

Sources and Factors Controlling the Distribution of Metals in Mudflat Sedimentary Environment, Ulhas Estuary, Mumbai

LINA FERNANDES and G. N. NAYAK
Department of Marine Sciences, Goa University, Goa- 403 206
E-mail: nayak1006@rediffmail.com

Abstract: Vertical variations for various physico-chemical parameters such as pH, TOC, TP, TN, sediment components and metals such as Fe, Mn, Cu, Pb, Co, Ni, Zn, Cr, V and Al of a sediment core collected from a mudflat bordering the Ulhas estuary, near Retibandar in Mumbai, was analysed at every 2 cm interval. Based on the distribution pattern of sediment, the core is divided into three parts. The upper and the lower portions are found to be dominated by clay and silt fractions while in the middle portion, sand is found to be in higher percentage. The varying thickness and the variations in sediment size of the three parts suggest that sedimentation rate and processes are not the same along the length of the core. The hydrodynamic conditions of the depositional environment of the mudflat was assessed using the Triangular diagram proposed by Pejrup (1988), which indicates that the sediment deposition took place under relatively calmer conditions. Higher TOC, TP and TN in the upper portion of the core compared to middle and lower portions indicate increasing impact of human activities on the estuary in recent years. The results of metal concentration indicate a significant upward enrichment of Cu and Pb, with the highest concentrations in the uppermost 0-12 cm layer, supporting the effect of increasing anthropogenic influence in recent years. Correlation coefficients, dendrogram hierarchical cluster and factor analysis has been applied to the data, to assess the diverse sources and mechanisms influencing the metal distribution in the sedimentary column of the estuary.

Keywords: Trace metals, coastal wetland, anthropogenic effect.

INTRODUCTION

Trace metal cycling and its fate in coastal wetland, a typical dynamic ecosystem, have fascinated many researchers, because they not only reveal the evolution processes of natural environment (Wang and Liu, 2003), but also indicate the intensity of human activities (Rabouille et al., 2007). The Estuarine environment and its associated mudflats play an important role in sediment deposition which acts as a sink for particle associated contaminants such as heavy metals. Both natural and anthropogenic activities may introduce trace metals to aquatic regions, but anthropogenic effects may seriously degrade the environment at local to regional scale (Siegel, 2002). Essentially, trace metals are introduced into the aquatic environment either insoluble or in particulate form through various sources. Riverine transported heavy metals originates from the weathering of natural rocks and mineralized deposits while anthropogenic sources include mining, smelting, electroplating and chemical manufacturing plants, as well as domestic discharges, shipping and boating activities. Input from marine through tides and tidal currents and also atmosphere cannot be neglected. In either case, physical, chemical and biological processes act to transform and translocate these contaminants.

Sediments form a crucial link in these processes and are the ultimate sink in the dispersion, accumulation and modification of pollutants in natural systems (Siegel, 2002; Jones et al., 2003). Therefore it is said that sediments are a major carrier phase for pollutants and provide useful spatial and temporal information (Maher et al., 1999; Birch et al., 2000; Birch, 2003; Singh and Nayak, 2009; Fernandes and Nayak, 2009).

The process of sediment deposition is common in intertidal flats of estuaries. Sediment grain size is an important factor in influencing the concentration of heavy metals, with metal concentrations significantly enriched in fine grained sediments, mainly clay and silt, which have high absorption capability due to their large specific surface area. Being formed by the deposition of fine particles with their associated contaminants, each layer of buried sediment represents a record of the environmental conditions, reflecting the water quality and possible effects of anthropogenic contamination at a certain period (Von Gunten et al., 1997). The elemental variation in core sediments reflects the geochemical history including any anthropogenic impact of a given region. Therefore, the study of undisturbed sediment cores from marine and coastal environments can provide historical record of various influences in the aquatic system by indicating both natural background level and

the man induced accumulation of elements over an extended period of time (Winkels et al., 1993; Buckley et al., 1995).

Mumbai, a metropolitan city, with a population of about ten million generates sewage of about 2000 million litres per day (mld). Large amounts of these untreated/partially treated industrial and domestic effluents are released into the coastal and marine environment. Several studies have been undertaken along the Mumbai coast, for the determination of trace metals, as indicators of pollution, in coastal sediments. The transport and distribution of trace metals as well as radionuclides in water, suspended particulate matter and sediment in inshore areas of Mumbai have also been extensively studied (Patel et al., 1975, 1985; Zingde and Desai, 1981; Bhosale and Sahu, 1991; Sharma et al., 1994, Jha et al., 2003; Ram et al., 1998, 2003, 2009). The present study was carried out to understand the sources and factors controlling the distribution of metals and to assess the impacts of fluvio-marine and geochemical processes in influencing the distribution of 10 metals (Fe, Mn, Cu, Pb, Co, Ni, Zn, Cr, Al and V) with time in a sediment core of 60 cm depth, collected from a mudflat of middle estuarine region of a tropical estuary.

STUDY AREA

The study was carried out in Ulhas Estuary, Mumbai which lies at longitude 72°53'52.2"E and latitude 19°17'18.4"N on the west coast of India (Figure 1). Ulhas River, about 135 km long, rises in the rainy ravines of the Bor Ghat and after flowing about 100 km, traversing through hilly tracks and mountainous terrain of the Western Ghats reaches Kalyan. From Kalyan onwards, it meanders through coastal plains and finally reaches the Arabian Sea at Vasai Creek (Bhosale and Sahu, 1991). The river is shallow having sandy basin, since the land

runoff carry huge sediments from its catchment area. An outlet of the river touches the head of the Thane creek south of Mumbra. Dredging activities near Mumbra resuspend the finer sediments and disturb the normal distribution of particulate and dissolved materials along its course. The region receives an annual mean rainfall of 2600-2800 mm during the monsoon season (June to September). The estuary is strongly influenced by tides, with spring tidal range varying from about 4.5 m at the mouth to 2.8 m at the upstream end. Barrages constructed upstream of the estuary and its associated tributaries allow only a limited river discharge to flow during the dry season. Several industrial complexes and estates located in Mumbra-Ambarnath segment release wastewater into the estuary either directly or indirectly. The estuarine flushing time varies between 73 and 211 tidal cycles (NIO, 1994) 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.

