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Distribution of Sediment Components and Metals in Recent Sediments within Tidal Flats along Mandovi Estuary

Ratnaprabha R. Siraswar and G. N. Nayak
Department of Marine Sciences, Goa University, Goa – 403 206
Email: ratna.siraswar@gmail.com

Abstract: Three short sediment cores from locations namely Betim representing lower estuarine region; Karyabhat - lower middle estuarine region and Ribander - upper middle estuarine region were collected from intertidal regions of the Mandovi estuary along west coast of India. The cores were subjected to sedimentological and geochemical analyses in order to understand the sediment texture, organic matter content and metal distribution (Fe, Mn, Cr, Cu, Co, Ni, Zn, Pb and Al) in the sediments with depth along the estuary. Results indicated that the sediments along the lower estuarine region were mainly composed of coarser sediments with less organic matter, whereas in the middle region finer sediments with high organic matter were deposited. Isocon diagram clearly indicated that most of the metals were deposited more towards the lower middle estuarine region when compared to other two locations. Calm environmental conditions must have facilitated deposition of finer sediments associated with high concentration of metals at Karyabhat. Role of sediment size, organic matter concentration and Fe – Mn oxy – hydroxides in distribution of trace metals down the core are discussed.

Keywords: Sediment Distribution, Metal Concentration, Tidal Flats and Mandovi Estuary.

INTRODUCTION

Estuarine tidal flats are transition zones between terrestrial and aquatic ecosystem and thus acts as important environmental interfaces (Meade, 1972). Vast amount of organic matter and metals are introduced into the estuarine waters through river run off, in-situ primary productivity, atmospheric deposition, diagenetic remobilization (Libes, 1992) and anthropogenic inputs. Source of anthropogenic material includes industrial and agricultural activities and also urban effluents which supply significant loads of toxic metals to the estuaries (Gavriil and Angelidis, 2005). The metal contaminants upon entering into the estuarine regions are partitioned to various phases (Prudencio, et al., 2007; Zhang et al., 2007) due to change in physico-chemical conditions and are adsorbed onto suspended particulate matter. The suspended particulate matter, both inorganic and organic, slowly gets deposited along with adsorbed metals and buried in tidal flats forming organic and metal rich sediments (Hegdes and Keil, 1995; Thornton and McManus, 1994). Thus, tidal flat sediments are considered as potential reservoir of metals (Karbassi and Amirnezhad, 2004). The role of organic matter in accumulation of heavy metals was emphasized earlier by Wakida et al. (2008). Remobilizations of trace metals are controlled by redox sensitive elements and are recycled with changing physicochemical conditions through the sediment–water interface (Sakellari et al., 2011; Graham et al., 2003). The mudflat environment may therefore continue to release metals into the water column of the estuary even after effluent discharge is ceased and hence understanding the level of concentration of metals is essential in mudflat environment.

Grain size is directly related to hydrodynamics with deposition of finer sediments towards upper estuarine regions and coarser in lower regions. It is well documented that due to their greater surface area, fine particles have greater efficiency in binding Fe- Mn oxyhydroxides and trace metals in association with organic matter (Santschi et al., 2001). Organic matter generally decreases with increasing grain size (Renjith and Chandramohanakumar, 2010). Several researchers (Gonzalez et al., 2006 and Kalbitz and Wennrich, 1998) have stated that organic matter could act as a sink for trace elements due to its strong complexing capacity for metal contaminants.

STUDY AREA

Mandovi estuary and its tributaries for most of their lengths pass through regions of extensive mining activity. There are 27 major mines within Mandovi River basin and annually more than 1.5 million tonnes of iron and manganese ores are transported along the rivers to the nearby Mormugao harbor (Nayak, 2002). Industrial and mining activities are at a peak during October–May at several points along the estuary and discharge nutrients, heavy metals, and other pollutants in the form of organic and inorganic industrial waste into the estuary (Alagarsamy, 2006; Ramaiah et al., 2007). Mandovi estuary also receives contaminant inputs from municipal waste waters, direct industrial discharges and harbour related activities. The estuarine channel of the Mandovi

River is also used to transport large quantities of iron and ferromanganese ores from hinterland to Marmugao harbour throughout the year. Considering this, an attempt has been made in the present study on mudflats of Mandovi estuary with an aim to understand the distribution of sediment characteristics and selected metals (Fe, Mn, Al, Cr. Cu, Co, Zn, Ni and Pb) in pre - monsoon season along the estuary.

