

Mudflats in lower middle estuary as a favorable location for concentration of metals, west coast of India

Ratnaprabha Siraswar & G. N. Nayak

Department of Marine Sciences, Goa University, Goa – 403 206

[E-mail: gnnayak@unigoa.ac.in]

Received 14 May 2010; revised 26 July 2010

Present study was an attempt to understand hydrodynamic conditions and the main factors regulating the distribution of metals in mudflats in the recent past along Mandovi Estuary. Sediment cores of 20 cm length were collected from three mudflats viz. near the mouth, lower middle and upper middle regions representing monsoon season from Mandovi Estuary. Cores were sub sampled at every 2 cm interval and analyzed for sand, silt, clay, organic carbon and selected metals. Sand percentage is the highest in the mudflat situated near the mouth (Betim) and finer sediments are higher in the lower (Karyabhat) and upper (Ribander) middle regions of the estuary. Organic matter associated more with finer sediment fractions at Karyabhat and Ribander (2.19% to 2.37%) mudflat cores as compared to Betim (0.13%). The sediments of Betim fall in the class I to IV, whereas sediments of two cores collected from middle estuarine region fall largely in class III. Sediment samples were analyzed for selected metals. Fe is highest in Ribander mudflat as compared to other cores. Cr, Co, Cu and Pb distribution agrees largely with the pattern of Fe in all the cores. Distribution of Cu and Pb also agrees with that of Mn. Zn and Ni follow the pattern of Co agreeing Fe distribution pattern. Concentration of Fe and Mn along with Ni, Zn, Cr, Pb and Cu are higher in Karyabhat.

[Keywords.: Madflats, Metal deposition, Manovi Estuary]

Introduction

Intertidal mudflats are prominent sub-environments found on the fringe of estuaries and in low relief sheltered coastal environments¹. The fine grained sediments of the intertidal mudflats (70 - 90%) are derived from terrestrial and marine regions^{2,3}. Mudflats act as a major sink for trace metals⁴, Metals which are discharged into aquatic environments from various sources may admix or interact with fine suspended sediments and are subsequently removed from the water column thus facilitating deposition in the inter-tidal regions leading to trapping of contaminants into the estuaries⁵. Estuarine mudflats are potential sites for deposition of organic matter derived from terrigenous, marine, atmospheric and anthropogenic sources and are mainly associated with fine grained particles which get trapped in this environment thus acting as trap for trace elements⁶⁻¹². Deloffre et al., (2005)¹³ stated that hydrodynamics control the fluvial sediment dynamics on an intertidal mudflat. Further, chemical processes such as oxidation-reduction, precipitation, dissolution, adsorption and also microbial processes regulate the cycling of elements in mudflats. Present study

consists the distribution and concentration of metals in mudflats and the factors influencing their distribution.

Material and Methods

The Mandovi River is about 70 km long and originates from the Parwa Ghats, a section of Western Ghats in Karnataka state. It is a drowned river valley type estuary¹⁴ with spring tide range of 2 to 2.4 m, while neap tide is 0.3 to 0.5 m. Inter-tidal flats are present in the lower and middle portion of Mandovi estuary. Sediment cores of 20 cm each were collected at 3 locations covering lower and middle regions of the Mandovi estuary. Sampling was carried out using PVC coring tube during low tide in August 2008 representing monsoon season. One core was collected towards the mouth of the estuary at station Betim representing lower estuary and two cores were collected from different parts of the middle estuary at station Karyabhat and Ribander (Fig. 1). Among the three locations, Betim and Ribander were from mudflats of main river channel whereas station Karyabhat is located in the sub channel of Mandovi estuary. All the sediment cores were sub sampled at

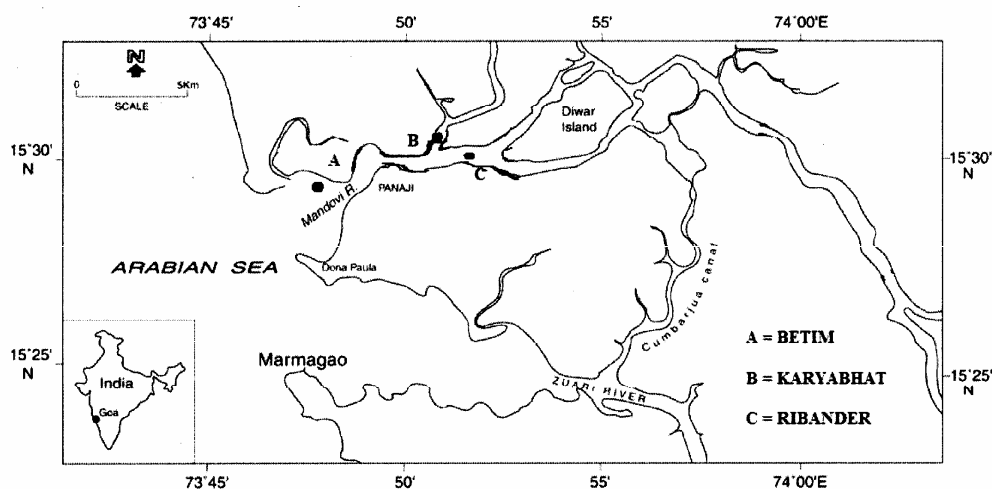


Fig. 1—Map showing the core locations along Mandovi estuary

2 cm interval using plastic sterile knife and was kept in zip lock plastic bags and transferred to lab in ice box. The samples were stored in a deep freezer at 20°C . Before the analysis they were thawed, dried at $50\text{--}60^{\circ}\text{C}$ in an oven and part of the sediment was disaggregated in an agate mortar. This part was used for total metal analysis and organic carbon. Other part of the sediment was used for granulometric analysis to obtain sand, silt and clay components. All sample containers and laboratory glass wares were pre-cleaned with detergent, soaked in HNO_3 (10%) for 24 h and rinsed with deionised distilled water before use. Acids and standard solutions used for the digestion and analyses were of supra-pure grade.

Total organic carbon: Organic carbon was determined using the standard method¹⁵ in which an aliquot of dried sediment (0.5 g) was treated with (10 ml) dichromate solution and 20 ml of acid mixture (silver sulphate dissolved in sulphuric acid). The mixture was then allowed to stand for 30 minutes. This was then followed by addition of a mixture of H_3PO_4 and NaF, and excess dichromate was then back titrated with standard ammonium solution using Diphenyl as an indicator. Dextrose was taken as standard for the determination of organic carbon.

Sediment component analysis was carried out using pipette method¹⁶, in which sand, silt and clay percentage in sediments was estimated by wet sieving. Before the analysis sediment was treated with sodium hexametaphosphate to remove carbonates and hydrogen peroxide to remove of organic matter from the sediment.

For metal analysis a small portion (0.2gm) of finely ground sediment sample was digested with $\text{HNO}_3\text{--HF--HClO}_4$ (7:3:1) on hot plate at 150°C in Teflon beakers. The above solution after drying was mixed with 5 ml of the same acid mixture and dried on hot plate for 1 hr then 2 ml of concentrated HCl was added again and was completely dried. After complete digestion of sediment sample the residue was dissolved in 10 ml of 1:1 HNO_3 . Thereafter, the contents from Teflon beakers were transferred into acid washed polypropylene volumetric flasks and solution was made up to 50 ml with millique (18 ohm's) water. Metals were determined on Varian AAS model AA240FS.

Results and Discussion

Sediment component distribution:

The abundance and distribution of sediment components namely sand, silt and clay together with total organic carbon of the three cores are described below separately. In the core collected at Betim, which is from the lower estuary, sediment largely consists of a higher percentage of sand (avg. 88.29%). The data obtained shows a range of 71.02% - 94.28% sand, 0.17% - 26.26% (avg. 7.97%) silt, and 2.44% - 8.16% (avg. 3.52%) clay. Sand percentage from bottom to surface remains almost constant except prominent decreasing peaks at 16 cm and 8 cm (Fig. 2a). Distribution of silt compensates the variations of sand throughout the length of the core. Clay shows increased peak at 18 cm, further towards

the surface it maintains almost constant trend but for relatively higher values at 10 cm, 8 cm and 4 cm. Organic carbon percentage values are low and ranges from 0.02% to 0.3% (avg. 0.13%). Relatively higher values are seen between 10 cm and 8 cm. Increased peak of organic carbon at 8 cm coincides with increased peak of silt, decreased peak of sand and increased values of clay. Further, in the upper part of the core, organic carbon values decrease along with sand. The low organic carbon values obtained might be due to the result of marine sedimentation and mixing processes at the sediment water interface where the rate

of delivery as well as rates of degradation by microbial-mediated processes can be high¹⁷.

