

Reading source and processes with time from mangrove sedimentary environment of Vaitarna estuary, west coast of India

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Two mangrove sediment cores collected from Vaitarna estuary were studied for the distribution of sediment components (sand, silt, clay and organic carbon), major elements (iron, manganese and aluminium) and trace metals (copper, zinc, cobalt, nickel and lead). Both the cores showed a gradual decrease in sand and an increase in clay component from bottom to surface. This change in the type of sediment deposited was attributed to the change in hydrodynamic energy conditions resulting from both natural (decrease in rainfall) as well as anthropogenic activities (construction of dams, freshwater diversion, etc.). Metals were found to be strongly associated with sand, silt and clay, while Fe-Mn oxyhydroxides and organic matter were found to play a minor role. They also showed similarity in their distribution patterns, thus suggesting a common lithogenic source. Enrichment of iron and zinc in core S5 and manganese, copper, cobalt and lead in core S6 towards surface however suggested increase in anthropogenic additions in recent years.

[**Keywords:** Sediment components, Metal distribution, Lithogenic source, Vaitarna estuary]

Introduction

Mangrove ecosystems are a prominent feature of many tropical and subtropical estuaries¹. They stabilize the environment from erosion and act as a buffer zone between land and sea². Sediment dynamics in mangrove ecosystem is mainly regulated by both internal (flocculation, dissolution, mixing, etc.) and external (river input, agricultural runoff, pollution) factors³. Sediments are generally rich in organic matter and have a high capacity to retain trace elements from tidal and river outflows⁴. Metals of both natural as well as anthropogenic origin are deposited simultaneously within the sediments. Their behavior, transport and fate however are determined by nature of association with solid substrate and/or organic material⁵. Sedimentological (e.g., grain size) parameters are known to vary within an estuarine system and therefore can be used to understand local dynamic processes⁶. Geochemical studies on sediment cores have been found to be an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environments of estuaries⁷⁻¹¹.

Vaitarna estuary is one of the major estuaries of Konkan region, west coast of India. However no geochemical data is available for mangrove sediments of this estuary. Thus aim of the present study is to understand the sources of metals and the processes governing their distribution within the mangrove sediments of this estuary.

Materials and Methods

Thane is the northernmost district of Konkan and extends between 20°20' N latitude and 73°45' E longitudes. Konkan is a narrow coastal plain adjoining the Arabian Sea. Along the western margins of Maharashtra, Konkan coast is separated from the Deccan plateau by the Sahyadri escarpment with an average elevation of 1000 meters¹². Thane district is blessed with abundant natural resources in the form of perennial rivers, extensive seashore and high mountainous range¹³. It is also one of the most industrialized districts in the Maharashtra state¹⁴. Vaitarna, is the largest of Konkan rivers. It has a number of tributaries, the most important of which are Pinjal, Surya and Tansa¹⁵. Mangrove species

reported from this region are *Avicennia alba*, *Avicennia marina*, *S. apetala*, *A. officinalis*, *Rhizophora mucronata* and *R. apiculata*.

Two mangrove sediment cores were collected from Vaitarna estuary during the field survey conducted in May 2009. Core S5 of length 102 cm ($19^{\circ}28'56.3''\text{N}$; $72^{\circ}46'58.7''\text{E}$) was collected closer to the mouth while core S6 of length 60 cm ($19^{\circ}31'35.0''\text{N}$; $72^{\circ}53'37.5''\text{E}$) was collected from the upper middle estuary (Fig. 1). Hand held Global Positioning System (GPS) was used to locate the sampling stations, while hand operated PVC corer was used to collect the sediment cores. Following the collection, sub sampling was done at 2 cm interval with the help of a plastic knife. The subsamples were sealed in clean plastic bags, labeled and stored in ice box and transferred to the laboratory.

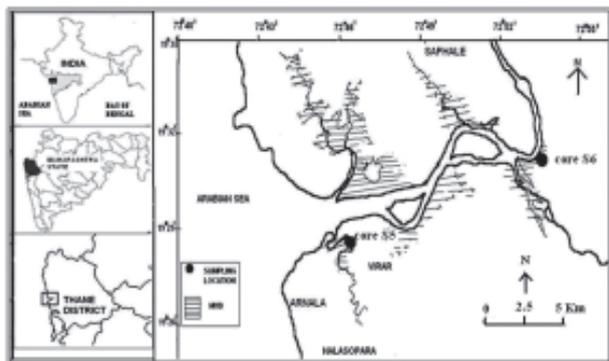


Fig. 1— Location of mangrove core samples collected from Vaitarna estuary

Sediments were oven dried at 60°C in the laboratory. Portion of the dried samples was powdered and homogenized using an agate mortar and pestle. Un-ground sediment samples were used for the analysis of sediment components (sand: silt: clay). While, powdered and homogenized samples were used for the estimation of total organic carbon and bulk sediment chemistry. To determine the sand: silt: clay ratio, pipette analysis was carried out following Folk¹⁶. The organic carbon in sediment sub-samples was estimated using Walkey-Black method¹⁷. For total 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, HNO₃ and HClO₄