METHODOLOGY

Sediment core of 60 cm length was collected, using a hand driven PVC tube of 5.5 cm diameter from the middle of the tidal flat bordering the estuarine region of Ulhas River (Figure 1). In the laboratory, the core was sub-sampled at 2 cm intervals, transferred to labelled polyethylene bags, determined for pH values with a pH meter (Thermo Orion 420 A+ model) and stored frozen to -20°C till further analysis.

For sedimentological and geochemical parameters, the sediment samples were dried in an oven at 60°C. Analysis of sediment component was carried out using standard sieve and pipette techniques after destruction of organic matter with H₂O₂ (Folk, 1974). Sediment samples were finely ground with mortar and pestle for

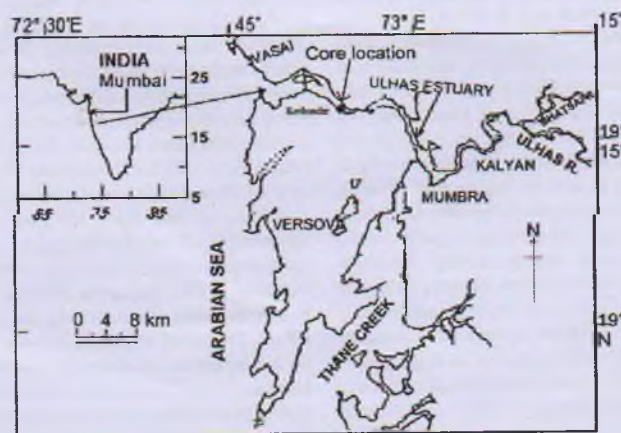


Fig. 1. Map showing the sampling location.

geochemical analysis. Total organic carbon (TOC) content was determined employing a rapid titration method (in chromic acid environment) (Walkley and Black, 1934). For Total Phosphorus (TP) and Total Nitrogen (TN) in sediment, standard procedure (Grasshoff, 1999) was employed wherein the sediment sample was autoclaved with persulphate, boric acid and sodium hydroxide mixture and then analysed for TN, as a azo dye complex, at 543 nm, while, TP was measured using the ammonium molybdate method with ascorbic acid reduction proposed by Murphy and Riley (1962). Sediment samples for trace metal analysis were digested using a HF-HClO₄-HNO₃ total dissolution technique (Jarvis and Jarvis, 1985). The digested samples were aspirated for Al, V, Fe, Mn, Cu, Pb, Co, Ni, Zn and Cr with the help of Varian AA 240 FS flame Atomic Absorption Spectrometry (AAS) with an air/acetylene flame for all of the above elements except for Al and V for which nitrous oxide/acetylene flame was employed at specific wavelengths.

The analytical results were statistically processed with factor analysis to group metals with similar behaviour and with cluster analysis to identify sections with varying levels of association in the sediment profile. Pearson's correlation coefficient was also computed. All statistical analyses were performed using the computer software STATISTICA 6.

RESULTS AND DISCUSSION

Sediment components

The depth wise plots of pH, TOC, TP, TN, and sediment components (sand, silt and clay) are shown in Figure 2. The values for pH are found in the range of 6.96-8.42 while for TOC the values are in the range from 0.97-1.56 %. For TP and TN, the data varies from 0.19-0.64 mg/g and 0.28-2.34 mg/g respectively. Sand percentage varies from 0.59- 45.76 % while for silt and clay the values range from 25.04-51.41 % and 29.20-69.68 % respectively. The distributions of sediment components show a fluctuating trend of sand-silt-clay, especially in the middle portion of the core. Based on the distribution of sediment components, the core is divided into three parts; lower portion from 60 to 44 cm, middle portion from 44 to 24 cm and the upper portion from 24 to 0 cm. In the lower portion, pH is found to increase from bottom to 44 cm depth while TOC, TP, TN show a fluctuating increasing and decreasing trend whereas sand and silt exhibits a corresponding opposite trend to each other, with lower percentage of sand between 60 and 48 cm, which is then followed by an increasing trend of sand and decreasing trend of silt. The lower portion is found to be dominated by clay and silt fractions with average values of 45.49 and 42.65 %

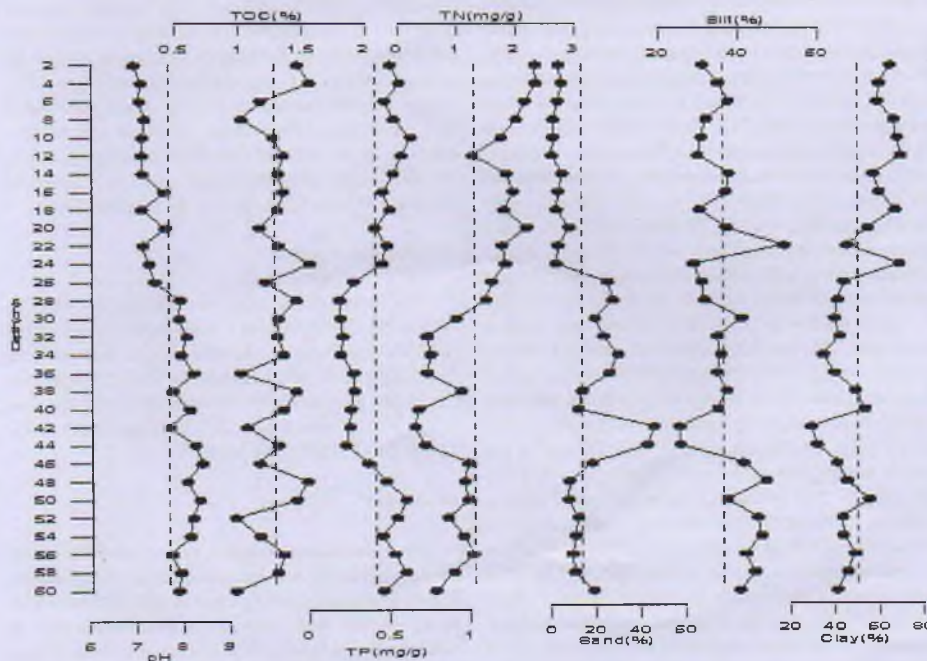


Fig. 2. Downcore variations of pH, TOC, TP, TN and sediment components with vertical lines of average values.

respectively. pH, TP, TN along with clay show a peak value at 50 cm depth which co-incidentally corresponds to the highest concentration of TP (0.603 mg/g) and clay (55.36 %) while TOC and silt show an increased peak at 48 cm depth which also corresponds to the highest concentration of TOC (1.54 %) for this portion of the core. Clay is found to associate significantly with TP (0.88) and TN (0.75) while silt shows good association with TP (0.64) and TN (0.60). TP with a correlation of 0.53 shows good association with TN. Sand shows significant negative association with TP (-0.88) and TN (-0.79) and also with silt (-0.86) and clay (-0.86).