MATERIAL AND METHODS

Sampling

Three short sediment cores of 20 cm each were collected from tidal flats (Fig. 1) during low tide from lower (Core A), lower middle (Core B) and upper middle (Core C) using hand held PVC corer during pre-monsoon season. It is important to mention here that Core B was collected from the inner channel of the lower middle estuary. GPS was used to locate the sampling areas. Sub-sampling of the sediment core was done at every 2 cm interval and placed in zip lock bags and transferred to the laboratory and stored at 4° C. Plastic wares were used to avoid metal contamination.

Laboratory Analysis

The sub samples were oven dried at 60° C. Grain size analysis was performed to obtain percentage of sand, silt and clay (Folk, 1974). Organic carbon within the sediment samples was analyzed using procedure given by Walkey and Black (1934) and Gaudette et al. (1974). For metal analysis a small portion of finely ground sediment samples were digested with HNO_3–HF-$HClO_4$ (7:3:1) on hot plate at 150°C in Teflon beakers (Jarvis and Jarvis, 1985). The digested samples were analysed for Al, Fe, Mn, Cu, Pb, Co, Ni, Zn and Cr using Varian AA 240 FS - flame Atomic Absorption Spectrometry (AAS). Together with the samples, certified reference standard from the Canadian National Bureau of Standards (BCSS-1) was digested and run, to test the analytical and instrument accuracy. The recoveries were between 86 and 91% for Fe, Cu, Ni and Al; 87-92% for Mn and Co; 80-85% for Pb and Zn; 90-95% for Cr, with a precision of ±6%.

RESULTS AND DISCUSSION

Sediment Components

Lower estuary (Betim - Core A): Sand, silt, clay and organic carbon values range from 94.73 - 97.28% (av. 96.25 %); 2.4 - 4.9% (av. 3.4 %); 0.1 - 0.47% (av. 0.39 %) and 0.1 - 0.42% (av. 0.23 %) respectively in this core. Down core distribution profiles of sand, silt, clay and organic carbon are presented in figure 2 (a). Sand percentage decreases from 18 to 8 cm and then increases towards surface. It is clearly seen from the distribution pattern that sand and silt compensates each other throughout the length of the core. Clay shows almost a constant trend from bottom (18 cm) to 8 cm with slight decrease between 18 and 14 cm, and with a considerable increase between 8 and 6 cm before maintaining a constant trend towards the surface. Organic carbon shows a fluctuating trend from 18 to 6 cm and decreasing values towards surface.

Lower middle estuary (Karyabhat – Core B): The sediment core collected from tidal flat of sub channel of Mandovi estuary is dominated by silt 43 to 60% (av. 47.50%) and clay 42 to 51% (av. 46.99%) accompanied with lesser proportion of coarser components (sand) which ranges from 4 to 7.2% (av. 5.49%). Sand value fluctuate from depth 18 cm up to surface (Fig 3 a). Relatively higher sand value is observed at depth of 18, 12, 8 and 4 cm accompanied with lesser sand concentration in between. Down core profiles of both silt and clay show opposite distribution pattern throughout the length of the core. Organic carbon ranges from 1.66 to 3.33% (av. 2.31%). High organic carbon occurs at 4 cm depth followed by 10 and 16 cm. Distribution of Organic carbon values largely agrees with that of silt between 18 and 14 cm.

