Students” scheme. Authors are thankful to the India Meteorological Department for providing the monsoon data.

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