In the middle portion of the core, pH decreases, TOC and TP fluctuate with decreasing and increasing trend while TN shows an increasing trend towards the surface. Higher percentage of sand is observed in this portion of the core compared to the lower and upper portions with an average value of 26.54 %. This indicates supply of more coarser material from the catchment area probably due to large scale agricultural practices/ anthropogenic activities including sand mining supported by high rainfall. Sand and silt show larger variations compared to clay. Clay shows a general increasing trend towards the surface. pH, TOC, TN, silt and clay show a decrease at 42 cm depth which corresponds to the lowest concentration for TN (0.28 mg/g), silt (25.04 %) and clay (29.20 %) within the middle portion. However, sand percentage is found to be maximum at this depth (45.76 %) when the entire length of the core is considered. At 38 cm depth, TOC, TP, TN and silt show a distinct peak. In general, TP and TN are found largely to show an opposite trend to the sand distribution profile. Clay shows significant correlation with TOC (0.64), TP (0.79) and TN (0.60) while TN shows good association with TOC (0.57) and TP (0.49). Sand shows negative correlations with TOC (-0.61), TP (-0.57) and TN (-0.53). In the upper portion, pH decreases and TN increases, whereas TOC and TP fluctuates with overall increasing trend for TP. Sand, in general, shows largely a constant trend with silt decreasing and clay increasing towards the surface. Silt and clay with average values of 34.78 % and 61.92 %, are found to dominate the upper portion of the core. TOC and clay show a sharp peak at 24 cm depth. Good association is shown by sand with TN (0.61) while clay shows strong negative association with silt (-0.96) and to some extent with sand (-0.59). In general, in the lower portion of the core, clay shows good association with TP and TN and in the middle portion clay shows good correlation with TOC, TP and TN. This reflects an incorporation of organic matter to the finest fractions of sediments by adsorption phenomenon (Salomons and Forstner, 1984). Negative correlation between organic matter (TOC, TP, TN) and sand indicates preferences of organic matter to finer fractions and not to associate with coarser sediments. However, in the upper portion of the core sand shows association with TN.

When the variations of parameters are viewed with respect to the average values drawn, it is seen that in the lower portion of the core pH and silt are found to be the dominant components while the concentration of TOC is found to be the lowest. In the middle portion, sand is present in higher percentage compared to lower and the upper portions while TP and TN are found to show the lowest concentration. TOC, TP, TN and clay show the highest concentration in the upper portion of the core while sand percentage is the lowest along with pH. Lower percentage of sand is observed in the upper portion of the core compared to the middle and bottom portion and might be due the construction of barrages in the upstream region of the estuary which restricts the normal flow of water and as such results in settling of more finer particles.

Further, an attempt has been made to understand the hydrodynamic condition of the depositional environment of the study area by using the ternary diagram proposed by Pejrup (1988). The diagram (Figure 3a) describes the hydrodynamic condition by using clay percentage in the mud fraction represented by sections I to IV, which reflects increasing violent hydrodynamic conditions. Further, the sediments are also classified according to their sand percentage represented by four sections viz, A to D. In the present study, it is seen that the sediment fractions fall largely under group II and III of sections C and D (Figure 3a), indicating that the sediment deposition took place under less violent to relatively calmer conditions. Also textural class of sediment is understood by plotting the sediment component data on the ternary diagram proposed by Reineck and Siefert (1980). In this diagram (Figure 3b), muddy intertidal sediments are commonly subdivided into Sand flats, Mixed flats, Mudflats and Mature mudflats on the basis of sand or mud contents. When the data points are plotted (Figure 3b), it is observed that the sediments fall largely in the mudflat class.

Metal geochemistry

The distribution of selected metals viz; Fe, Mn, Cu, Pb, Co, Ni, Zn, Cr, Al and V with depth is represented graphically in Figure 4. The data is found to range from 4.15-5.04 % for Fe, 636-1320 ppm for Mn, 87-199 ppm for Cu, 29-104 ppm for Pb, 30-107 ppm for Co, 61-154 ppm for Ni, 104-147 ppm for Zn, 221-7163 ppm for Cr, 4.45-7.90 % for Al and 45-286 ppm for V.

Fe and Mn

From the bottom to surface, Fe and Mn show almost similar decreasing and increasing trend except at few depths where an opposing trend is observed viz, from 46-42 cm and from 10-2 cm. A general decrease in concentration is seen in case of Fe and Mn from bottom to surface with some fluctuations in mid-portion of the

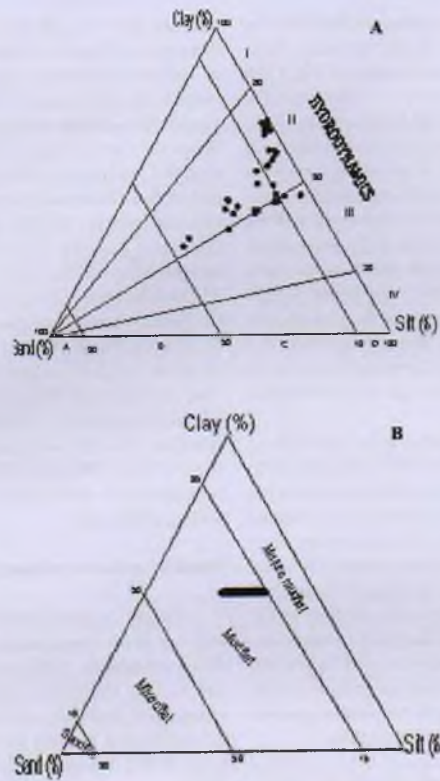


Fig. 3a. Triangular diagram for the classification of hydrodynamic conditions after Pejrup (1988), b. Ternary diagram for a revised textural classification of sediments on the basis of Sand/Mud ratios after Reineck and Seifert (1980).