Upper middle estuary (Ribander – Core C): Sand, silt and clay varies from 5 to 7.4% (av. 5%); 53 to 61.15% (av. 54.32%); 35 to 45% (av. 40.66%) in the core collected from Ribander. Organic carbon ranges from 1.6 to 2.6% (av. 2.14%). The down core plots of sand, silt, clay and organic carbon are shown in figure 4(a). Sand shows higher values in lower portion of the core i.e. from 16 to 12 cm and a positive peak at 8 cm and for the remaining portion of the core comparatively lower values are observed. Silt and clay profiles compensate each other throughout the length of the core. Organic carbon values fluctuate throughout the length of the core. Higher organic matter is present in surface sediments i.e. at 6 cm (2.62%) followed by 10 cm (2.4%) and 14 cm (2.3%) and lower values are noted at the lower portion of the core i.e. at 20 cm (1.6%) depth.

The distribution pattern of the sediment components in the sediments of the different regions of the estuary indicated significant spatial variations. The sediment composition in the cores collected within the three regions of the estuary show variable admixture of components viz. sand, silt and clay with overall texture ranging from sandy to clayey. The variation can be attributed to processes namely estuarine mixing, suspension-resuspension and flocculation-deflocculation (Jonathan et al., 2010; Sarkar and Bhattacharya, 2010). Grain- size variation reflects change in energy and processes involved in deposition of sediments. The coarser sediment fractions are more dominant in the lower region as compared to areas within middle estuarine region. The sandy sediments reveal the strong hydrodynamic conditions prevailing towards