Second core which was collected from lower region of middle estuary at Karyabhat has, sand, silt and clay components in the range of 0.52% – 8.1% (avg. 4.01%); 46.46% – 80.67% (61.09%) and 18.2% – 46.76% (34.89%) respectively with a high average value (95.98%) of finer sediments (silt and clay). Sand profile shows an alternate decrease and increase throughout the core with minimum at 16 cm and maximum value at a depth of 6 cm (Fig. 3a). Silt and clay distribution compensates with each other. Sand and clay show a similar trend from 20 cm to 16 cm and 12 cm to surface. Organic carbon varies from 1.55% to 2.57% (avg. 2.19%) at depth 18 cm and 12 cm respectively. Distribution of organic carbon largely agrees with that of silt between 18 cm and 10 cm. Finer sediments are associated with organic carbon in this core. Organic carbon is generally dependent on sediment grain size distribution and thus gets enriched in finer fractions of estuarine sediments^{18,19} as C-org /surface is higher for finer sediments than coarser fractions like sand particles^{20, 21}. However, the balance between accumulation and degradation rate of organic matter is probably the key factor which controls concentration of organic matter in sediments and anoxic decomposition of organic matter is intrinsically slower than oxic decomposition²². Further though generally organic matter is associated

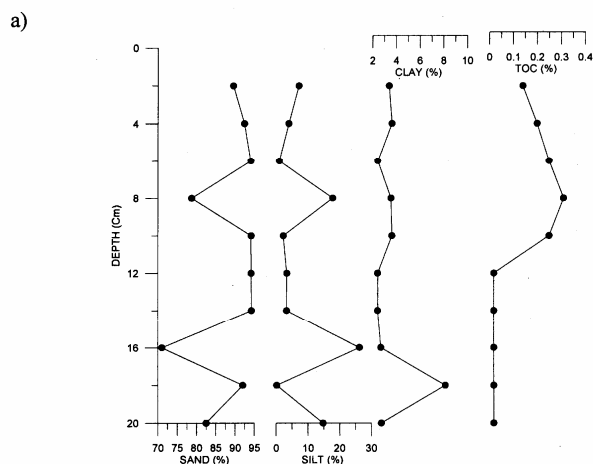


Fig. 2a) — Down core variation of sediment components (sand, silt, clay and organic carbon) in Betim mudflat.

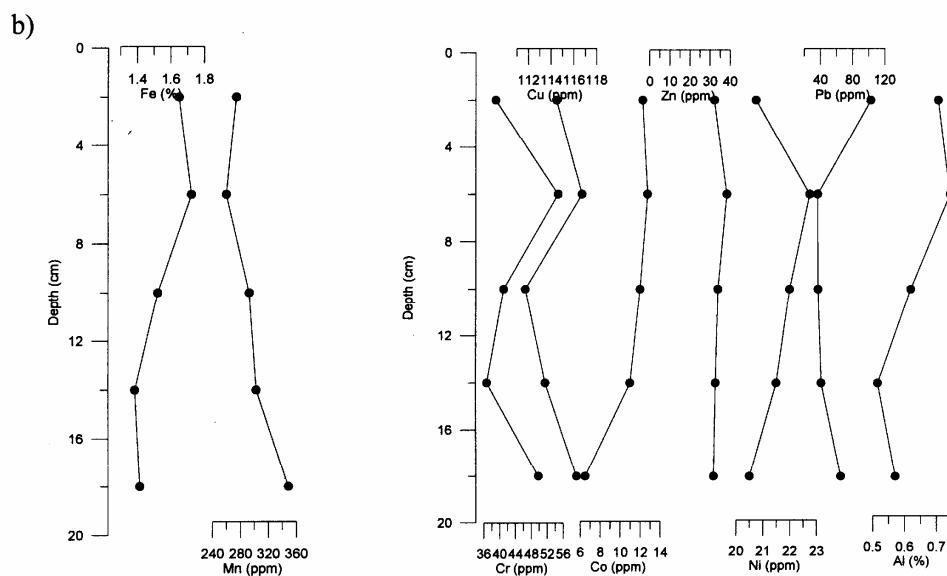


Fig. 2b) — Down core variation of metals (Fe, Mn, Cr, Cu, Co, Zn, Ni, Pb, Al) in mudflat sediment.

with the finer sediments association of organic matter with the size of sediments depends on the type of organic material and the source²³.

Core collected at Ribander, which is towards the upstream side of the middle estuary, shows a range of 4.76% - 37.35% (avg. 15.90%) sand, 36.09% - 55.76% (avg. 48.42%) silt and 26.56% - 46.4% (avg. 35.67%) clay. Sand shows an increasing trend from bottom to 12 cm and then decreases up to 4 cm.

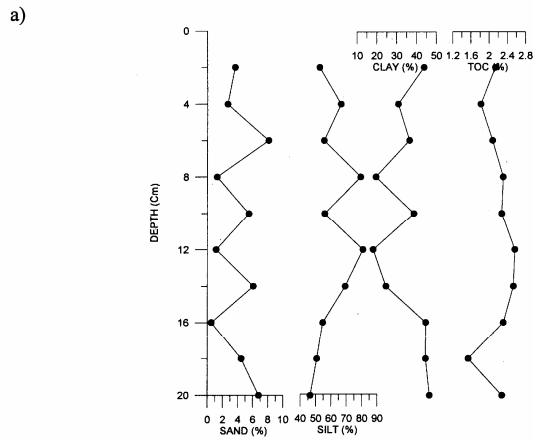


Fig. 3a) — Down core variation of sediment components (sand, silt, clay and organic carbon) in Karyabhat mudflat.

Distribution trend of silt and clay is largely opposite to that of sand with decreasing values up to 12 cm and then increase up to 4 cm in case of clay and 6 cm for silt (Fig. 4a). Organic carbon ranges from 1.72% (12 cm) to 2.75% (4 cm) with an average value of 2.37%. Distribution pattern of organic carbon largely agrees with finer fractions namely clay and silt except between 18 cm and 16 cm. Percentage of organic matter is very high in this core and is attributed to large amount of land runoff due to increase in rainfall during monsoon²⁴. Sorption behaviour is known to differ according to the origin and composition of the organic material^{25, 26}.

When the sediment components of the three cores are compared, it is seen that percentage of coarser fraction is high at Betim which is collected from the lower estuary, as compared to the other two cores. Higher hydrodynamic condition near the mouth of the estuary must be facilitating the deposition of coarser sediment fraction carrying away finer sediment components towards the middle region of the estuary. Organic matter is comparatively lesser in Betim. Further, when the two cores of middle estuary are compared it is observed that in Karyabhat the concentration of finer sediments is higher than Ribander, whereas organic carbon percentage is

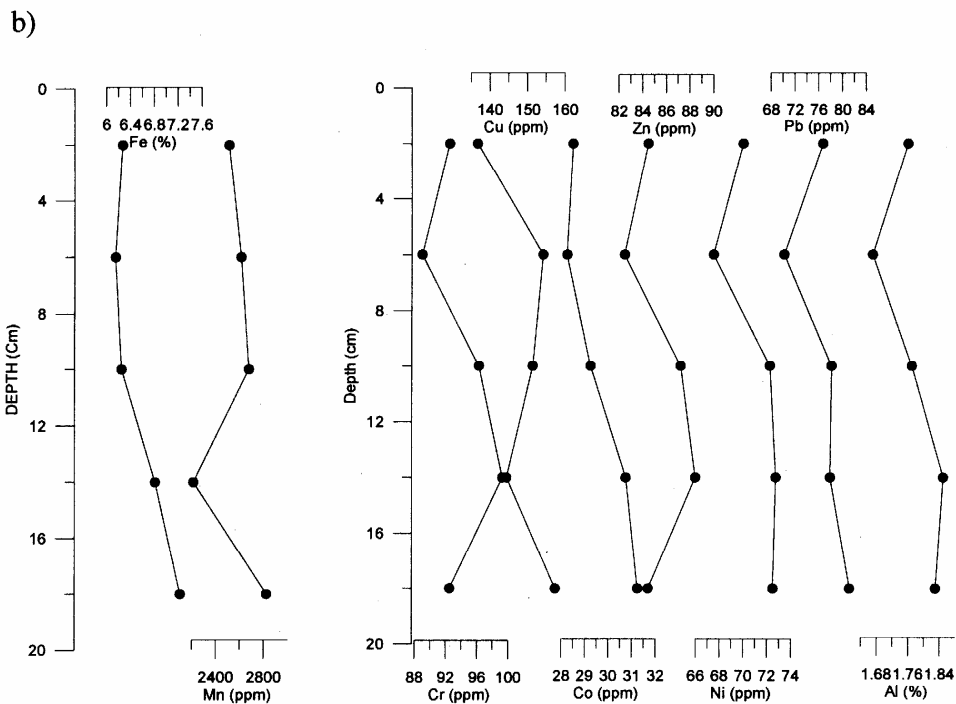


Fig. 3b) — Down core variation of metals (Fe, Mn, Cr, Cu, Co, Zn, Ni, Pb, Al) in mudflat sediment.

slightly higher in Ribander. As stated earlier Karyabhat core was collected from sub-channel of Mandovi estuary, which must be facilitating deposition of finer sediments.