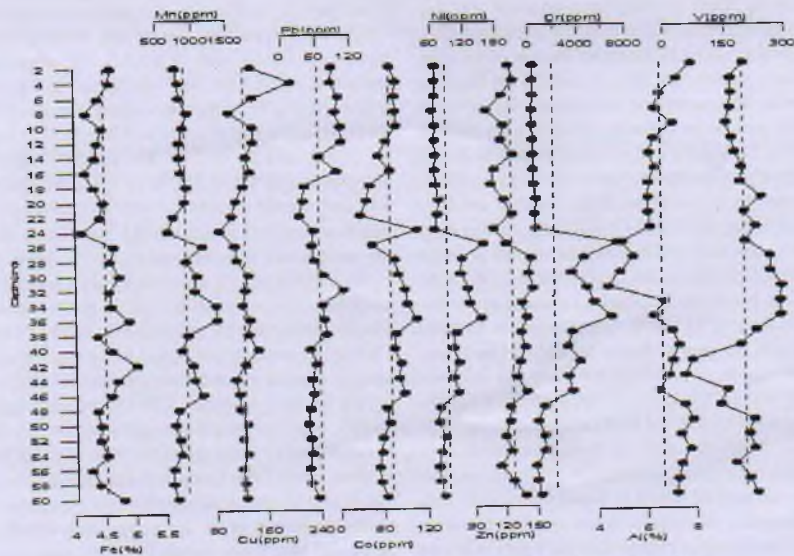


Fig. 4. Downcore variations of metals with vertical lines of average values.

core. Two significant peaks are observed for both the elements at 26 cm and 36 cm depth, the latter depth corresponding to the highest concentration of Mn (1320 ppm) when compared for the entire core. However, for Fe the highest concentration (5.04 %) is seen at 42 cm depth. At depth of 24 cm, a decreased peak is observed for Fe and Mn wherein both the metals show the lowest concentration, 4.15 % for Fe and 636 ppm for Mn when seen for the entire core. When the distribution of Fe and Mn is analysed separately for the different portions of the core, it is observed that both the elements show a more constant trend in the lower and upper portion when compared to the middle portion of the core wherein a large fluctuating trend is seen. However, the concentration of Fe is found to have increased in the upper few cm of the core whereas that of Mn has decreased.

Fe and Mn oxides/hydroxides have a high affinity with most trace metals and Fe often correlates with concentrations of other metals in aquatic environments (Zabetoglou et al., 2002). Heavy metals co-precipitated with Fe and Mn oxides might be released to pore water during reduction and re-adsorbed in the oxic zone (Finney and Huy, 1989). Hence cycling of Fe and Mn may partly control the vertical profiles of most of the metals especially in the zone of diagenetic enrichment of Fe and Mn. In view of the importance of Fe and Mn documented above, the distribution pattern of the selected elements studied is explained with respect to the distribution pattern of Fe and Mn profiles.

Trace and Major metals (Cu, Pb, Co, Ni, Zn, Cr, Al and V)

Cu with Zn and Pb with Co project similar decreasing and increasing trend for the entire length of the core from bottom to surface, with Cu and Zn increasing while Pb and Co decreasing at the upper few cm of the core. In the lower portion, Cu, Pb, Co and Zn are found to show similar decreasing and increasing trend while in the middle portion an opposite trend to each other is seen for Cu, Pb and Co and to a less extent for Zn. Ni and Cr show similar trend in their distribution pattern. From bottom to 26 cm depth, both elements exhibit a gradual increasing trend with Cr profile fluctuating more than Ni which is followed by a decreased peak at 24 cm depth. Above this depth, the concentration of both the elements is found to be almost constant up to the surface. In case of Al and V, large variations in metal concentration are seen at depths between 44 to 24 cm. Below this depth, concentration is found to decrease from 60 to 44 cm while above 24 cm, the trend is slightly increasing up to the surface for Al and decreasing for V.

In the sediment core, a broad concentration maximum is seen between 44 and 24 cm depth for most of the metals studied which is found to coincide with the concentration maxima for redox sensitive elements Fe and Mn and a colour change from dark grey to brown

between 36 to 30 cm depth is also observed to fall within this portion. The colour of the lower half is characteristic of sediment containing diagenetic sulphide minerals indicating permanently reduced sediments and significant sulphate reduction (Buckley et al., 1995). When the vertical trend of Mn and Ni is observed, it is seen that both the elements exhibit similar distribution pattern from bottom to 10 cm depth while above this an opposite trend is seen. The average metal concentration in all three portions of the core is computed separately and it is observed that, in the lower portion of the core, Al exhibits higher concentration while Cu, Mn, Pb and Co show lower concentration while in the middle portion Fe, Mn, Co, Ni, Zn, Cr and V concentrations are found to show higher values while Al exhibits low concentration. However, in the upper portion of the core, the concentration of Cu and Pb are found to be more whereas Fe, Ni, Zn, Cr and V display lower concentrations. It is specifically observed that elemental concentrations show higher variations in the middle portion of the core.

Metal Vs sediment components

a. Correlation Coefficient: Correlation of metals with sediment components and organic matter in the different portions of the core are listed in Tables 1a, b and c. It is stated that inter-element and sediment component relationships can provide interesting information on element sources and pathways (Manta et al., 2002). When the relevant data of correlations is analysed separately for the different portions of the core, it is observed that in the lower portion, significant association is seen between sand and Fe (0.70), Ni (0.70) and Cr (0.72) while good association is seen with Mn (0.64) and Co (0.63), clay associates strongly with Cu (0.67), Al (0.69) and less strongly with V (0.65). Silt shows good correlation with V (0.65). TP significantly associates with Cu (0.74), V (0.79) and to a less extent with Al (0.63), Fe strongly associates with Pb (0.87) and Zn (0.84) while less strongly with Mn (0.53), Co (0.56), Ni (0.60) and Cr (0.54). Mn exhibits significant association with Co (0.91), Ni (0.97) and Cr (0.99) and also shows good association with Zn (0.64). pH shows significant correlation with Mn (0.67) and Co (0.74). From the associations it is observed that in the lower portion of the core, Pb and Zn are strongly associated while Cu to a less extent is associated with Fe oxide compared to Mn, indicating that the redistribution of Pb, Zn and also Cu may be strongly controlled by Fe cycling than Mn cycling. Similar observations were made by Allen et al. (1990) for Severn estuary, UK. On the other hand, Mn oxide is found to contribute significantly to the binding of Co, Ni and Cr in the sediment. Also finer fraction and to some extent TP is found to control the distribution of Cu, Al and V. Almost all the elements except for Ni and Co show a peak at 54 cm depth coinciding with the peaks of Fe and Mn. Trace metals formerly associated with