was added slowly to the sample. Care was taken to avoid excessive frothing. The mixture was kept overnight and later dried completely on a hot plate at 70°C . After drying, again 5 mL of the above 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 HNO₃ 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 digested solutions were aspirated into the flame of atomic absorption spectrophotometer (AAS) (Varian AA240FS) for the analyses of the metals viz. iron (Fe), manganese (Mn), aluminium (Al), copper (Cu), zinc (Zn), cobalt (Co), nickel (Ni) and lead (Pb). Care was taken to avoid contamination at every step. Certified reference standard from the Canadian National Bureau of Standards (BCSS-1) was also treated following the same procedure and analyzed along with the sample solutions. The accuracy of the analytical procedure was assessed using certified standard reference material (BCSS-1). Accuracy was 5% for Mn and Co, 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 (1000 mg/l). Reproducibility of the instrument was checked by analyzing duplicate random samples. The precision obtained for the metals was as follows: Fe 2.19%, Mn 3.04%, Al 3.24%, Co 2.16%, Cu 2.75%, Ni 2.89%, Pb 2.26% and Zn 3.67% of the standard deviation (%SD).

Statistical correlation, t-test and principal component analyses (PCA) were carried out on sediment components, organic carbon and metals of the studied cores by using the software SPSS.

In order to understand the level of metal enrichment in mangrove sediments of Vaitarna estuary, Enrichment factor (EF) and Index of geoaccumulation (I_{geo}) were computed. Enrichment

factor (EF) proposed by Simex and Helz¹⁸ was calculated as follows

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

Where, C_{sample} and C_{crust} was the concentration of the element in the sample and in the continental crust respectively. $\text{Al}_{\text{sample}}$ and Al_{crust} represent concentration of Al in the sample and in the continental crust respectively^{19,20}. Al was used as a normalizer, since; it was a conservative element and has no significant anthropogenic source. While geoaccumulation index as proposed by Müller²¹ was calculated as

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

Where, C_n and B_n was the concentration of the studied element 'n' and the geochemical background value taken from global average shale respectively. Factor 1.5 was used to compensate for lithogenic variations in background data. Both EF and I_{geo} were divided into seven classes of contamination as shown in table 4a, b.

Results and Discussion

Distribution of sediment components (sand: silt: clay)

The range and average values for sediment components are shown in Table 1a, b. Average sand

percentage was noted to be significantly higher in core S5 collected closer to the mouth as compared to core S6 collected from the upper middle estuary (Table 2). Silt and clay showed relatively higher percentages in core S6 as compared to core S5; however result of t-test indicated significant difference for silt and no significant difference for clay between the two cores. The observed variation in sand, silt and to some extent clay percentages at the two locations therefore may be attributed to difference in tidal energy conditions at the two locations. Decrease in tidal current velocities must have resulted in relatively higher deposition of fine grained sediments²² within the upper middle estuary.

Based on the distribution pattern of sediment components, the two cores were divided into three sections. Section I in core S5 ranged from 102 cm to 80 cm depth, section II varied from 78 cm to 50 cm while uppermost section III ranged from 48 cm to surface of the core (Fig.2a). In section I, sand percentage was high and exhibited a decreasing trend. In section II, further decrease in sand percentage was noted. While in section III, sand percentage was almost constant and remained lower than the average. Clay was found to compensate for the variation in sand percentage in all the three sections. Silt was

Table 1a:—Core S5

	N	Minimum	Maximum	Mean	Std. Deviation
sand	51	1.62	74.76	20.6254	20.38275
silt	51	18.04	49.82	25.5982	5.46173
clay	51	7.2	80.08	53.7765	19.62127
OC	51	0.21	1.97	0.9475	0.43443
pH	51	6.12	6.94	6.4612	0.19493
Fe	28	4.15	9.83	7.7343	1.57751
Mn	28	278	904.33	456.64	176.23018
Al	28	6.91	11.51	9.5157	1.0141
Cu	28	88.77	126.33	109.45	9.56916
Zn	28	154.37	362.63	233.49	57.67559
Co	28	58.67	97.33	72.5357	10.01248
Ni	28	102.67	158.33	126.26	17.26395
Pb	28	21.97	74.9	50.1714	13.89373