To understand the hydrodynamic conditions in which the sediments have been deposited the data of three cores were plotted (Fig. 5) on a Ternary diagram proposed by Pejrup²⁷. The hydrodynamics are

distinguished in the diagram into four sections labeled as I to IV. Section I indicates very calm hydrodynamic condition and section II to IV indicate increasingly violent hydrodynamic conditions. Further, sections A to D provides environment with respect to size of the sediments. In Betim, 3 out of 9 points fall in Division IV (B) indicating their deposition in extreme violent condition, retaining comparatively higher percentage of sand whereas remaining six points fall between I to III (A) facilitating sediment deposition in relatively calmer environment. Overall at this station coarser sediment has deposited in a large range of hydrodynamic conditions. Sediments collected from two locations of middle estuarine region, when plotted on Ternary diagram fall in Division III which indicates that these locations provide less violent condition for deposition. Between the two locations, sediments of Karyabhat fall in D and that of Ribander fall in C and D (Fig.5b). This indicates that station Karyabhat facilitates deposition of uniformly finer sediments.

Mandovi Estuary mainly experiences violent hydrodynamic conditions i.e. high energy turbulent conditions towards the mouth and therefore finer grains do not settle instead they are carried away and get settled in low energy conditions²⁸. Further, in general estuary maintains relatively strong hydrodynamic

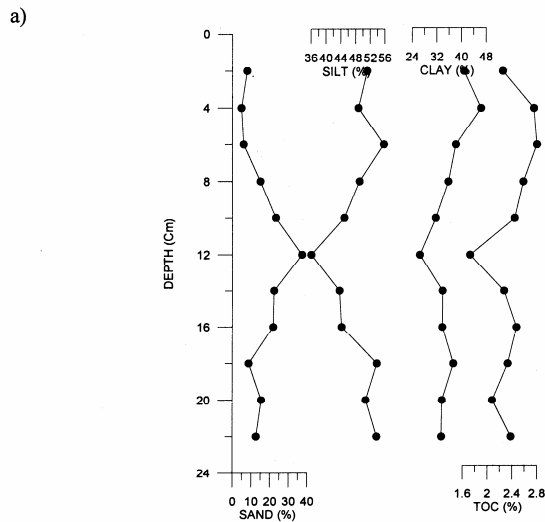


Fig. 4a) — Down core variation of sediment components (sand, silt, clay and organic carbon) in Ribander mudflat.

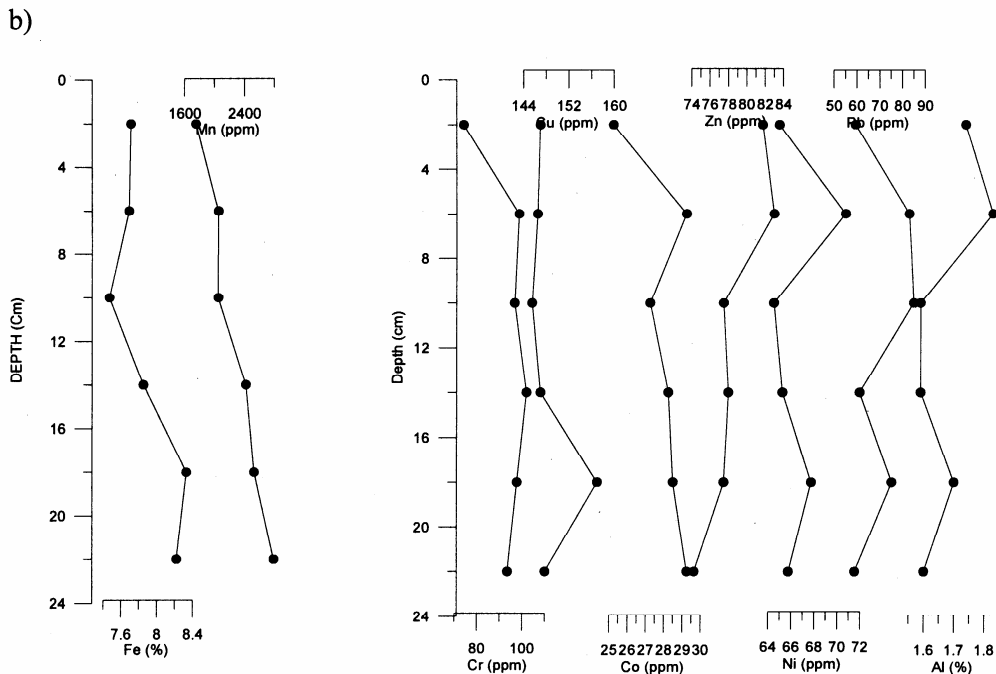


Fig. 4b) — Down core variation of metals (Fe, Mn, Cr, Cu, Co, Zn, Ni, Pb, Al) in mudflat sediment.

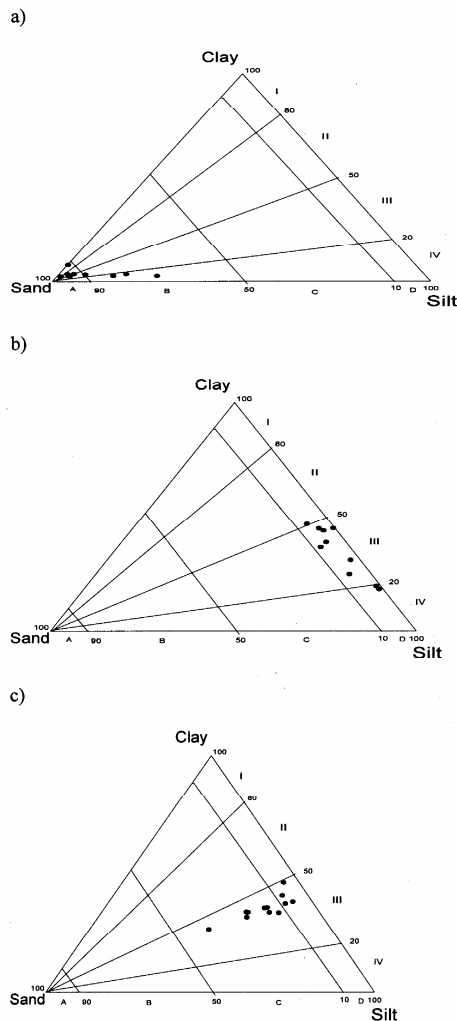


Fig. 5 — Traingular diagram for classification of hydrodynamic conditions of (a) Betim (b) Karyabhat (c) Ribander. (after Pejrup, 1988)

conditions during monsoon and as a result more percentage of sand is retained in both upper as well as lower estuarine region. Due to this higher percentage of sand is seen at Betim.

Trace elements

Betim

In the core collected from lower estuary (Betim), the Fe concentration varies from 1.39% to 1.72% (avg. 1.53%). Iron in the upper portion is higher than average compared to lower portion. Increase is specially seen between 14 cm and 6 cm, while in the lower end from 18 cm to 14 cm and also upper end from 6 cm to 2 cm Fe shows a decreasing trend. Mn

concentration ranges from 260 ppm to 349 ppm with (avg. 296 ppm). Largely Mn shows a decreasing trend from bottom up to 6 cm and increase towards surface from 6 cm. Mn enrichment seen in younger sediments may be due to reprecipitation of Mn in the form of insoluble oxy hydroxides. The vertical distribution of some metals such as Fe and Mn can be affected upon deposition by diagenetic processes that solubilize the elements in the anoxic portions of the core and redeposit them in the upper oxic layers²⁹. Fe and Mn distribution shows opposite trend in the upper portion, but shows similar distribution pattern in lower portion of the core (18 cm to 14 cm) which indicate the strong association of these elements in the lower portion. Abu-Hilal and Badran (1990)³⁰; Nohara and Yokota (1978)³¹; El-Sayed (1982)³² have reported that the distribution of Fe and Mn is controlled by different factors including hydrodynamics, churning and dredging.