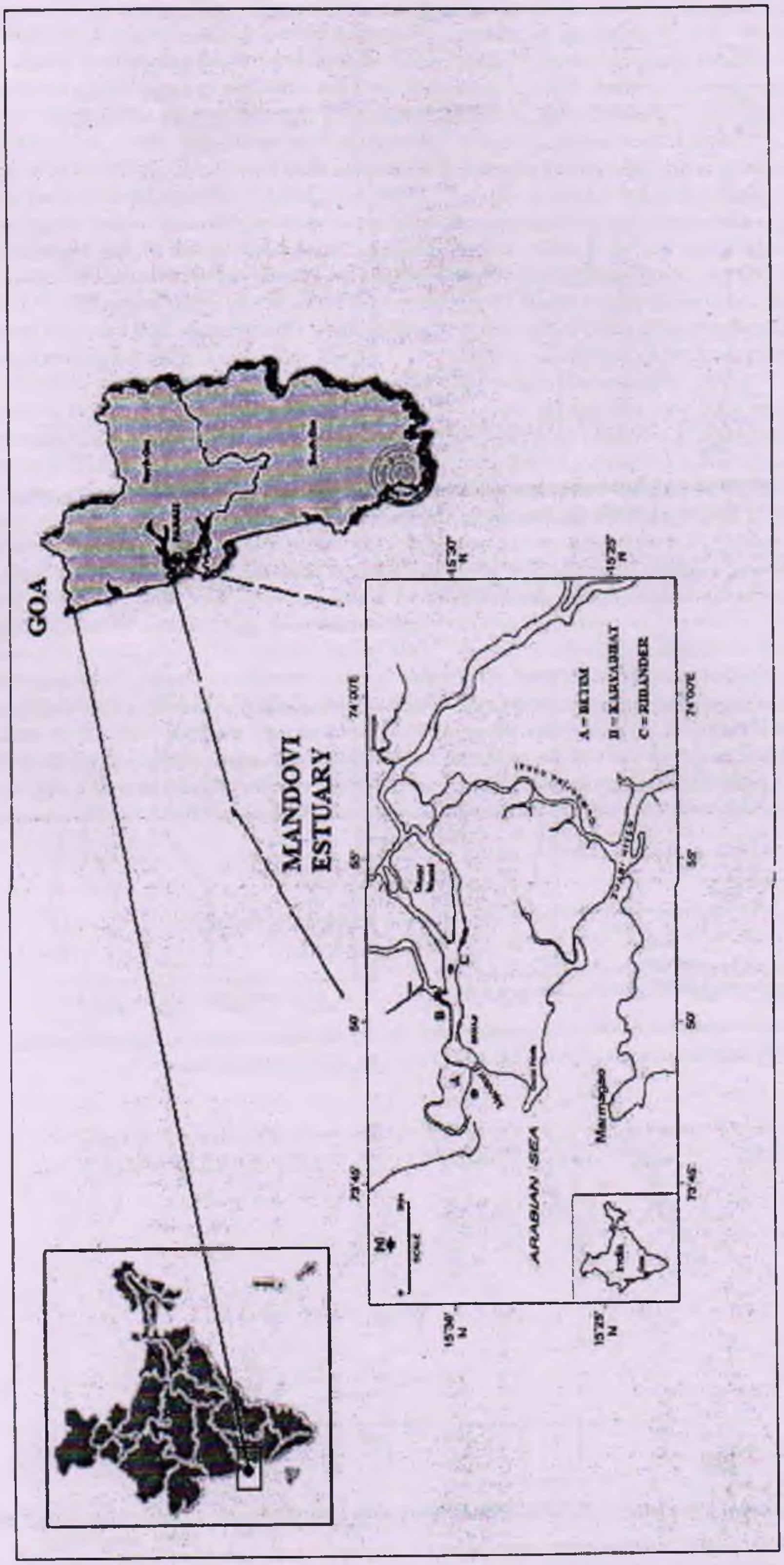

Fig. 1. Map showing the core locations along Mandovi estuary.

BETIM

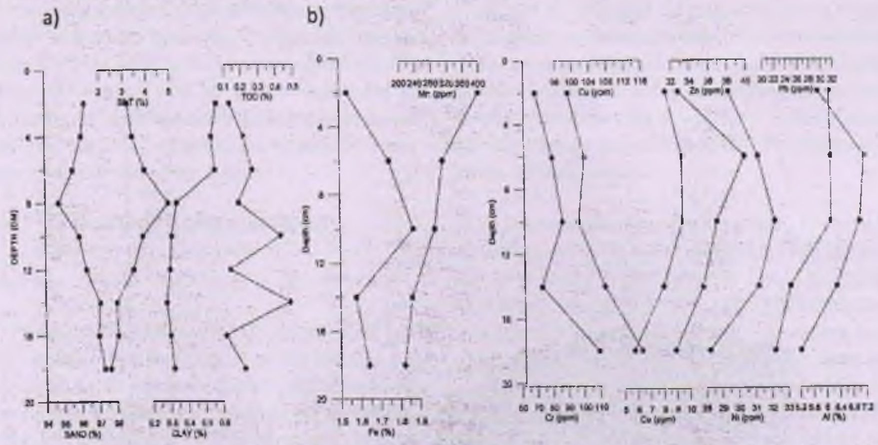

Fig. 2 a. Down core variation of sediment components (sand, silt, clay and organic carbon) in Betim mudflat.
b. Down core variation of metals (Fe, Mn, Cr, Cu, Co, Zn, Ni, Pb, Al) in mudflat sediment.

KARYA BHAT

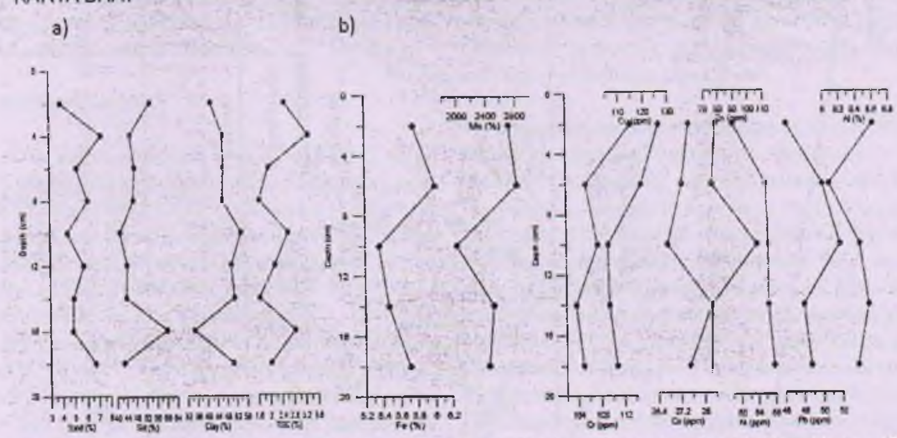

Fig. 3 a. Down core variation of sediment components (sand, silt, clay and organic carbon) in Karyabhat mudflat.
b. Down core variation of metals (Fe, Mn, Cr, Cu, Co, Zn, Ni, Pb, Al) in mudflat sediment.