Table 1b.—Core S6

	N	Minimum	Maximum	Mean	Std. Deviation
sand	30	3.32	21.45	11.1709	5.1029
silt	30	28.16	39.68	33.8105	2.68944
clay	30	43.04	62.24	55.0187	4.06095
OC	30	1.04	1.52	1.2377	0.09134
pH	30	6.29	6.97	6.598	0.16412
Fe	30	3.26	10.99	6.0809	1.6034
Mn	30	1614.33	2054	1767.6	117.36381
Al	30	8.08	9.95	9.1531	0.53526
Cu	30	118.33	156.67	133.07	8.78321
Zn	30	107.67	154	128.7	11.89106
Co	30	60.33	87.67	73.0333	8.35714
Ni	30	122.33	146.67	134.84	6.15243
Pb	30	49	107	77.4333	15.68125

Table 2—Paired-samples t-test for the comparison of means of studied parameters in core S5 and core S6

Pairs of variables	Difference of means	t	df	P (2-tailed)
Sand _{core S5} -Sand _{core S6}	1.077	3.435	27	0.002
Silt _{core S5} -Silt _{core S6}	-7.557	-5.338	27	0.000
Clay _{core S5} -Clay _{core S6}	-3.221	-0.968	27	0.342
OC _{core S5} -OC _{core S6}	-0.275	-3.307	27	0.003
Fe _{core S5} -Fe _{core S6}	1.804	4.956	27	0.000
Mn _{core S5} -Mn _{core S6}	-1.316	-26.541	27	0.000
Al _{core S5} -Al _{core S6}	0.399	1.970	27	0.059
Cu _{core S5} -Cu _{core S6}	-2.405	-14.151	27	0.000
Zn _{core S5} -Zn _{core S6}	1.061	8.500	27	0.000
Co _{core S5} -Co _{core S6}	-0.488	-0.162	27	0.873
Ni _{core S5} -Ni _{core S6}	-7.904	-2.795	27	0.009
Pb _{core S5} -Pb _{core S6}	-2.845	-7.921	27	0.000

almost constant from bottom to surface except slight increase between 54 cm and 44 cm depths. While in core S6, section I varied from 60 cm to 44 cm depth, section II ranges from 42 cm to 14 cm while uppermost section III varied from 12 cm to surface

of the core (Fig. 2b). Sand showed a gradual decreasing trend similar to that in core S5. It indicated values higher than average in section I, close to the average in section II and lower than the average in section III. Clay compensated for the variation in sand.

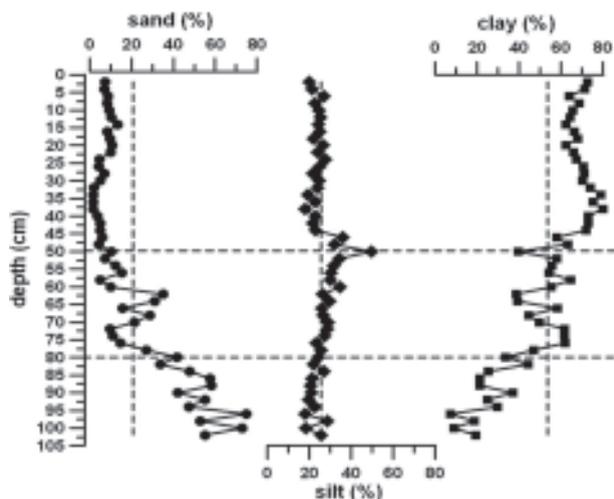


Fig. 2(a)—Distribution of sediment components in core S5

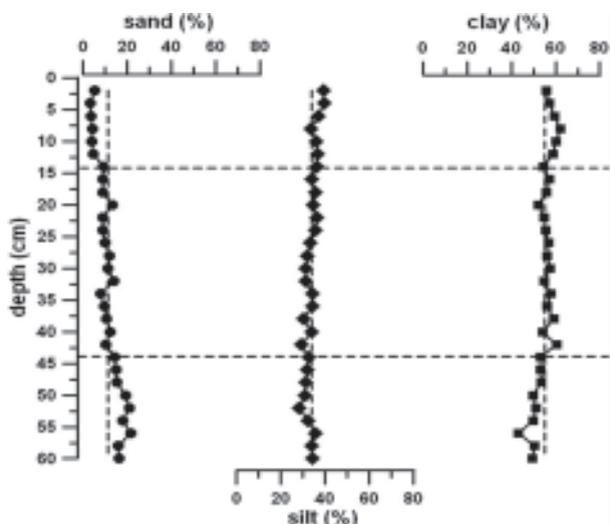


Fig. 2—(b) Distribution of sediment components in core S6

Silt was constant from bottom to surface of the core except slight increase above 6 cm depth.