The concentration of Cr, Cu, Co, Zn, Ni, Pb and Al in this core ranges from 37 - 55 ppm, 112 - 117 ppm, 7 - 13 ppm, 32 - 39 ppm, 21- 23 ppm, 37 - 103 ppm, 0.52 - 0.74%. Trace element distribution is presented in (Fig. 2b). Cr shows a decreasing trend from 18 cm - 14 cm depth followed by an increasing trend up to 6 cm depth and towards surface its concentration decreases. Cu shows decreasing trend from bottom up to 10 cm which then increases up to 6 cm, from here it decreases towards the surface. Co, Ni and Zn experiences an increase from bottom up to 6 cm depth from where towards surface they show decreasing trend. Pb shows a decreasing trend from bottom to 6 cm and further shows increasing trend towards the surface. This reveals that increase of Pb flux in surface sediments is probably due to increased vehicular traffic or may be due to increased anthropogenic and industrial discharges into coastal environments in the recent years. Al largely follows trend of Cr showing decreasing values from bottom to 14 cm and increasing up to 6 cm and further shows decreasing trend towards surface.

From the above observations it can be stated that Cr, Co, Ni, Zn along with Al show an increasing trend between 14 cm and 6 cm, from here towards the surface concentration of all these elements decreases. Between 18 cm and 14 cm however, these elements can be grouped into two. Co, Zn and Ni show an increasing trend while Cr and Al decreasing trend. Cu agrees largely with Cr but except for its decrease between 14 cm - 10 cm. Pb shows largely opposite

trend i.e. it decreases from bottom up to 6 cm and shows increasing trend towards the surface indicating its increase in concentration in recent years. Distribution pattern of Cr and Cu can be largely compared to that of Fe indicating co precipitation of these elements. Also distribution pattern of Co, Ni and Zn between 14 cm and 6 cm is similar to that of Fe distribution. Distribution pattern of Pb largely agrees with distribution pattern of Mn through out the length of the core. Pb distribution together with Mn pattern may be attributed to local redox conditions, which allows Pb to co precipitate with Mn during Mn oxide formation^{33,34}. This indicates that Fe and Mn oxides play a major role in the distribution and concentration of trace metals at this location.

In the core collected from lower middle estuarine region (Karyabhat), Fe varies from 6.15% to 7.24% at depths 6 cm and 18 cm respectively. Fe shows a decreasing trend from bottom 18 cm up to 6 cm followed by a slight increase towards surface. Mn concentration ranges from 2214 ppm to 2824 ppm with avg. 2567 ppm. Mn shows a decreasing trend from depth 18 cm up to 14 cm followed by an increase up to 10 cm and there after decreases up till surface. Fe and Mn show similar pattern of distribution except from depth 14 cm to 10 cm and 6 cm to surface (Fig. 3b). The concentrations of Cr, Cu, Co, Zn, Ni, Pb and Al ranges from 89 - 99 ppm, 137 - 158 ppm, 28 - 31 ppm, 83 - 89 ppm, 68 - 73 ppm, 70 - 81 ppm, 1.67 - 1.85% respectively. Cr shows an increasing trend from 18 cm to 14 cm, followed by a decrease from 14 cm to 6 cm and further shows an increasing trend towards the surface. Cu shows an opposite trend to that of the distribution pattern of Cr showing an increasing trend from depth 14 cm to 6 cm and with decreasing trend between 18 cm and 14 cm in the lower portion of core and towards surface from 6 cm. Co shows a decreasing trend from depth 18 cm to 6 cm before showing slight increasing trend towards surface. Zn, Ni along with Al largely follows trend of Cr showing an increase from bottom to 14 cm followed by a decrease between 14 cm and 6 cm from where they show an increasing trend towards surface. Pb shows alternate decrease and increase through out the length of the core with decrease in values from depth 18 cm to 14 cm and depth 10 cm to 6 cm whereas, increase is seen from depth 14 cm to 10 cm and towards the surface from 6 cm.

From the above observations Co largely agrees with the distribution pattern of Cr, Zn, Ni and Al from

depth 14 cm to 6 cm showing a decreasing trend and increase from 6 cm to surface. The distribution pattern of Cu, Co and Pb largely agrees in lower portion of core wherein their concentration decreases from 18 cm to 14 cm, whereas increase is observed from 6 cm up to surface in both Co and Pb except for Cu where decrease is noted. Between 14 cm and 10 cm Cr, Co, Ni, Zn and Al all show decreasing trend whereas Pb and Cu show increasing trend. Co agrees with the distribution pattern of Fe throughout the length of the core. Also Ni, Zn, Cr show a similar pattern to that of Fe between 14 cm and 6 cm and increase towards surface from 6 cm. Trace metal co-precipitation with Fe oxides may be related to pore water movement during reduction and re adsorption in the oxic zone³⁴. Cu agree with the distribution pattern of Fe between 18 cm and 14 cm and Pb agrees with Fe from 18 cm to 14 cm and also between 10 cm and 6 cm. Distribution pattern of Pb largely agrees with Mn profile from depth 18 cm to 6 cm. Cu and Mn also maintains a similar profile from depth 18 cm up to 10 cm and 6 cm to surface. Ni, Zn, Co, Cr, Pb show a similar distribution pattern to that of Fe and Mn showing a decrease from depth 10 cm to 6 cm indicating the role of Fe-Mn oxides in the concentration of these metals. Pb, Ni, Zn, Co and Cr show increased concentration towards the surface which indicates that they are mobilized and partially re adsorbed on to Fe oxy hydroxides in oxic sediment layer. This strongly supports that the diagenetic processes influence the modification of sediments thus facilitating distribution of trace metals in sediments.

In the core collected from upper middle estuary (Ribander) Fe concentration ranges from 7.47% to 8.33% with avg. 7.87%. Increase in Fe content is observed between 22 cm to 18 cm and from depth 10 cm up to surface and a decrease from 18 cm to 10 cm. Mn ranges from 1752 ppm to 2792 ppm with avg. 2267 ppm. Largely Mn shows a decreasing trend between 22 cm and 10 cm and towards the surface from 6 cm and slight increase between 10 cm and 6 cm (Fig. 4b). Fe and Mn show an opposite trend in lower portion of core i.e. from depth 22 cm to 18 cm and also from 6 cm to surface. However, they show similar distribution pattern between 18 cm and 6 cm with a decrease between depth 18 cm and 10 cm followed by an increase between 10 cm and 6 cm. The concentration of Cr, Cu, Co, Zn, Ni, Pb and Al ranges from 74 - 102 ppm, 146 - 157 ppm, 25 - 29 ppm,

74 - 83 ppm, 65 - 71 ppm, 59 - 85 ppm, 1.59 - 1.83% respectively. Cr shows an increasing trend from depth 22 cm up to 14 cm there after maintains a decreasing trend from 14 cm up to surface. Cu shows an increase between depth 22 cm and 18 cm followed by a decrease up to 10 cm before showing an increasing trend towards surface. Co experiences a decreasing trend from bottom up to depth 10 cm further shows an increase from 10 cm to 6 cm and decrease from 6 cm up till surface. Largely Zn shows increase in the lower portion of core i.e. from 22 cm to 14 cm and also from 10 cm to 6 cm whereas it shows decreasing trend in the middle portion of core i.e. from 14 cm to 10 cm and also towards surface from 6 cm. In case of Ni decrease is seen between 18 cm and 10 cm and towards surface from 6 cm. Between 22 cm and 18 cm and also 10 cm and 6 cm it shows increasing trend. Pb shows an increase from bottom up to 18 cm and from 14 cm and 10 cm and decrease between 18 cm and 14 cm and from 10 cm up to surface. In case of Al distribution pattern largely shows an alternate increase (22 cm - 18 cm and 10 cm - 6 cm) and decrease (18 cm - 14 cm and 6 cm - surface) with a constant trend in the middle portion of the core (14 cm - 10 cm).