Table 1a. Pearson's correlation between different parameters in the lower portion of the core (0-24 cm).

	pH	TOC	TP	TN	Sand	Silt	Clay	Cu	Fe	Mn	Pb	Co	Ni	Zn	Cr	Al
TOC	-0.19	1.00														
TP	-0.59	0.09	1.00													
TN	0.05	0.04	-0.35	1.00												
Sand	0.45	0.02	-0.57	0.61	1.00											
Silt	0.13	-0.17	-0.31	0.09	0.35	1.00										
Clay	-0.24	0.14	0.43	-0.25	-0.59	-0.96	1.00									
Cu	-0.29	0.34	0.48	0.31	0.13	-0.08	0.03	1.00								
Fe	-0.40	0.18	0.31	0.41	0.36	0.14	-0.23	0.65	1.00							
Mn	0.16	-0.71	0.20	0.07	0.04	-0.18	0.15	0.18	0.07	1.00						
Pb	-0.25	-0.04	0.56	-0.02	-0.49	-0.43	0.51	0.49	0.07	0.18	1.00					
Co	-0.14	0.34	0.22	0.11	-0.41	-0.62	0.66	0.09	-0.29	-0.32	0.60	1.00				
Ni	0.29	0.03	-0.35	0.16	0.69	0.55	-0.67	0.06	0.53	-0.08	-0.57	-0.69	1.00			
Zn	-0.31	0.37	0.21	0.21	0.44	0.48	-0.54	0.50	0.75	-0.35	-0.08	-0.28	0.57	1.00		
Cr	0.52	0.15	-0.74	0.09	0.58	0.23	-0.37	-0.47	-0.07	-0.39	-0.77	-0.28	0.63	0.05	1.00	
Al	-0.48	0.37	0.44	0.51	-0.06	-0.29	0.27	0.61	0.67	-0.07	0.54	0.37	-0.11	0.38	-0.44	1.00
V	0.58	0.19	-0.82	0.20	0.57	0.12	-0.27	-0.53	-0.15	-0.36	-0.70	-0.20	0.50	-0.08	0.93	-0.32

Table 1b. Pearson's correlation between different parameters in the lower portion of the core (24-44 cm).

	pH	TOC	TP	TN	Sand	Silt	Clay	Cu	Fe	Mn	Pb	Co	Ni	Zn	Cr	Al
TOC	-0.30	1.00														
TP	-0.65	0.29	1.00													
TN	-0.75	0.57	0.49	1.00												
Sand	0.37	-0.61	-0.57	-0.53	1.00											
Silt	0.21	0.14	-0.30	0.00	-0.50	1.00										
Clay	-0.51	0.64	0.79	0.60	-0.93	0.14	1.00									
Cu	0.63	-0.43	-0.58	-0.70	0.10	0.55	-0.36	1.00								
Fe	0.45	-0.90	-0.58	-0.64	0.77	-0.13	-0.83	0.52	1.00							
Mn	0.40	-0.65	-0.55	-0.42	0.49	0.28	-0.68	0.37	0.61	1.00						
Pb	0.24	-0.08	-0.27	-0.24	-0.09	0.50	-0.12	0.30	-0.03	0.29	1.00					
Co	0.20	0.05	0.32	-0.21	-0.17	0.03	0.18	-0.10	-0.15	-0.02	0.33	1.00				
Ni	0.20	-0.65	-0.50	-0.16	0.34	0.27	-0.51	0.34	0.55	0.84	0.27	-0.36	1.00			
Zn	0.76	-0.26	-0.83	-0.53	0.27	0.49	-0.52	0.75	0.47	0.38	0.51	0.01	0.37	1.00		
Cr	0.20	-0.67	-0.49	-0.18	0.41	0.16	-0.54	0.32	0.58	0.82	0.19	-0.39	0.99	0.35	1.00	
Al	0.17	-0.02	0.20	-0.40	0.13	-0.30	-0.02	0.19	0.06	-0.11	-0.48	0.20	-0.39	-0.20	-0.31	1.00
V	0.00	0.21	-0.07	0.28	-0.55	0.76	0.30	0.13	-0.31	0.26	0.57	0.25	0.34	0.32	0.26	-0.51

Table 1c. Pearson's correlation between different parameters in the lower portion of the core (44-60 cm).

	pH	TOC	TP	TN	Sand	Silt	Clay	Cu	Fe	Mn	Pb	Co	Ni	Zn	Cr	Al
TOC	0.02	1.00														
TP	-0.34	0.11	1.00													
TN	-0.01	0.41	0.53	1.00												
Sand	0.26	-0.16	-0.88	-0.79	1.00											
Silt	-0.30	-0.11	0.64	0.60	-0.86	1.00										
Clay	-0.15	0.38	0.88	0.75	-0.86	0.48	1.00									
Cu	-0.20	-0.24	0.74	0.33	-0.68	0.50	0.67	1.00								
Fe	0.27	-0.51	-0.67	-0.71	0.70	-0.52	-0.70	-0.16	1.00							
Mn	0.67	-0.16	-0.82	-0.20	0.64	-0.44	-0.66	-0.65	0.53	1.00						
Pb	-0.03	-0.69	-0.49	-0.54	0.42	-0.11	-0.62	-0.06	0.87	0.39	1.00					
Co	0.74	0.03	-0.72	-0.22	0.63	-0.59	-0.49	-0.60	0.56	0.91	0.33	1.00				
Ni	0.60	-0.31	-0.79	-0.35	0.70	-0.48	-0.72	-0.65	0.60	0.97	0.48	0.89	1.00			
Zn	0.36	-0.35	-0.53	-0.38	0.46	-0.26	-0.53	-0.20	0.84	0.64	0.81	0.70	0.68	1.00		
Cr	0.65	-0.10	-0.86	-0.29	0.72	-0.52	-0.72	0.54	0.99	0.36	0.92	0.96	0.61	1.00		
Al	-0.20	0.32	0.63	0.32	-0.59	0.34	0.69	0.68	-0.48	-0.78	-0.52	-0.68	-0.87	-0.66	-0.78	1.00
V	-0.24	-0.37	0.79	0.38	-0.76	0.65	0.65	0.95	-0.21	-0.61	0.02	-0.60	-0.57	-0.14	-0.70	0.51

Fe/Mn oxides may reprecipitate in the sulphate reduction zone as sulphides (Shaw et al., 1990). A number of trace metals including Cu, Pb and Zn commonly co-precipitate with sulphides below the redox-cline and therefore may show enrichment at depth (Cundy and Croudace, 1995; Zwolsman et al., 1993).