Distribution of sediment components (sand, silt and clay) along the length of the core is important in understanding the source, transport, history and process of sediments²³. Mangrove sub-environment of Vaitarna estuary seems to have favored higher deposition of sand in the past and clay in recent years. Heavy rainfall leads to washing of the surrounding area/bedrock and greater influx of material of varying sizes and geochemical composition in estuarine region. The study area experienced heavy rainfall in the past (1953-1961), which further decreased in

successive years (Fig. 3). Rate of sedimentation for the area available is 0.7–1.9 cm/yr²⁴ and 0.24–2.72 cm/yr²⁵. Average sedimentation considered for the area based on the data available is 1.4 cm/yr.

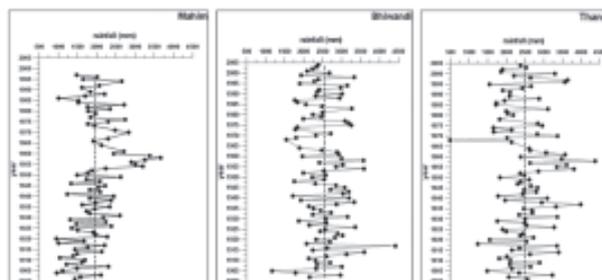


Fig. 3—Rainfall data of last hundred years for Thane district

Mangrove cores collected in the present study therefore represent less than seventy five years of sediment accumulation. Higher river runoff therefore seems to have brought along with it coarser particles from the surrounding catchment to the estuarine environment. Prevalence of higher hydrodynamic energy conditions must have facilitated higher deposition of coarser particles and lead to washing away of finer particles to the offshore region in the past. Further change in particle size i.e higher deposition of finer particles towards surface suggested a transition from high-energy environment to lower-energy environment²⁶. The decrease in rainfall in successive years²⁷, diversion of river water for agricultural and drinking purposes, as well as construction of large dams and other small structures within the catchment area might have impounded runoff²⁸. All these processes together must have resulted in less influx of river brought particles. It must have also resulted in increased marine inundation or salinity, greater flocculation and deposition of finer clay particles in recent years.

Distribution of organic carbon (OC)

The range and average values for OC in core S5 and core S6 are shown in table 1a and 1b. In section I of core S5, OC showed an increasing trend with larger fluctuations from bottom to 88 cm depth (Fig. 4a). In this section OC was noted to be lower than the average. In section II, OC maintained higher

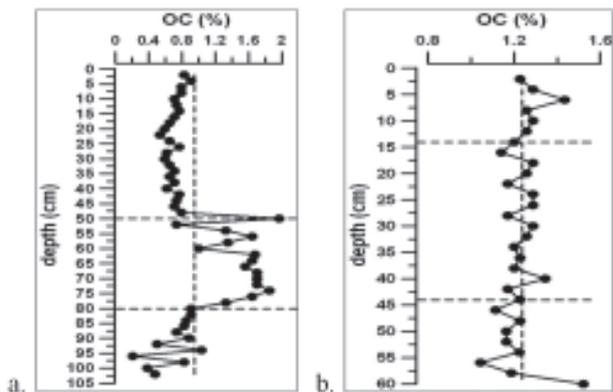


Fig. 4—Distribution of OC in a. core S5 and b. core S6

than average values. While, in section III lower than average values were noted. Wherein, OC showed slight decreasing trend up to 22 cm, followed by an increase towards the surface. While in core S6, OC indicated fluctuating increasing trend with highest value observed at the bottom of the core (Fig. 4b).

OC in core S5 did not show similarity with the distribution pattern of sediment components. However, relatively higher OC percentage in the middle section probably suggests greater deposition of organic matter in the past and/or partial decomposition and preservation of refractory organic matter (e.g. leaf litters, root exudates) in the sediments²⁹. Increasing trend of OC in core S6 similar to that of clay suggests their association and co-sedimentation due to similarity in settling velocity³⁰ as well as due to larger surface to volume ratio of the fine-grained particles³¹.

Distribution of major elements (Fe, Mn and Al)

The range and average values for major elements are shown in Table 1a and 1b. Major elements showed spatial variation in the distribution pattern, wherein, average Fe and Al concentration was noted to be higher towards the mouth while average Mn concentration was noted to be high towards the upper middle estuary. Al however showed no significant difference between the two locations (Table 2).

In core S5, Al indicated lower than average values from 102-86 cm, at 70 cm and 64 cm and above 26 cm depths; while, higher than average values were

noted between 80-74 cm and 60-30 cm depths (Fig. 5a). Vertical distribution pattern indicated a decrease from bottom to 94 cm depth followed by an increase till 74 cm of section II. Relatively lower values were noted between 74 and 60 cm depths. Above 60 cm, Al decreased gradually up to 6 cm followed by an increase at the surface. The distribution pattern of Al indicated no similarity with that of clay. However, it showed some similarity with silt component; wherein, both Al and silt indicated higher values between 60 cm and 40 cm depths. Correlation analysis also indicated significant positive association of Al with silt (Table 3a). In addition to that of clay minerals, Al therefore seems to be a part of other sedimentary minerals such as anorthite, albite, etc. that predominates in silt and sand size particles³².