From the above observations it is noted that Pb and Cu show a similar profile between depth 22 cm and 14 cm followed by an opposite trend up to surface. Cu and Ni show a similar trend from bottom to 6 cm (Fig.4b). Zn and Co maintains a similar profile from 14 cm to surface but from bottom to 14 cm an opposite trend is observed. Al and Ni largely show similar distribution except in the middle portion of core i.e. from 14 cm to 6 cm where Al maintains a constant trend and Ni shows a slight decrease. Cu agrees with Co, Ni and Al from depth 18 cm to 6 cm except for Al which shows constant trend between 14 cm and 10 cm. Pb and Cr experiences similar distribution pattern between 10 cm and surface and from bottom up to 18 cm. However, between 18 cm and 14 cm Pb decreases and Cr increases and between 14 cm and 10 cm Pb shows an increase where as decrease is noted in case of Cr. Co and Ni shows a similar profile except from bottom to 18 cm. Zn and Cr experiences similar distribution pattern from depth 22 cm up to 10 cm and in surface beyond 6 cm except between 10 cm to 6 cm. In lower portion of the core similar distribution pattern i.e. increase from bottom to 18 cm followed by a decrease i.e. from 18 cm to 14 cm is mainly observed in Al, Pb, Ni and Cu out of

which Al and Ni together with Co and Zn show a similar distribution pattern beyond 10 cm up to surface. In top portion of the core i.e. from 6 cm up to surface similar pattern of metal distribution is observed in case of Cr, Co, Zn, Ni, Pb and Al. Cu largely agrees with the distribution pattern of Fe from bottom up to the surface. Ni shows a similar distribution pattern to that of Fe between 22 cm and 6 cm but beyond 6 cm it reflects the pattern of Mn with a decrease. Al and Pb reflects the pattern of Fe between 22 cm and 14 cm with increase seen between 22 cm and 18 cm followed by decrease up to 14 cm. Co largely agrees with distribution profile of Mn throughout the length of the core it also reflects the Fe distribution pattern (14 cm - 6 cm) together with Mn distribution pattern. Al and Zn agree with Fe distribution pattern between 10 cm - 6 cm and in case of Zn similarity in pattern is also seen between 22 cm-18 cm. Cr agrees with Fe in lower portion of core i.e. between 22 cm and 18 cm and 14 cm and 6 cm followed by an decrease towards surface which agrees with Mn distribution pattern. Al also agrees with Mn distribution pattern between 18 cm and 14 cm where decrease is observed followed by an increase between 10 cm and 6 cm and showing decrease towards surface. Ni shows a similar distribution pattern to that of Mn from 18 cm onwards up to surface, except in lower portion of core between 22 cm-18cm where it agrees with Fe, whereas Zn agrees with Mn profile between 14 cm till surface. Cr and Cu shows similar distribution pattern to that of Mn between 14 cm - 10 cm and beyond surface and between 18 cm - 6 cm respectively. In top portion of core largely all metals except Cu show a decrease in surface reflecting the distribution pattern of Mn whereas in lower portion of core largely elements except Co agree with Fe between 22 cm and 18 cm. Hence Fe and Mn may partly control the vertical profile of trace metals in this core.

Correlation coefficient:

Pearson's correlation coefficient is used to determine interrelation among several parameters existing in sediments with $r = \pm 0.9$ with $p = 0.1$ and 0.05 depending on correlation. In the core collected from lower estuary (Betim), show significant positive correlation between organic matter and metals such as Fe, Ni, Zn, Co and Al ($p < 0.05$) and significant negative correlation with Mn (Table 1a). Positive correlation of organic matter with the metals infer that

Table 1a)—Pearsons correlation between different sediment components (sand, silt, clay and total organic carbon) and elements in sediment core (Betim)

	Sand (%)	Silt (%)	Clay (%)	OC (%)	Fe	Mn	Cr	Cu	Co	Zn	Ni	Pb	Al
Sand (%)	1.00												
Silt (%)	-0.65	1.00											
Clay (%)	-0.31	-0.43	1.00										
OC (%)	0.22	-0.01	-0.48	1.00									
Fe	-0.22	0.25	-0.45	0.77	1.00								
Mn	-0.04	-0.44	0.87	-0.73	-0.83	1.00							
Cr	0.17	-0.70	0.31	0.29	0.42	-0.01	1.00						
Cu	-0.22	-0.34	0.32	-0.15	0.33	0.05	0.79	1.00					
Co	0.15	0.49	-0.93	0.72	0.67	-0.96	-0.21	-0.32	1.00				
Zn	0.51	-0.36	-0.51	0.73	0.69	-0.68	0.64	0.34	0.57	1.00			
Ni	0.73	-0.32	-0.67	0.74	0.49	-0.67	0.35	-0.04	0.67	0.92	1.00		
Pb	-1.00	0.70	0.26	-0.27	0.19	0.03	-0.26	0.17	-0.12	-0.55	-0.75	1.00	
Al	-0.30	0.22	-0.32	0.75	0.99	-0.75	0.47	0.38	0.58	0.64	0.40	0.25	1.00

Table 1b)—Pearsons correlation between different sediment components (sand, silt, clay and total organic carbon) and elements in sediment core (Karyabhat)

	sand (%)	Silt (%)	Clay (%)	OC (%)	Fe	Mn	Cr	Cu	Co	Zn	Ni	Pb	Al
sand (%)	1.00												
Silt (%)	0.35	1.00											
Clay (%)	-0.53	-0.98	1.00										
OC (%)	0.27	0.80	-0.78	1.00									
Fe	-0.34	0.09	-0.01	-0.47	1.00								
Mn	-0.16	-0.88	0.83	-0.84	0.11	1.00							
Cr	-0.22	0.74	-0.63	0.63	0.29	-0.59	1.00						
Cu	0.44	-0.27	0.15	-0.56	0.34	0.66	-0.30	1.00					
Co	-0.28	0.29	-0.20	-0.25	0.96	-0.02	0.53	0.32	1.00				
Zn	-0.20	0.72	-0.60	0.63	0.24	-0.55	1.00	-0.27	0.49	1.00			
Ni	-0.52	0.31	-0.18	0.06	0.67	-0.10	0.81	0.03	0.82	0.81	1.00		
Pb	-0.76	-0.03	0.19	-0.26	0.73	0.16	0.56	0.02	0.78	0.55	0.92	1.00	
Al	-0.54	0.40	-0.24	0.03	0.80	-0.26	0.76	-0.11	0.89	0.73	0.93	0.88	1.00

organic matter present in sediments provides active sites for sorption of these metals as it has a high complexation ability with trace metals in marine environment^{35,36}. Further, it is well established that organic matter is important factor in the distribution and concentration of trace metals³⁷. Clay shows a significant positive correlation with Mn ($r = 0.87$) whereas it shows negative correlation ($r = -0.93$) with Co (Table 1a). Ni shows a good correlation with coarser fractions ($r = 0.73$) of the sediment. Pb shows a good correlation with silt fractions ($r = 0.70$). Fe shows significant correlation with Al ($r = 0.99$) indicating that they are from same namely terrigenous source. Fe also shows positive correlation with Co ($r = 0.67$) and Zn ($r = 0.69$) which reveals Fe - oxides plays a role in concentration of these trace metals in the sediments.

In Karyabhat silt shows good correlation with organic carbon ($r = 0.80$) as well as with Cr ($r = 0.74$) and Zn ($r = 0.72$). Clay shows a negative correlation with organic carbon however, it shows good association with Mn ($r = 0.83$). The clay minerals are the main carriers of trace metals during mobilizing and diffusing³⁸. Cr and Zn display a significant correlation with organic carbon (Table 1b). It is observed that total organic carbon did not play much role in metal sorption except for Cr and Zn, as there is little evidence to suggest the association of metals with organic carbon because correlation values are poor for Fe, Co, Ni, Al except for Zn and Cr. This may be due to oxygen-depleted, more protected and muddy sediment in which there is less conditions of aeration and hence no degradation of organic matter³⁹. Further, in this condition finer sediment fractions

along with redox sensitive elements (Fe and Mn) must have played a role in sorption of metals. Fe showed significant correlation with Co, Ni, Pb and Mn with Cu indicating the role of Fe and Mn oxides in the distribution of these elements. During monsoon higher salinity is expected to be available in the lower and lower middle estuary facilitating Mn adsorption, precipitation and finally association with clay size sediments.