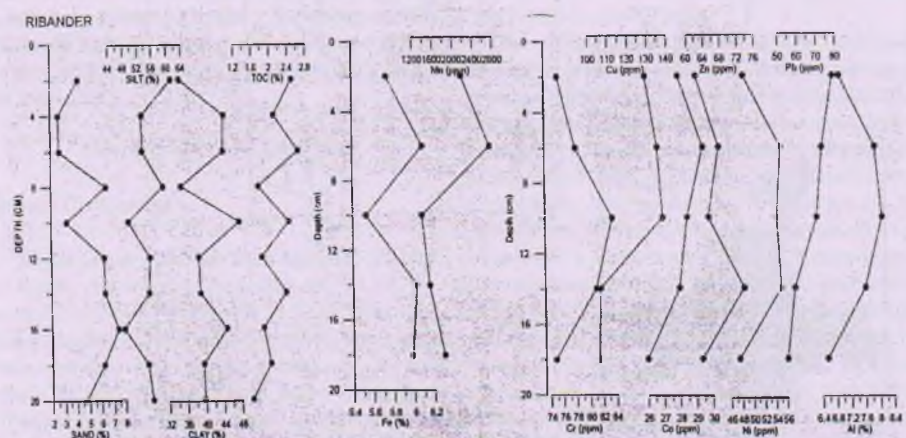

Fig 4 a. Down core variation of sediment components (sand, silt, clay and organic carbon) in Ribander mudflat.
b. Down core variation of metals (Fe, Mn, Cr, Cu, Co, Zn, Ni, Pb, Al) in mudflat sediment.

the mouth of the estuary. This indicates that the strong wave activity along with associated currents which are responsible for removing the finer sediment fractions from lower estuarine regions carry them away towards middle regions of the estuary (Badr et al., 2008; Gheith and Abou Ouf, 1996). This allows retaining coarser material which includes largely sand and some time silt in the lower intertidal sediments (Chatterji et al., 2006). Low organic carbon values obtained at lower estuarine region might also be due to high rate of microbial degradation in coarser sediments (Canuel and Martens, 1993) as high permeability of the sandy sediments enables advective pore water transport which leads to more organic matter decay (Franke et al., 2006).

From the mouth of the estuary towards the middle estuarine region, sediment size decreases. Higher percentage of finer sediment fractions present at Karyabhat along with high organic matter (av. 2.31%) indicates presence of lower energy hydrodynamic conditions at this location. Higher organic carbon concentration in surface layers can be attributed to influx of organic matters from flora and fauna communities from surrounding (Man et al., 2004) as well as from enhanced input of organic matter from anthropogenic sources in recent years. The organic matter from overlying water column settles down along with accumulation of fine grained inorganic materials (Janaki-Raman et al., 2007) and gets incorporated into the sediments. Further, during summer the consequence of algae lysis is more pronounced which is seen soon after the onset of bloom. Microbial biomass decomposition is also more intense in summer (Dellwig et al., 2007a) resulting in production of sticky carbohydrate which colligate suspended organic and inorganic particles in water column thereby forming larger aggregates (Passow, 2002; Chen et al., 2005). Significant amounts of these aggregates must be depositing on the tidal-flat sediments forming a fluffy layer of organic-rich material on the sediment surface (Chang et al., 2006). Incorporation of organic matter rich aggregates into the surface sediments by tidal forces was explained earlier by Rusch and Huettel (2000) and also Billerbeck et al. (2006). Higher organic matter values obtained at 10 and 16 cm depth of Core – C must be due to sudden burial of organic matter that must not have undergone extensive degradation (Deflandre et al., 2002).