Fe in this core indicated higher than average

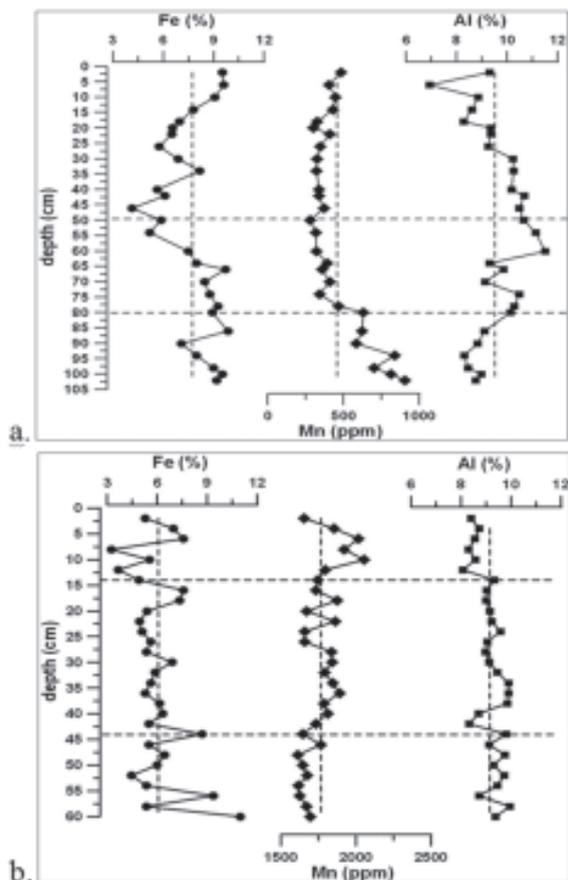


Fig. 5—Distribution of major elements in a. core S5 and b. core S6

Table 3a: -Core S5

	sand	silt	clay	OC	pH	Fe	Mn	Al	Cu	Zn	Co	Ni	Pb
sand	1												
silt	-0.236	1											
clay	-0.951**	-0.078	1										
OC	-0.111	.577**	-0.07	1									
pH	.647**	-0.349	-0.552**	-0.248	1								
Fe	.505**	-0.391*	-0.393*	0.066	.377*	1							
Mn	.896**	-0.35	-0.808**	-0.302	.725**	.506**	1						
Al	-0.35	.383*	0.237	0.317	-0.383*	-0.435*	-0.460*	1					
Cu	-0.842**	.467*	.715**	0.319	-0.536**	-0.381*	-0.856**	.494**	1				
Zn	-0.600**	-0.127	.656**	-0.391*	-0.347	-0.178	-0.488**	-0.315	.395*	1			
Co	.543**	.514**	-0.721**	.447*	0.21	0.166	0.336	0.089	-0.161	-0.599**	1		
Ni	.910**	0.076	-0.958**	0.26	.543**	.491**	.745**	-0.191	-0.641**	-0.727**	.769**	1	
Pb	-0.645**	0.259	.579**	0.274	-0.585**	-0.246	-0.685**	0.285	.644**	0.289	-0.125	-0.483**	1

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

Table 3b: Core S6

	sand	silt	clay	OC	pH	Fe	Mn	Al	Cu	Zn	Co	Ni	Pb
sand	1												
silt	-0.611**	1											
clay	-0.852**	0.106	1										
OC	-0.345	0.287	0.243	1									
pH	.700**	-0.581**	-0.495**	0.05	1								
Fe	0.295	0.093	-0.432*	0.311	0.197	1							
Mn	-0.686**	0.293	.668**	0.309	-0.397*	-0.156	1						
Al	.503**	-0.403*	-0.365*	-0.135	.444*	0.118	-0.349	1					
Cu	-0.772**	.597**	.574**	.422*	-0.612**	-0.038	.531**	-0.469**	1				
Zn	.812**	-0.604**	-0.621**	-0.26	.650**	0.26	-0.575**	.655**	-0.697**	1			
Co	-0.283	.510**	0.018	0.208	-0.326	0.134	0.234	-0.543**	.445*	-0.304	1		
Ni	.735**	-0.429*	-0.639**	-0.25	.546**	0.227	-0.487**	.496**	-0.536**	.718**	-0.197	1	
Pb	-0.376*	0.19	0.346	-0.111	-0.378*	-0.253	0.312	-0.377*	.391*	-0.427*	.414*	-0.471**	1

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

values from bottom to 64 cm and above 14 cm depths. While lower than average values were noted between 60 cm and 18 cm depths. The vertical distribution pattern of Fe in the lower section I, showed a gradual decrease up to 90 cm followed by an increase till 86 cm; above 86 cm, up to 46 cm depth of section III, Fe indicated a gradual decreasing trend. Above which, it showed an increase till 34 cm followed by a decreasing trend up to 26 cm and an increase towards the surface.