In Ribander clay exhibits significant correlation with Zn ($r = 0.73$) and Al ($r = 0.83$). Silt displays a significant correlation with Ni ($r = 0.71$) and Al (0.70). The elements Zn and Ni are mainly concentrated in the fine-grained size fraction of the solid phase^{40,41}. Organic carbon shows significant correlation with Ni and Pb indicating the role of organic carbon in governing distribution of these elements in sediments. Fe shows significant correlation with Mn and Cu and Mn with Cr and Co, indicating role of Fe and Mn oxide in the distribution and concentration of Cu, Cr and Co. Fe and Mn shows a significant correlation ($r = 0.80$) with each other (Table 1c) indicating they are derived from similar source or have similar post depositional behaviour. Fe shows significant correlation with Cu ($r = 0.78$), whereas Mn displays a significant correlation with Co ($r = 0.74$), Cr ($r = 0.55$) and negative correlation with Zn ($r = -0.82$). This behaviour of negative correlation of Zn may be because of different sources probably from anthropogenic input⁴².

Inter metal association between elements were observed in all three cores collected at different locations. In Betim Fe exhibits significant correlation with Al ($p < 0.1$, $r = 0.99$) and Zn ($p < 0.05$, $r = 0.69$).

Despite the fact that Fe is a major element in mineral phase of sediments, its significant correlation with Al suggests that Fe is also of lithogenic origin⁴³. Zn also shows a significant correlation ($p < 0.05$) with Al ($r = 0.64$) and Ni ($r = 0.92$). Co exhibits significant correlation ($p < 0.05$, $r = 0.67$) with Fe and Ni. In Karyabhat core Mn showed negative correlation with many elements (Cr, Co, Zn and Ni), suggesting that Mn-oxide may be only a minor host phase for these elements in the estuarine environments. Similar poor associations of Mn with trace metals in sediments were also noticed earlier by⁴⁴ from Mandovi estuary. Mn and Cr showed negative correlation which may be due to influence of redox conditions of sedimentary environment. In pore waters, their oxidation states are determined by ambient redox conditions and hence these elements have different mobility in oxic and anoxic environments. Mn is enriched in oxic zone of sediment. In reducing environment, it gets mobilized to pore waters and get depleted in solid phase⁴⁵. In contrast, Cr is found to be depleted in the oxic zone and gets enriched in reducing strata⁴⁶. Cr exhibits a significant correlation with Zn ($r = 1.00$), Ni ($r = 0.81$) and Al ($r = 0.76$). Inter-metal relationship revealed that high degree of correlation existed indicating their identical behaviour during transport in estuarine environment⁴⁷. Co displays a significant correlation with Pb ($r = 0.78$), Fe ($r = 0.96$), Ni ($r = 0.82$) and Al ($r = 0.89$). Pb also shows significant correlation with Ni ($r = 0.92$), Fe ($r = 0.73$) and Al ($r = 0.88$). Mn showed a significant association with Fe ($r = 0.80$) in Ribander. Cu and Fe displays a significant correlation ($r = 0.78$, $p < 0.1$), whereas Mn shows negative correlation with Zn ($r = -0.82$); Pb ($r = -0.27$) and with

Table 1c)—Pearsons correlation between different sediment components (sand, silt, clay and total organic carbon) and elements in sediment core (Ribander)

	sand (%)	silt (%)	clay (%)	OC (%)	Fe	Mn	Cr	Cu	Co	Zn	Ni	Pb	Al
sand (%)	1.00												
silt (%)	-0.93	1.00											
clay (%)	-0.84	0.57	1.00										
OC (%)	-0.33	0.46	0.06	1.00									
Fe	-0.35	0.48	0.07	-0.30	1.00								
Mn	0.14	0.13	-0.50	-0.17	0.80	1.00							
Cr	0.41	-0.19	-0.62	0.36	0.16	0.55	1.00						
Cu	-0.37	0.39	0.25	-0.25	0.78	0.43	0.15	1.00					
Co	-0.05	0.34	-0.39	0.51	0.47	0.74	0.81	0.21	1.00				
Zn	-0.48	0.22	0.73	0.46	-0.54	-0.82	-0.32	-0.23	-0.35	1.00			
Ni	-0.67	0.71	0.42	0.81	0.16	0.01	0.33	0.25	0.57	0.50	1.00		
Pb	0.03	0.06	-0.16	0.68	-0.40	-0.27	0.44	0.04	0.23	0.28	0.47	1.00	
Al	-0.85	0.70	0.83	0.59	-0.11	-0.50	-0.27	0.12	-0.03	0.84	0.79	0.29	1.00

Al ($r = -0.50$). Al shows a significant correlation with Zn ($r = 0.84$) and Ni ($r = 0.79$). Significant correlation of Al with several elements in all three cores indicates that metals are dominantly associated with clay minerals especially aluminosilicates, probably as lattice-bound components⁴⁸. Fe and Mn seem to play an important role in governing the distribution of trace elements in the mudflats. It is a known fact that

Fe and Mn oxy hydroxides are important scavengers of trace metals⁴⁹. The redox-driven cycling of Fe and Mn occurring at oxic-anoxic boundaries in many water bodies influences the cycling of other elements by scavenging on the surfaces of freshly formed Fe- and Mn-oxides⁵⁰. The exclusive role played by Mn oxides in cycling of Co has been reported earlier by⁵¹. Metal enrichment occurs in organic rich silty

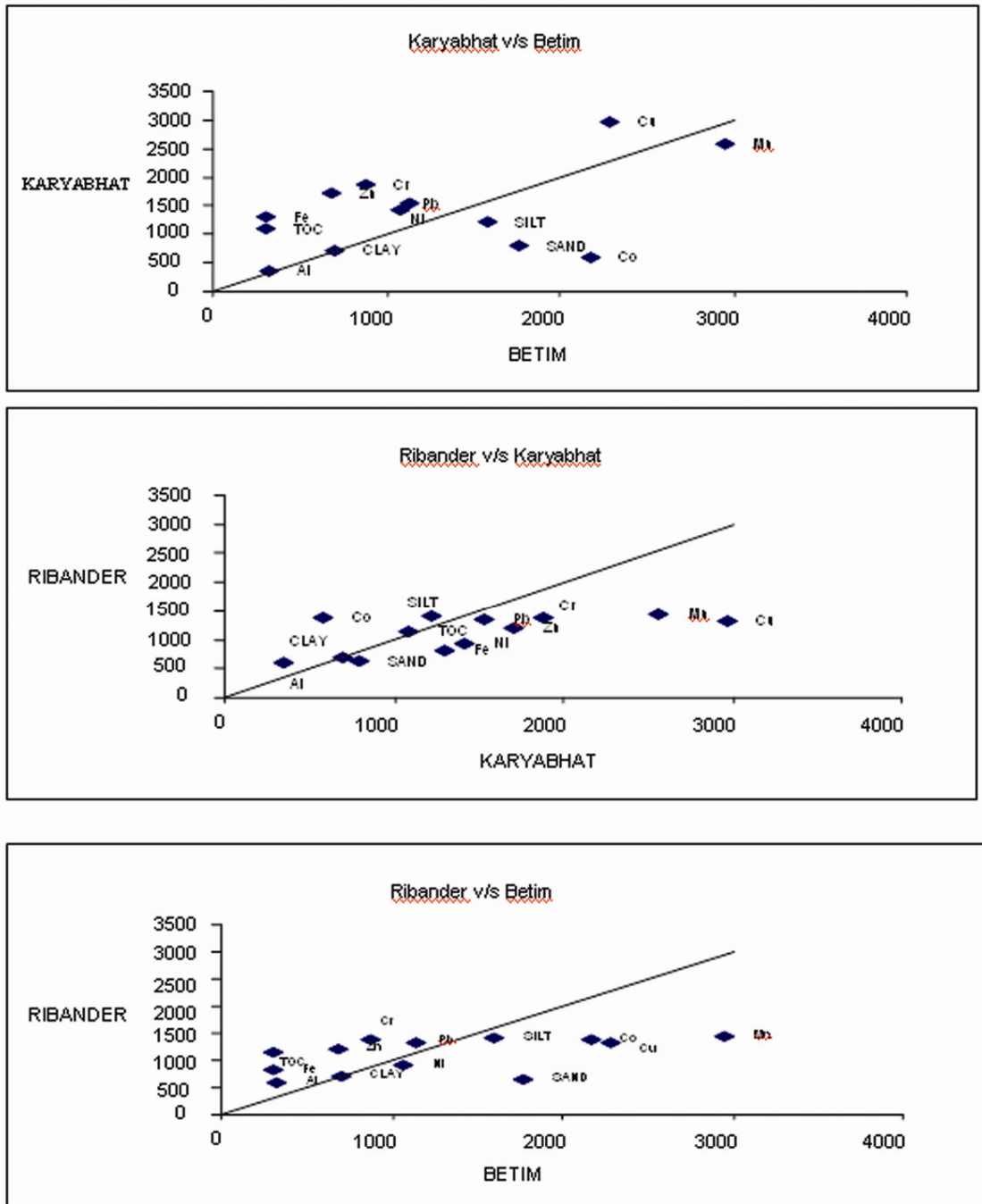


Fig. 6—Isocon diagram (Grant, 1986) individual points represent average value of sediment component and element in each core.

clay fractions^{52,53} which have high cation exchange capacities, larger surface area and surface charge⁵⁴.