In the middle portion of the core, sand significantly associates with Fe (0.77) while silt associates significantly with V (0.76). Fe shows significant association with Mn (0.61) and to less extent with Ni (0.55), Zn (0.47) and Cr (0.58) while Mn goes well with Ni (0.84) and Cr (0.82). Ni also strongly correlates with Cr (0.99). pH shows significant association with Zn (0.76) and good association with Cu (0.63). In general, in this portion of the core, strong association of metals with Fe and Mn and also coarser fraction of the sediments is observed. It is important to mention here that average sand percentage in the middle portion is higher compared to lower and upper portions of the core. Further, TP and TN values are found to be lower in this portion. This indicates the role of Fe and Mn oxides in the distribution of trace elements when the sediment size is relatively coarser. Further, such an environment facilitates higher mobility and retention of trace elements as can be seen from their concentrations. Different metals bind with Mn and Fe through adsorption, co-precipitation and complexation in sediment-water interface. A peak is seen at 36 cm depth shown by Fe, Mn, Co, Ni, Zn, Cr and V which may be caused by remobilization and reprecipitation of heavy metals on Fe/Mn oxides and oxyhydroxides coatings. The oxides and hydroxides of Fe and Mn are considered responsible for the concentration and accumulation of metals in marine and fluvial sediments (Yucesoy and Ergin, 1992; Summerhayes and Thorpe, 1996). Pb, Co and V along with TOC, TN and clay show another peak at 24 cm depth. Heavy metals resulting from anthropogenic contamination are either associated with organic matter present in the thin fraction of the sediments, or adsorbed onto Fe/Mn hydrous oxides, or precipitated as hydroxide, sulphides and carbonates (Forstner, 1985).

In the upper portion of the core, clay shows significant association with Co (0.66) and good association with Pb (0.51) while sand associates well with Ni (0.69), Cr (0.58) and V (0.57). Cr associates strongly with V (0.93) and Ni (0.63). The strong association of Ni, Cr and V indicate that they may share a common origin. pH shows good association with V (0.58) and Cr (0.52). Fe is found to associate with Cu (0.65), Zn (0.75), Ni (0.53) and Al (0.67). Fe in the form of oxyhydroxides has the affinity to scavenge other metals such as Cu and Zn as they pass through the water en route to the sediments (Waldichuk, 1985). In the upper portion, Fe oxide and also coarser fractions are found to contribute to the distribution of metals such as Ni and Zn while Cr and V are found to be dependent on the pH along with coarser sediment. The distribution and concentration of trace metals Cu and Pb are seemed to

be controlled by finer fractions and organic components in addition to Fe oxide. Under sub-oxic conditions, the degradation of sedimentary organic matter involves the use of trace metals (e.g. Mn and Fe) as secondary oxidants and the reduction of Fe and Mn results in the mobilization and upward diffusion of these metals to oxic surface sediments where they are reprecipitated either as oxides or occasionally as carbonates (Farmer and Lovell, 1984).

b. Cluster analysis: Cluster analysis (CA) is a multivariate technique, whose primary purpose is to classify the objects of the system into categories or clusters based on their similarities. The result of a hierarchical clustering procedure can be displayed graphically using a tree diagram, also known as a dendrogram, which shows all the steps in the hierarchical procedure (Richard and Dean, 2002; Alvin, 2002). Cluster analysis was performed to understand the relationship between metals; sediment components (sand, silt, clay); Organic Matter (TOC, TP, TN) and Fe-Mn oxides as they are the major binding fractions. The analysis was performed separately for the different portions of the core and the cluster plots are shown in Figure 5. Based on the analysis, the whole distribution is grouped into 2 distinct clusters for the upper, middle and the lower portion of the core which is further divided into sub-clusters. This suggests that there might be different environmental settings of deposition or different sources of metals in the sediments.

When the grouping of cluster plots is seen, it is observed that in the lower portion of the core, coarser fraction comprising of sand is found to form a strong group with metals such as Cr, Ni, Co, Zn and oxides/hydroxides of Fe and Mn whereas finer fraction mainly clay forms group with TN, Cu, Pb and V while silt with Al, TP and pH forms another cluster. From this association, it is seen that sediment components are the dominant factors that control the distribution of the metals along with organic matter and so are accordingly grouped, i.e. sand forms one group while silt with clay forms the other group. Physical factors, such as grain size, can exert a significant effect on sediment-associated trace element concentrations (Horowitz, 1995). The lower portion possibly represents sulphide formation zone and corresponds to the trapping of most of the metals as insoluble sulphides, a process which has been inferred in other studies (Cundy and Croudace, 1995). In the middle portion of the core, similar observation is noticed i.e. sand and silt along with clay form the dominants groups, however, the association of metals with organic matter and sediment components is found to be slightly different. Co which was earlier found to associate with sand, TOC, Fe and Mn exhibits formation of a new sub-cluster with TOC and V, while clay in addition to previous metal association also links with silt, Al and TP. Associations between Pb, Al, Cu and organic matter (TP, TN) in the marine sediments