Mn indicated higher than average values in lower section I and lower than average values in middle and upper sections II and III respectively. It showed a gradual decreasing trend from bottom to 74 cm depth. Above which it remained constant except a slight increasing trend from 20 cm to surface of the core. Both Fe and Mn therefore showed a similar decreasing trend with higher values in lower part of the core. Amongst the sediment components, sand percentage had shown a similar decrease. Gradual decreasing trend of Fe and Mn from bottom to approximately 60 cm depth similar to that of sand therefore suggested that these metals were probably derived from similar source and were associated with coarser sand particles³³. Further, increased concentration of Fe towards the surface probably suggests additional anthropogenic input in recent years and/or diagenetic enrichment³⁴.

In core S6 collected from the upper middle estuary, Al showed a decreasing trend from bottom to surface of the core similar to that observed for sand (Fig. 5b). Wherein higher than average values were noted in the lower section I. Al in this section showed fluctuating trend. In middle section II, Al indicated a decrease at 42 cm followed by increase till 38 cm. Further, it remained constant up to 34 cm and then decreased till 30 cm. Between 30 and 14 cm depths Al remained constant around the average line. While in upper section III, Al showed lower than average values. It indicated a sudden decrease at 12 cm, above which it remained almost constant. Al in this core seems to be associated with coarser sand component.

Fe indicated large variation in distribution pattern from bottom to surface of the core. None of the sediment components showed such large variation in

their distribution pattern in this core. The point to point variation pattern of Fe however showed large similarity with that of OC. In lower section I, Fe indicated highest concentration at 60 cm depth as well as prominent peaks at 56 cm and 44 cm depths. In section II, it remained almost constant up to 20 cm, followed by an increase between 18-16 cm depths. While in section III, it fluctuated with lower than average values between 14 cm and 8 cm depths, above which it showed a sudden increase at 6 cm, followed by a decrease towards the surface.

Mn indicated an increasing trend from lower section I to upper section III similar to that of clay. The vertical distribution pattern showed lower than average values in section I, while in section II, Mn fluctuated around the average line. In section III, it showed a large increase between 12 cm and 4 cm depths. Mn showed similarity in distribution pattern with that of Fe in section III. Higher concentration of Mn above 12 cm depth suggests additional anthropogenic input in recent years. While its similarity in distribution pattern with that of clay further suggested their association and higher concentration in recent years. In general major elements (Fe, Mn and Al) did not show much similarity in their distribution pattern suggesting

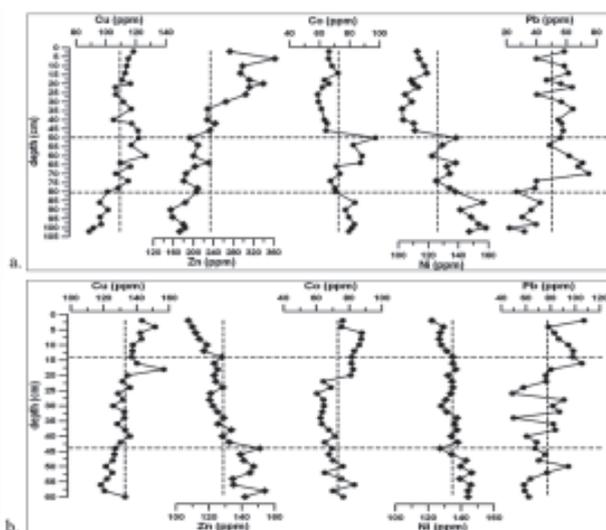


Fig 6—Distribution of trace metals in a. core S5 and b. core S6

difference in their sources as well as processes of deposition.

Distribution of trace metals (Cu, Zn, Co, Ni and Pb)

The range and average values for trace metals were shown in table 1a and 1b. All the studied trace metals except Co showed significant difference in their distribution at the two locations (Table 2). The studied trace metals except Zn were noted to be higher in core S6 as compared to core S5. The vertical distribution patterns of Zn, Pb and Cu in core S5 indicated an overall increasing trend from bottom to surface (Fig. 6a). These metals showed similarity in their distribution patterns at various depths and also agreed with the distribution pattern of clay. Thus, suggesting their association with clay and a similarity in sources and/or post depositional behavior³⁵. Reduction in freshwater inflow in recent years must have resulted in accumulation of these metals within the estuary along with clay. Clays act as adsorbents and play an important role in ion exchange reactions³⁶. While, Ni and Co showed a decreasing trend similar to that of sand, Mn and to some extent Fe. These metals therefore seem to be associated with coarser particles as well as Fe and Mn probably as oxyhydroxides. Further, higher concentration of Co between 66 cm and 46 cm depths agreed with that of silt and OC, thus suggesting their association.