In order to understand the difference in depositional processes between three locations with respect to facilitating metal concentration, an attempt is made to plot (Fig. 6) the data on the Isocon diagram⁵⁵. When the cores between lower estuary and lower region of the middle estuary are compared, it is seen that Al and clay mostly fall on the isocon line indicating not much variation in both cores with respect to these components. However, Betim core showed high concentration of Co, Mn, silt and sand indicating presence of coarser sediment fractions which facilitates association of Mn and Co. Whereas, organic carbon, Fe, Zn, Cr, Pb and Ni are more enriched in Karyabhat core indicating role of organic matter along with Fe oxide in concentration of trace elements. When cores collected from different parts of middle estuary are compared, it is observed organic carbon, Pb, silt, clay and sand fall close to isocon line indicating not much variation between the cores. Metals such as Mn, Cu, Fe, Ni, Zn, and Cr are enriched in Karyabhat core, indicating the role of Fe and Mn oxides in distribution of these trace elements in addition to finer sediments and organic matter. In inter-tidal flats if extent of water percolation is limited it creates anoxic zone where in sulphate reduction is dominant as a result metal ions get precipitated⁴⁵. This process may account for higher metal concentration in Karyabhat as it is from sub channel of Mandovi estuary. Al and Co is high in Ribander core. Lastly when comparison is made between Ribander and Betim it is seen that Al, clay, Pb, silt fall close to isocon line indicating no variation observed between the cores. Sand, Co, Cu and Mn are more pronounced in Betim core indicating that in the presence of coarser sediments role of Mn in distribution of Co and Cu, whereas organic carbon, Zn, Cr, Fe and Al are more enriched in Ribander core indicating the role of organic matter and clay together with Fe oxides in metal distribution. It is clear from the present study that among all three cores, Karyabhat provides favourable location for deposition of trace metals as compared to other two locations. Fe and Al displays a good correlation with each other in Betim and Karyabhat cores which suggests that iron is associated with aluminium in aluminosilicate phases⁵⁶. The positive correlation of trace metals and Al is related to the abundance of clay⁵⁷ minerals and role of the clay minerals in the distribution of metals.

Conclusion

Sediment cores of 20 cm length collected from three mudflats, near the mouth, lower middle and upper middle regions representing monsoon season from Mandovi Estuary revealed that sand percentage is the highest in the mudflat situated near the mouth (Betim) and finer sediments are higher in the lower (Karyabhat) and upper (Ribander) middle regions of the estuary indicating changes in energy conditions and progressive sorting of sediments by tidal currents along the estuary. Selected metals studied with space and depth in Mandovi estuary indicated that trace metal distribution and concentration is regulated by presence of finer sediments, organic matter and Fe and Mn oxides. Further, among the three locations trace metal concentrations is found to be higher in Karyabhat core which was collected from lower middle estuarine region and from sub channel of Mandovi estuary. The study reveals that this location as a favorable region for concentration of metals.

Acknowledgement

Author (RRS) wish to thank COE - Marine Microbiology, Goa University, supported by Ministry of Earth Sciences, Govt. of India for the financial assistance in the form of Research Fellowship. Authors also wish to thank the anonymous reviewer/s for their comments.

References

- O'Brien, D. J., Whitehouse, R. J. S. and Cramp, A., The cyclic development of a macrotidal mudflat on varying timescales. *Cont. Shelf Res.*, 20 (2000) 1593-1619.
- Lesueur, P., Lesourd, S., Lefebvre, D., Granaud, S. and Brun-Cottan, J., Holocene and modern sediments in the Seine estuary (France): a synthesis. *J. Quar. Sci.*, 18 (1) (2003) 3-16.
- Shi, Z. and Chen, P. Y., Morphodynamics and sediment dynamics on intertidal mudflats in China. *Cont. Shelf Res.*, 16 (15) (1996) 1909-1926.
- Lindsay, P., Bell, F. G. and Hytiris, N., Contamination of sediments in Forth Estuary, Scotland. Geological Society, London, Engineering Geology special publications 14 (1998) 179-187.
- Cearreta, A., Irabian, M. J., Leorri, E., Yusta, I., Croudace, I. W. and Cundy, A. B., Recent anthropogenic impacts on the Bilbao estuary, Northern Spain: Geochemical and Microfaunal evidence. *Estuar. Coast. Shelf Sci.*, 50 (2000) 571-592.
- Billion, G., Ouddane, B. and Boughriet, A., Chemical speciation of sulphur compounds in the surface sediments from the bays (Fresnaye, Seine and Authie) in Northern France and identification of some factors controlling their generation: *Talanta*, 53 (2002) 971-981.