An attempt has also been made to infer the hydrodynamic conditions of depositional environment using textural analysis (Fig 5). For this purpose, a ternary diagram proposed by Pejrup (1988) has been used. 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, all the data points lie in section IV (A) revealing their deposition in very violent conditions indicating wave action facilitates coarser sediments to get deposited. Sediments collected from the middle estuarine regions both lower and upper middle, when plotted on Ternary diagram falls in Division III which indicates that these locations provide less

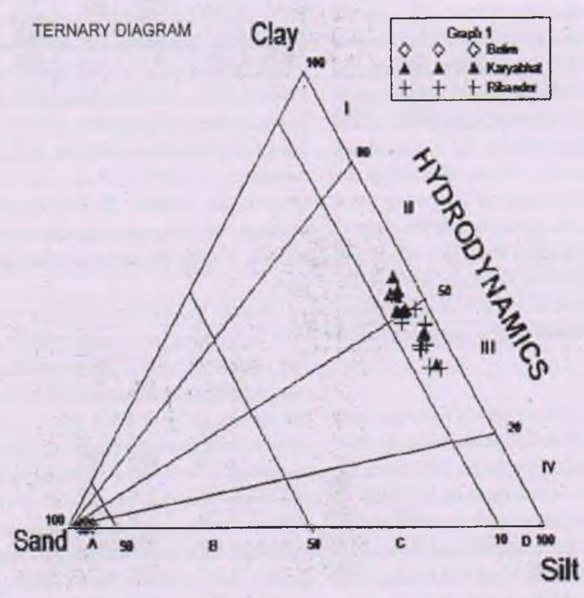

Fig. 5. Traingular diagram for classification of hydrodynamic conditions of (a) Betim (b) Karyabhat (c) Ribander. (after Pejrup, 1988).

violent conditions for sediment deposition. The plots in Karyabhat region mostly lie between section II (D) and III (D) with single point been part of III (D) indicating less violent conditions prevailed there facilitating deposition of finer sediments. In the upper middle estuarine region all the points lie in section III (D) indicating less violent conditions.

Metal Distribution

The concentration of metals in sediments of three mudflats (Betim, Karyabhat and Ribander) collected from different regions of the estuary namely lower, lower middle and upper middle are presented graphically in figures 2 (b), 3 (b) and 4 (b) respectively.

Lower estuary (Betim): In the core collected from lower estuarine region (Betim) Fe varies from 1.54 - 1.9% (av. 1.7%), Al ranges from 5.24 – 7.17 % (av. 6.31 %). and Mn ranges from 207 – 399 ppm (av. 285 ppm). Vertical distribution of Fe is characterized by presence of increasing peak at depth of 10 cm followed by decreasing concentration towards surface above 10 cm and to some extent in lower portion of the core. Al values show an increasing trend from bottom up to 6 cm and then decreases towards the surface. Mn shows markedly increasing pattern throughout the sediment core.

Cr, Cu, Co, Zn, Ni, Pb ranges from 70 – 110 ppm (av. 84 ppm); 99 – 116 ppm (av. 105.2 ppm); 6 – 10 ppm (av. 8.2 ppm); 32 - 40 ppm (av. 35.35 ppm); 28 – 32 ppm (av. 31 ppm) and 22 - 32 ppm (av. 28 ppm). Except for Cu and Pb the average concentrations obtained for metals are lower than average crustal concentrations at this location. Cr largely shows a decreasing trend from 18 – 14 cm thereafter shows an increasing trend up to 10 cm before showing decreasing values towards the surface. Cu shows a decreasing trend from bottom of the core up to 10 cm followed by a slight increase between 10 – 6 cm before decreasing towards surface. Co maintains an increasing pattern between 18 – 10 cm from where the value decreases. Zn values show an increasing trend up to 6 cm followed by a decrease towards the surface. Ni maintains an increasing trend from 18 - 10 cm and show decreasing trend between 10 cm and surface. Pb exhibits substantial increase in lower half of sediment core (18 - 10 cm) and maintains almost constant trend in the upper portion.