In core S6, Zn and Ni decreased gradually from bottom to surface of the core (Fig. 6b). Similar decreasing trend was also noted for sand and petrogenetic element Al³⁷. The decrease in Zn and Ni may therefore be attributed to reduction in deposition of coarser particles towards the surface of the core, as these metals seem to be associated with sand. They therefore appear to have a common lithogenic source from physical weathering of basaltic rocks. Cu, Co and Pb showed similarity in their distribution patterns at various depths. Cu indicated a gradual increasing trend from bottom to surface of the core similar to that of silt, clay, OC and Mn. Co decreased gradually from bottom to 26 cm depth, followed by a fluctuating increasing trend till 20 cm. Above 20 cm, Co increased up to 6 cm, followed by a decrease towards the

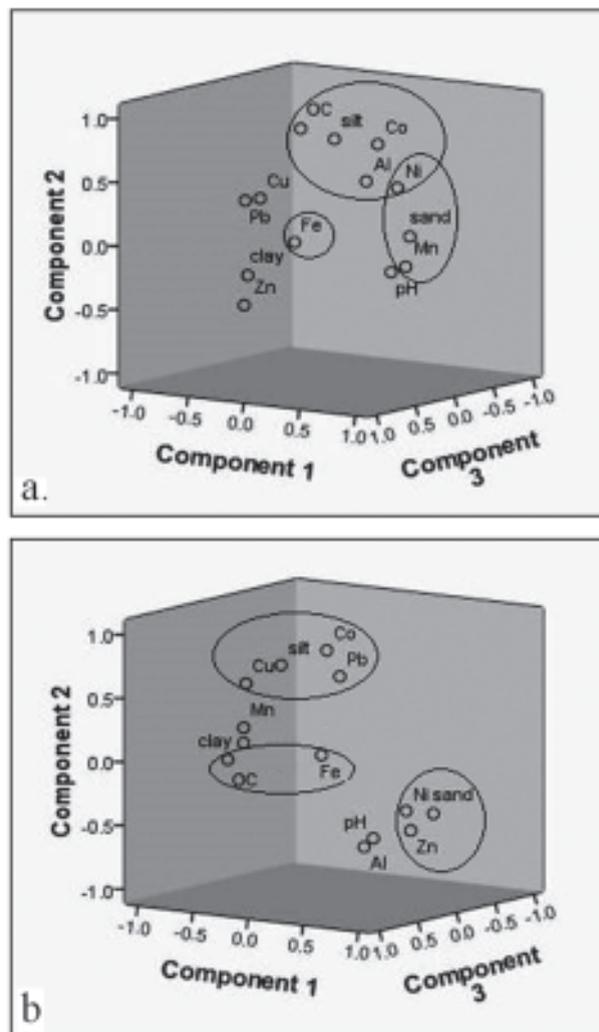


Fig. 7—Result of Principal component analysis (PCA) in a. core S5 and b. core S6

surface. Pb showed a large fluctuating with overall increasing trend from bottom to surface of the core. Increase in concentration of Cu, Co and Pb towards the surface therefore suggested higher accumulation of these metals in recent years along with finer particles.

Correlation analysis and Principal Component Analysis (PCA)

Further, to understand the sources and factors controlling metal distribution and the inter-relationship between the studied parameters, correlation and Principal component analyses were carried out. In core S5, Fe, Mn, Co and Ni were

strongly positively correlated with sand (Table 3a). The result of PCA also indicated higher loadings of sand, Mn and Ni in the first Principal component which explained 43.8 % of the total variance (Fig.7a). While, Co, Al and Cu showed strong association with silt; whereas, clay controlled the distribution of Cu, Zn and Pb (Table 3a). Similarly, silt, OC, Al, Co and Ni were found to have their high loadings in second Principal component which explained 22.1% of the total variance. Fe showed high loading in third Principal component which explained 14.7 % of the total variance. Thus all the sediment components (sand, silt and clay) played a significant role in metal distribution in this core. Strong positive association of Cu with Al, Zn and Pb, Ni with Fe, Mn and Co further suggested their common source. Fe-Mn oxyhydroxides and OC did not play a major role

in metal distribution in this core except for Ni and Co respectively. The trace metals transported from human activities are often associated with organic matter, adsorbed on Fe-Mn hydrous oxides, or precipitated as hydroxides, sulphides and carbonates³⁸. Physically comminuted, but not chemically decomposed, material containing some or all of the original minerals with their inherited load of heavy metals of all grain sizes, therefore seem to have been transported to, and deposited³⁹ in sediments closer to the mouth of Vaitarna estuary.