- 7 Dickinson, W. W., Dunbar, G. B. and Mcleod, H., Heavy metal history from cores in wellington harbour, New Zealand. *Environ. Geol.*, 27 (1996) 59-69.
- 8 Fatoki, O. S. and Mathabatha, S., An assessment of heavy metal pollution in the East London and Port Elizabeth harbours. *Water SA*, 27 (2001) 233-240.
- 9 Gogou, A., Bouloubassi, I. and Stephanou, E. G., Marine organic geochemistry of the Eastern Mediterranean: 1. Aliphatic and polyaromatic hydrocarbons in Cretan Sea surficial sediments. *Mar. chem.*, 68 (2000) 265-282.
- 10 McCready, S., Birch, G. F. and Long, E. R., Metallic and organic contaminants in sediments of Sydney harbour, Australia and vicinity – A chemical dataset for evaluating sediment quality guidelines. *Environ. Inter.*, 32 (2006) 455-465.
- 11 Poulton, D. J., Morris, W. A. and Coakley, J. P., Zonation of contaminated bottom sediments in Hamilton harbour as defined by statistical classification techniques. *Water Qual. Res. J. Can.*, 31 (1996) 505-528.
- 12 Wang, X. C., Sun, S., Ma, H. Q. and Liu, Y., Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments of Jiaozhou Bay, Qingdao, China. *Mar. Pollut. Bull.*, 52 (2006) 129-138.
- 13 Deloffre, J., Lafite, R., Lesueur, P., Lesourd, S., Verney, R. and Guezennec, L., Sedimentary processes on a fluvial estuarine mudflat: The macrotidal Seine example (France). *Estuar. Coast. Shelf Sci.*, 64 (4) (2005) 710-720.
- 14 Murty, C. S., Das, P. K., Nair, R. R., Veerayya, M. and Varadachari, V. V. R., Circulation and sedimentation processes in and around the Aguada Bar. *Indian J. Mar. Sci.*, 5 (1976) 9- 17.
- 15 Gaudette, H. E., Flight, W. R., Toner, L. and Folger, D. W., An inexpensive titration method for the determination of organic carbon in recent sediments. *J. Sedi. Petro.*, 44 (1974) 249 - 253.
- 16 Folk, R. L., *Petro Sedi Rocks*, (Hemphills Austin) 1968, pp. 177.
- 17 Canuel, E. A. and Martens, C. S., Seasonal variability in the sources and alteration of organic matter associated with recently deposited sediments. *Org. Geochem.*, 20(5) (1993) 563-77.
- 18 Hunt, C. D., Regulation of sedimentary cation exchange capacity by organic matter, *Chem. Geol.*, 34 (1981) 131-149.
- 19 Poppe, L. J. and Commeau, J. A., Mineralogy of silt fractions in surficial sediments from united states mid-Atlantic shelf, slope and rise. *Mar. Geol.*, 103 (1992) 185-197.
- 20 Wakeham, S., Diagenesis of organic matter at water-sediment interface. In: A. Gianguzza, E. Pelizzeti and S. Sammartano (eds). *Chemistry of Marine water and sediments*. (Springer Berlin) 2002, pp. 146-164.
- 21 Hedges, J., Sedimentary organic matter preservation and atmospheric oxygen regulation. In: A. Gianguzza, E. Pelizzeti and S. Sammartano (Eds). *Chemistry of marine water and sediments*. (Springer Berlin) 2002, pp. 105-123.
- 22 Murray, J. W., Stewart, K., Kassakian, S., Krynytzky, M. and Dijulio, D., Oxic, Suboxic and Anoxic conditions in Black sea. In: A. Gilbert, V. Yanko- Hombach and N. Panin (eds) *Climate change and coastline migration as factors in human adaptation to the circum- pontic region: from past to forecast*. (Kluwar publications) 2005, pp. 1-26.
- 23 Schorer, M., Pollutant and organic matter content in sediment particle size fractions. (*Freshwater Contamination*, proceedings of Rabit Symposium S4, IAHS publication) 1997, pp. 243.
- 24 Krupadam, R. J. and Anjaneyulu, Y., 'Hydrogarphic features and distribution of nutrients in the Kakinada bay, East Coast of India', *Asian J. Microbial Biotech. Enc. Sci.*, 4(1) (2002) 21-36.
- 25 Chen, J. H., Lion, L. W., Ghiorse, W. and Shuler, M., Mobilization of adsorbed cadmium and lead in aquifer material by bacterial extracellular polymers. *Water Res.*, 29 (1995) 421-430.
- 26 Flemming, H. C., Schmitt, J. and Marshall, K. C., Sorption properties of biofilms. In: *Sediments and Toxic Substances* (ed. by W. Calmano), (Springer, Berlin) 1996, pp. 115-157.
- 27 Pejrup, M., The triangular diagram used for classification of estuarine sediments: a new approach. In de Boer, P. L., van Gelder, A., Nios, S. D., (Eds), *Tide – influenced sedimentary environments and facies*. (Reidel, Dordrecht) 1988, pp. 289 – 300.
- 28 Nayak, G. N., Grain size parameters as indicator of sediment movement around a river mouth, near Karwar, West Coast of India, *Indian J. Mar. Sci.*, (1996) 346-348.
- 29 Nathalie, J. Valette- Silver., The use of sediment cores to reconstruct historical trends in contamination of estuarine and coastal sediment. *Estuaries*, 16 (1993) 577- 588.
- 30 Abu-Hilal, A. H. and Badran, M. M., Effect of pollution sources on metal concentration in sediment cores from the Gulf of Aqaba (Red Sea). *Mar. Pollut. Bull.*, 21(4) (1990) 190-7.
- 31 Nohara, M. and Yokota, S., The geochemistry of trace elements in pelagic sediments from the central Pacific Basin. *J. Geol. Soc., Japan*, 84 (4) (1978) 165-75.
- 32 El-Sayed, M. K., Effect of sewage effluent on the sediment of Nordasvatnet (a land-locked fjord), Norway. *Mar. Pollut. Bull.*, 13 (1982) 85-8.
- 33 Kumar, S. P. and Edward, P. J. K., Assessment of metal concentration in the sediment cores of Manakudy Estuary, South west coast of India. *Indian J. Mar. Sci.*, 38 (2) (2009) 235-248.
- 34 Finney, B. P. and Huy, C., History of metal pollution in the Southern California Bight: an update. *Environ. Sci. Tech.*, 23 (1989) 194-303.
- 35 Boszke, L., Sobczynski, T., Glosinska, G., Kowalski, A. and Siepak, J., Distribution of mercury and other heavy metals in bottom sediments of middle Odra river (Germany/ Poland). *Polish J. Environ. Studies*, 13 (5) (2004) 495-502.
- 36 Mantoura, R. F. C., Dickson, A. and Riley, J. P., The complexation of metals with humic materials in natural waters. *Estuar. Coast Mar. Sci.*, 6 (1978) 387-408.
- 37 Rubio, B., Nombela, M. A. and Vilas, F., Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution. *Mar. Pollut. Bull.*, 40 (2000) 968-80.
- 38 Horowitz, A. J., *A Primer on Sediment-Trace Element Chemistry*. Chelsea, MI: (Lewis Publishers) 1991, pp. 136.
- 39 Singh, Ksh. Tomchou and Nayak G. N., Distribution of sediment parameters and depositional environment of mudflats of Mandovi estuary, Goa, India. *J. Coast. Res.*, 25(2) (2009) 641 – 650.
- 40 Breslin, V. T. and Sanudo-Wilhelmy, S. A., High spatial resolution sampling of metals in the sediment and water

- column in Port Jefferson Harbor, New York. *Estuaries*, 22 (1999) 669–80.
- 41 Zhu, F.G., Wang, Z. F. and Zhang, B. Z., Clay mineral distributions and their effects on the transfer of the polluting elements in the Changjiang Estuary and the adjacent shelf. In: YuGH, Martin JM, Zhou JY, (eds). *Biogeochemical study of the Changjiang Estuary*. (Beijing: China Ocean Press) 1990, pp. 437–49.
- 42 Forstner, U. and Wittman, G. T. W., *Metal pollution in the aquatic environment*. (Springer-Verlag, Berlin) 1983, pp. 486.
- 43 Nath, B. N., Kunzendorf, H. and Pluger, W. L., Influence of provenance, weathering and sedimentary processes on the elemental ratios of the fine-grained fraction of the bed load sediments from the Vembanad Lake and the adjoining continental shelf, southwest coast of India. *J. Sedi. Res.*, 70 (2000) 1081-1094.
- 44 Alagarsamy, R., Distribution and seasonal variation of trace metals in surface sediments of the Mandovi estuary, west coast of India. *Estuar. Coast. Shelf Sci.*, 67 (2006) 333–9.
- 45 Somayajulu, B. L. K., Yadav, D. N. and Sarin, M. M., Recent sedimentary records from Arabian Sea, *Proc. Ind. Acad. Sci.*, 103, 1994, pp. 315-327.
- 46 Dean, W. E., Gardner, J. V. and Piper, D. Z., Inorganic geochemical indicators of glacial- inter glacial changes in productivity and anoxia on the California continental margin. *Geochim. Cosmochim. Acta.*, 61 (1997) 4507-4518.
- 47 Chatterjee, M., Filho Silva, E. V., Sarkar, S. K., Sella, S. M., Bhattacharya A., Satpathy K. K., Prasad, M. V. R., Chakraborty, S. and Bhattacharya B. D., *Distribution and possible sources of trace elements in the sediments cores of a tropical macrotidal estuary and their ecotoxicological significance*. (Elsevier) 2006, pp. 346- 356.
- 48 Rosales- Hoz, L., Cundy, A. B. and Bahena-Manjarrez, J. L., Heavy metals in sediment cores from a Tropical estuary affected by anthropogenic discharges: Coatzacoalcos estuary, Mexico, *Estuar. Coast. Shelf Sci.*, 58 (2003) 117-126.
- 49 Sigg, L., Sturm, M. and Kistler, D., Vertical transport of heavy metals by settling particles in Lake Zurich. *Lim. Oceano.*, 32 (1987) 112-130.
- 50 Hamilton- Taylor, J. amd Davison, W., Redox driven cycling of trace elements in lakes. In: A. Lerman et al. (ed). *Physics and Chemistry of lakes*. (Springer) 1995, pp. 218-263.
- 51 Klinkhammer, G. P., Early diagenesis in sediments from the eastern equatorial Pacific, H. Pore water metal results. *Earth and Planetary Science Letters*, 49 (1980) 81-101.
- 52 Lara, R. J., Gomez, E. A. and Pucci, A. E., Organic matter, sediment particle size and nutrient distribution in sewage affected shallow channel. *Mar. Pollut. Bull.*, 16 (1985) 360-364.
- 53 Warren, L. J., Contamination of sediment by lead, zinc and cadmium- A review, *Environ. pollut.*, (Series B) 2, (1981) 401- 436.
- 54 Horowitz, A. J., *A primer on trace metal- sediment chemistry*. (U.S. Geological survey water supply paper) 1985, pp. 2277.
- 55 Grant, J. A., The isocon diagram—a simple solution to Gresen’s equation for metasomatic alteration. *Econ. Geol.*, 81 (1986) 1976 – 1982.
- 56 Alagarsamy, R. and Zhang, J., Geochemical characterization of major and trace elements in coastal sediments of India. *Environ. Monit. Assess.*, (2008), 669-735.
- 57 Horowitz, A. J., Elrick, K. and Callender, E., The effect of mining on the sediment-trace element geochemistry of cores from the Cheyenne River arms of Lake OaheSouth Dakota, USA. *Chem. geol.*, 67 (1988) 17–33.