Lower middle estuary (Karyabhat): Fe ranges from 5.31 to 6.01% (av. 6%), Al from 8.07 to 8.61% (av. 8.41%) and Mn ranges from 1983 to 2709 ppm (av. 2483 ppm). Fe shows a decreasing trend from bottom up to depth 10 cm followed by an increase between 10 - 6 cm thereafter decrease towards surface. Al values increase from 18 to 16 cm and then decrease up to 6 cm before showing increase towards surface. Mn exhibits slight increase from bottom of the core up to 14 cm followed by decreasing trend up to 10 cm. Between 10 and 6 cm distribution of Mn agrees with that of Fe.

The concentration of Cr, Cu, Co, Zn, Ni and Pb varies from 104 – 113 ppm (av. 107 ppm); 105 – 126 ppm (av. 113 ppm); 26 – 28 ppm (av. 27.45 ppm); 75 – 105 ppm (av. 82 ppm); 58 – 68 ppm (av. 65 ppm) and 46 – 52 ppm (av. 49 ppm). The distribution patterns of Cr exhibits alternate decrease and increase throughout the length of the core with considerable increase in concentration towards the surface. Cu exhibits decreasing trend in lower half of the core and increasing trend in the upper half. Co values show an increase between 18 - 14 cm and also towards the surface above 10 cm and large decrease between 14 -10 cm. Zn shows opposite trend to that of Co from 18 to 16 cm and similar trend towards the surface. Ni shows overall decrease from bottom to surface. Pb shows decrease in concentration between 18 - 14 cm. The value increases from 14 to 10 cm and then again decreases towards surface.

Upper middle estuary (Ribander): Fe value varies between 5.53 - 6.09 % (av. 5.87 %), Al from 6.54 – 8.08 % (av. 7.41%) and Mn ranges from 1368 – 2721 ppm (av. 1914.4 ppm) in the core. Fe exhibits alternate increasing (18 - 14 cm and 10 - 6 cm) and decreasing (14 - 10 cm and 6 cm - surface) trend. Al exhibits increasing trend up to 10 cm followed by a decrease towards the surface. Mn also exhibits similar distribution pattern to that of Fe between 14 cm- surface and in lower portion it decreases is between (18 - 14 cm).

Trace elements vary between 75 - 84 ppm (Cr); 105 - 138 ppm (Cu); 26– 30 ppm (Co); 62 – 73 ppm (Zn); 48–55 ppm (Ni) and 54 – 78 ppm (Pb) with average values of 78.5; 122.3; 28; 66.25; 52.05 and 66.4 respectively. Distribution pattern of Cr shows an increasing trend from bottom of the core up to 10 cm followed by decrease towards surface, Cu shows a constant trend from 18 – 14 cm, an increasing trend between 14 – 10 cm and shows decreasing trend towards the surface. Co shows an increasing trend from 18 to 6 cm and then decreases towards the surface. Zn and Ni show an alternate increase and decrease with lower values towards the surface. Pb exhibits increase from bottom to top of the core.

Results indicate variation in metal concentration from lower estuarine to upper middle estuarine regions. The catchment area of Mandovi estuary is known for considerable anthropogenic activity in the form of open cast mining for Fe and Mn ores. All along the banks of Mandovi estuary, ore processing units which enrich the percentage of iron ore are operating and it is expected that these industries are forced to release associated elements to the waters of the estuary which is ultimately deposited in sediments. Barges carry the ore from loading platforms in the upper estuary to the Murmugao harbor located on the southern bank of Zuari estuary. The concentrations of Fe and Mn within the estuarine

Table 1 **a.** Pearsons correlation between different sediment components (sand, silt, clay and total organic carbon) and elements in sediment core (Betim), **b.** Pearsons correlation between different sediment components (sand, silt, clay and total organic carbon) and elements in sediment core (Karyabhat), **c.** Pearsons correlation between different sediment components (sand, silt, clay and total organic carbon) and elements in sediment core (Ribander).