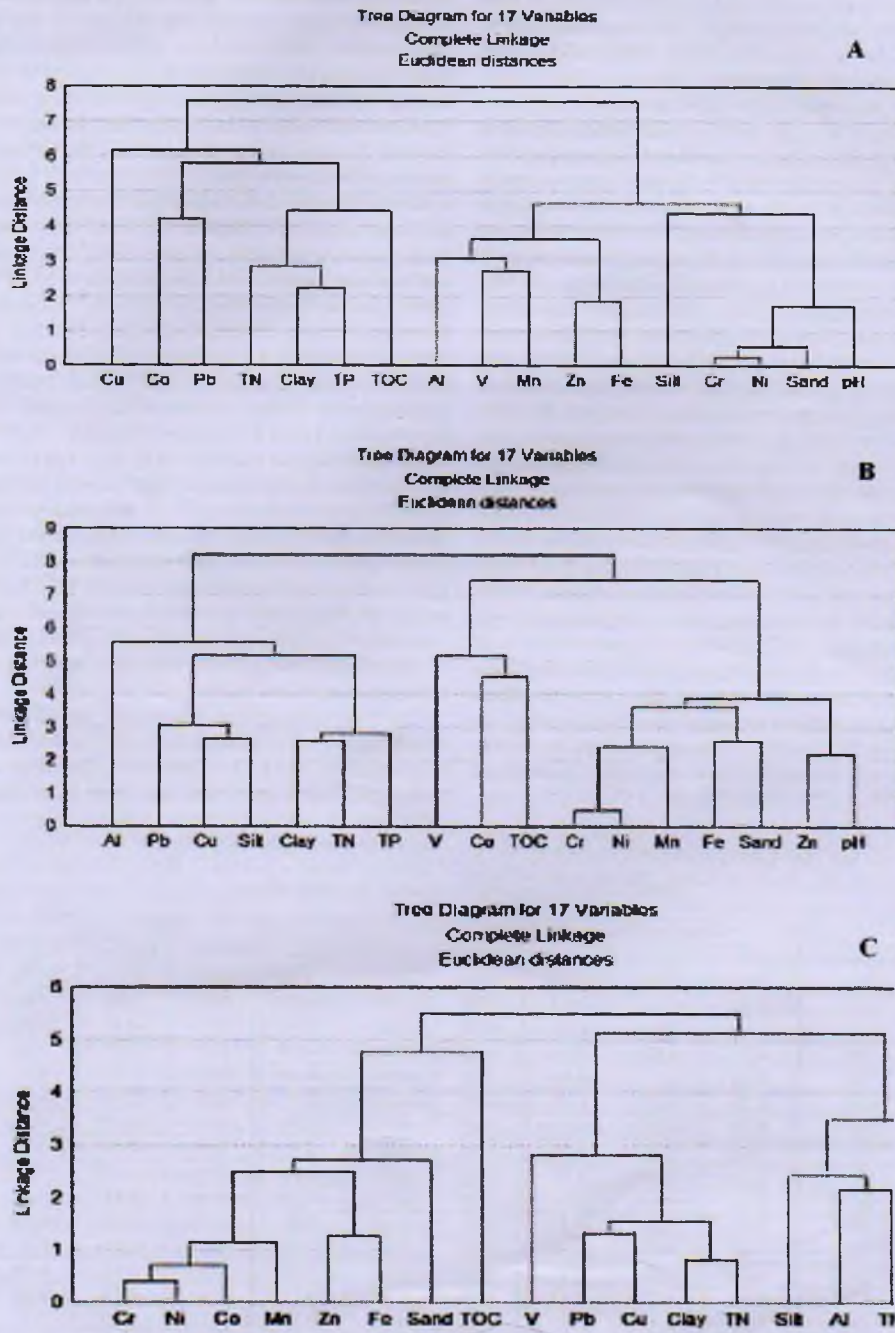


Fig. 5. Hierarchical Cluster analysis for the, (a) Upper portion, (b) Middle portion (c) Lower.

have often been related to the adsorption and complexation of metals by organic matter of both terrestrial and marine origin (Salomons and Forstner, 1984; Loder and Liss, 1985; Wangersky, 1986; Haraldsson and Westerland, 1991).

In the upper portion of the core, sand and silt with Fe, Mn, Al, V, Cr, Ni, pH and Zn form one group while clay with TOC, TP, TN, Cu, Pb and Co forms the other group. The heavy metals Pb, Co and Cu show a typical enrichment in the oxic zone which may be due to their association with particulate organic matter and so can be remobilized owing to the strong mineralization of these compounds in this zone (Klinkhammer et al. 1982; Schwedhelm et al., 1988). Also, it is observed that Co which was found to be associated with the coarser fraction in the lower and middle portions is found to be associated with the finer fraction in the upper portion of the core. From bottom to surface of the core, the pH in general is found to decrease which may be one of the factors resulting in such Co association. High pH values promote adsorption whereas low pH can actually prevent the retention of metals by sediment (Belzile et al., 2004). In the middle and lower portion of the core, Mn and Ni are found to be part of a cluster whereas in the upper portion such close association is not seen. Mn is mobilized in sediments under suboxic conditions (Froelich et al., 1979), which may lead to the loss of (adsorbed) Ni in the surface sediments. The redox status of the sediment determines the extent to which mobilization of Mn and associated Ni takes place, i.e. the presence of a distinct oxic top layer leads to efficient trapping of Mn and Ni (Shaw et al., 1990; Zwolsman et al., 1993).

c) Factor analysis: Factor analysis (FA) was carried out on the data set to confirm the associations between the metals and sediment components and to understand the sources of metals. In factor analysis, an Eigen-value gives a measure of the significance of the factors; the factors with highest Eigen-value are most significant and useful in explaining large variation in the data. The Eigen values computed for the different portions of the core are found to be greater than 1. The values of different factors and percentage variance accounted are given in Table 2. It is noted that, in the lower portion, three factors account for 85.77% of the total variance. Factor 1 with a total variance of 57.70 % shows good positive loadings on silt, clay, TP, Cu and V, to a less extent on TN and strong negative loading on sand, indicating strong association of these metals with finer fraction of the sediments and TP. This factor is associated with the finer fraction of the sediment. On the other hand, Factor 2 with a total variance of 16.76 % exhibits high positive loadings (>0.8) on Fe and Pb and to a less extent on Zn. However, high negative loading on TOC is also observed. This suggests strong association of Pb with Fe. This can be called the Fe-oxide controlled factor. Factor 3 with a total variance of 11.31 % exerts high positive loading on pH, Mn, Ni, Co and Cr which highlights the role of pH in retention of these metals in this portion of the core. Finer sediments, Fe, Mn and pH seem to control the metal associations in this portion.

In the middle portion of the core, three factors constitute 76.43 % of the total variance. Factor 1 with a total variance of 41.32 %, projects good positive loadings on Mn, Ni and Cr; with less extent on sand and

Table 2. Factor analysis matrix after varimax rotation.