Similarly in core S6, Al, Zn and Ni showed strong positive association within themselves as well as with sand (Table 3b). The result of PCA also showed higher loadings of sand, Zn and Ni in the first Principal component which explained 35.2% of the total variance (Fig.7b), thus suggesting a common lithogenic source for Zn and Ni. Cu was associated with both silt and clay. It was also found to be strongly positively associated with OC, Mn, Co and Pb. While Co and Mn showed strong positive correlation with silt and clay respectively. Second Principal component which explained 24.1% of the total variance also indicated higher loadings of silt, Cu, Co and Pb. Thus, Cu, Co and Pb seem to be affected by similar processes and/or have similar sources, both natural as well as anthropogenic. OC and Fe showed higher loadings in third Principal component which explained 12.5% of the total variance. Thus, similar to core S5, Fe-Mn oxyhydroxides in core S6 have been found to play insignificant role in metal distribution.

Table 4 a)—EF showing seven levels of contamination

b) I_{geo} class showing sediment quality	
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

b I_{geo}	I_{geo} classes	Sediment quality
< 0	0	Unpolluted
0 - < 1	1	Unpolluted to 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

EF and Igeo

The average EF (Table 5) and Igeo values (Table 6) in the two cores when compared, indicated higher magnitude of metal enrichment or contamination (except for Fe and Zn) in core S6 collected from the upper middle estuary as compared to core S5 collected closer the mouth. Mangrove sediments of upper middle estuary (core S6) were found to be moderately to highly polluted with Mn, Cu, Co and Pb, and that with only Co in sediment core collected closer to the mouth (core S5). Other metals except Mn were however moderately polluted in core S5 while core S6 was moderately polluted

Table 5—average values of EF in mangrove cores collected from Vaitarna estuary

	Avg. EF values in core S5	Sediment quality	Avg. EF values in core S6	Sediment quality
Fe	2.1	Minor enrichment	1.7	Minor enrichment
Mn	0.7	No enrichment	2.9	Minor enrichment
Cu	6.3	Moderately severe enrichment	7.9	Moderately severe enrichment
Zn	3.7	Moderate enrichment	2.1	Minor enrichment
Co	5.1	Moderately severe enrichment	5.4	Moderately severe enrichment
Ni	5.6	Moderately severe enrichment	6.1	Moderately severe enrichment
Pb	2.4	Minor enrichment	3.9	Moderate enrichment

Table 6—average values of I_{geo} in mangrove cores collected from Vaitarna estuary

	Avg. I_{geo} values in core S5	Sediment quality	Avg. I_{geo} values in core S6	Sediment quality
Fe	1.3	Moderately polluted	0.9	Unpolluted to moderately polluted
Mn	0.1	Unpolluted to moderately polluted	2.1	Moderately to highly polluted
Cu	1.9	Moderately polluted	2.1	Moderately to highly polluted
Zn	1.8	Moderately polluted	1.0	Moderately polluted
Co	2.5	Moderately to highly polluted	2.5	Moderately to highly polluted
Ni	1.5	Moderately polluted	1.6	Moderately polluted
Pb	1.9	Moderately polluted	2.5	Moderately to highly polluted

with Zn and Ni. Fe and Mn were found to be unpolluted to moderately polluted in sediment collected from the upper middle estuary (core S6) and closer to the mouth (core S5) respectively. The difference in metal enrichment at the two locations may be attributed to addition of metals to upper middle estuary from the adjoining river as well as influence of relatively higher tidal flushing of metals towards the mouth⁴⁰.

Conclusion

The two mangrove cores collected from Vaitarna estuary indicated a gradual change in the type of sediment particles deposited over a period of time. All the studied parameters except clay, Al and Co showed significant difference at the two locations. In core S5 Mn, Fe, Co and Ni showed similar distribution pattern to that of sand and also indicated significant positive association. Similarly in core S6, Zn and Ni

showed similarity in distribution with sand. These metals are therefore seemed to have a common lithogenic origin from physical weathering of source rock. Zn, Cu and Pb showed increasing trend in core S5 similar to that of clay, while in core S6 Mn, Cu, Co and Pb agreed with the distribution pattern of clay, thus suggesting their association and higher accumulation in recent years. It also pointed towards increase in anthropogenic addition of these metals in recent years. Metal contamination was however found to be higher in core S6, collected from upper middle estuary, as compared to core S5, collected near the mouth, and was attributed to higher input from adjoining river as well as greater flushing of metals towards the mouth.

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