Variance (%)	Upper portion			Middle portion			Lower portion		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
	35.18	23.30	14.05	41.32	20.76	14.35	57.70	16.76	11.31
pH	0.12	-0.66	-0.12	0.07	0.04	0.88	0.02	-0.05	0.80
TOC	-0.08	0.09	0.85	-0.70	0.23	-0.38	-0.15	-0.85	0.02
TP	-0.27	0.82	-0.15	-0.52	-0.16	-0.64	0.75	-0.29	-0.49
TN	0.36	0.11	0.40	-0.12	0.24	-0.90	0.69	-0.59	0.17
Sand	0.74	-0.29	0.26	0.61	-0.57	0.39	-0.88	0.33	0.27
Silt	0.75	-0.16	-0.20	-0.05	0.86	0.26	0.78	-0.06	-0.20
Clay	-0.86	0.22	0.10	-0.68	0.28	-0.57	0.74	-0.51	-0.26
Cu	0.23	0.78	0.23	0.15	0.25	0.79	0.78	0.19	-0.46
Fe	0.62	0.61	0.30	0.68	-0.32	0.55	-0.36	0.81	0.29
Mn	0.04	0.24	-0.73	0.75	0.20	0.37	-0.38	0.21	0.89
Pb	-0.49	0.68	-0.04	0.04	0.67	0.35	-0.11	0.94	0.20
Co	-0.76	0.17	0.45	-0.51	0.09	0.29	-0.37	0.14	0.88
Ni	0.86	-0.22	0.13	0.90	0.34	0.11	-0.41	0.35	0.82
Zn	0.70	0.42	0.39	0.23	0.40	0.78	-0.11	0.69	0.57
Cr	0.36	-0.81	0.34	0.92	0.24	0.10	-0.49	0.18	0.84
Al	-0.02	0.73	0.51	-0.37	-0.61	0.31	0.41	-0.37	-0.61
V	0.25	-0.84	0.40	0.02	0.94	-0.05	0.88	0.25	-0.37

negative loading on TOC. Factor 1 can be called the Mn-oxide controlled Factor. The second factor accounts for 20.76 % of the total variance and is dominated by high positive loadings (>0.8) on silt and V which reflects the adsorption of V on finer sediment fraction. Factor 3 with a total variance of 14.35 % is characterised by good positive loadings on pH, Cu and Zn and negative loadings on clay and Organic matter (TP, TN and TOC) which reflects an anthropogenic source. In this portion, finer sediment fractions along with Mn-oxide are found to be the dominant factors. In the upper portion of the core, three factors accounts for a total variance of 72.54 %. Factor 1 accounts for 35.18 % of the total variance and is characterised by high positive loadings (>0.7) on sand, silt, Ni, Zn and to some extent on Fe and high negative loadings on clay and Co. This factor could be identified as the natural factor comprising of lithogenic processes involving the weathering of natural parent materials such as rocks and soils. Factor 2 accounts for 23.30 % of the total variance and exhibits good positive loadings with TP, Cu and Al and to a less extent on Fe and Pb. Factor 2 can be called the Fe-oxide factor as it is observed to control the distribution of most of the metals along with TP. Factor 3 with a total variance of 14.05 % is positively loaded on TOC and negatively loaded with Mn. In this portion of the core, sediment grain size together with organic matter is found to control the distribution of most of the metals.

Sediments represent one of the ultimate sinks for heavy metals discharged into the aquatic environment (Luoma and Bryan, 1981). Sediment metal concentrations are influenced by a range of factors. They include physical and hydrological characteristics of the region and its benthos, atmospheric conditions, productivity, pH, soil texture, redox potential and cation exchange capacity among others. The fluctuations of metal concentration in certain depths of the core can be attributed to leaching and/or post-depositional remobilization (Ramanathan et al., 1996). The metal distribution in the profile can also be affected by other factors such as the river input, sediment properties and dredging activities (Salomons et al., 1988; Winkles et al., 1993). Strong relationships between some metals and Al exist in sediments that are relatively uncontaminated (Summers et al., 1996), and weak relationships are indicative of multiple sources of metals from both lithogenous and anthropogenic inputs (Luoma, 1990). The presence of a positive linear correlation between aluminium and fine grain size in the lower portion of the core indicates that alumino-silicate may be the primary metal bearing mineral. In the middle portion, large fluctuating trend of sediment components accompanied by a significant increase in sand percentage might indicate an episode of large river input or flooding in the region. Due to the high population density of Mumbai region resulting in the increasing demand for land, many low lying areas of the rivers flowing through

Mumbai Metropolitan Region (MMR) are reclaimed and this causes floods during the monsoon season (Phansalkar et al, 1997). This problem is aggravated by poor storm water drainage system of the city. Indiscriminate dumping of solid waste often clogs the combined storm water and municipal waste water drainage system resulting in coastal flooding and inundation during the monsoon months. A large increase in metal concentration for almost all the element studied is observed in the sandy sediments of middle portion compared to the finer sediment present in the lower and upper portions. The enrichment of metals in the middle portion may be due to the presence of detrital coarse particles rich in metals derived from catchment areas due to anthropogenic activities. Many industrial units manufacturing a wide range of products such as dyes, pharmaceuticals, metalurgical, fine chemicals, plastics, petro and agrochemical, fertilizers and refined petroleum products are present in the upstream region of the river, the discharge of which might have resulted in the observed high concentration of metals. Apart from the industrial input of metals, villages located along the coast also contribute, though in a small quantity. Organic matter and finer fractions especially silt is found to play a key role in the enrichment of most of the metals in the upper portion of the core. Cu and Pb concentration is observed to increase in the recent sediments. Release of sewage sludge, municipal waste discharge, and antifouling paints are some of the reasons for Cu increase while Pb is increasingly used in vehicle exhausts, commercial and fishing boats.

CONCLUSIONS

Sediment components, organic matter and selected metals were analysed in a sediment core collected from the intertidal region of Ulhas estuary, Mumbai, which showed three different episodes of sedimentation from the bottom to surface. Multivariate statistical technique comprising of factor and cluster analysis helped in providing a valuable insight in identifying the different processes and associations between the metals and organic matter along with the sediment components. The middle portion shows higher sand and metal concentration compared to the lower and upper portions. Finer fractions with Fe and Mn oxides are found to control the distribution of most of the metals in the lower portion, coarser fraction with Fe oxide have played an important role in the middle portion while the upper portion is characterised by clay and organic matter exerting a strong geochemical influence on the metals.

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