a. BETIM PRE MONSOON

	SAND	SILT	CLAY	TOC	Mn (ppm)	Fe (%)	Ni (ppm)	Zn (ppm)	Cr (ppm)	Cu (ppm)	Co (ppm)	Pb (ppm)	Al (%)
SAND	1.00												
SILT	-0.99	1.00											
CLAY	-0.62	0.48	1.00										
TOC	0.07	0.08	-0.72	1.00									
Mn (ppm)	-0.63	0.53	0.82	-0.53	1.00								
Fe (%)	-0.59	0.70	-0.19	0.40	-0.14	1.00							
Ni (ppm)	-0.61	0.71	-0.13	[illegible]	0.07	0.63	1.00						
Zn (ppm)	-0.75	0.79	0.22	0.40	0.05	0.65	0.78	1.00					
Cr (ppm)	0.43	-0.38	-0.44	-0.14	-0.65	0.27	-0.49	-0.28	1.00				
Cu (ppm)	0.80	-0.77	-0.57	0.02	-0.85	-0.19	0.58	-0.41	0.80	1.00			
Co (ppm)	-0.90	0.92	0.36	0.32	0.51	0.54	0.87	0.80	-0.65	-0.86	1.00		
Pb (ppm)	-0.95	0.92	0.64	-0.11	0.81	0.42	0.57	0.55	-0.59	-0.94	0.89	1.00	
Al (%)	-0.81	0.83	0.15	0.51	0.19	0.70	0.93	0.93	-0.44	-0.62	0.94	0.70	1.00

b. KARYABHAT PRE MONSOON

	SAND	SILT	CLAY	TOC	Mn (ppm)	Fe (%)	Ni (ppm)	Zn (ppm)	Cr (ppm)	Cu (ppm)	Co (ppm)	Pb (ppm)	Al (%)
SAND	1.00												
SILT	-0.52	1.00											
CLAY	0.34	-0.98	1.00										
TOC	-0.53	0.25	-0.16	1.00									
Mn (ppm)	0.01	0.74	-0.81	-0.39	1.00								
Fe (%)	0.23	0.57	-0.68	-0.19	0.87	1.00							
Ni (ppm)	0.70	-0.92	0.85	-0.50	-0.43	-0.24	1.00						
Zn (ppm)	-0.40	-0.42	0.54	0.69	-0.84	-0.65	0.12	1.00					
Cr (ppm)	-0.67	0.77	-0.70	0.78	0.16	0.12	-0.93	0.17	1.00				
Cu (ppm)	-0.39	0.96	-0.97	0.30	0.76	0.73	-0.83	-0.40	0.74	1.00			
Co (ppm)	0.14	0.13	-0.17	-0.77	0.42	-0.01	-0.03	-0.73	-0.30	-0.06	1.00		
Pb (ppm)	0.15	-0.72	0.75	0.18	-0.61	-0.27	0.68	0.70	-0.44	-0.57	-0.68	1.00	
Al (%)	-0.30	0.11	-0.05	0.22	-0.33	-0.63	-0.40	0.10	0.39	-0.12	0.37	-0.54	1.00

c. RIBANDER PREMONSOON

	SAND	SILT	CLAY	TOC	Mn (ppm)	Fe (%)	Ni (ppm)	Zn (ppm)	Cr (ppm)	Cu (ppm)	Co (ppm)	Pb (ppm)	Al (%)
SAND	1.00												
SILT	0.27	1.00											
CLAY	-0.56	-0.95	1.00										
TOC	-0.78	0.09	0.18	1.00									
Mn (ppm)	-0.48	0.37	-0.16	0.55	1.00								
Fe (%)	0.35	0.17	-0.26	0.09	0.50	1.00							
Ni (ppm)	-0.39	-0.58	0.63	0.57	-0.05	0.10	1.00						
Zn (ppm)	0.27	-0.25	0.13	0.16	-0.19	0.49	0.76	1.00					
Cr (ppm)	-0.26	-0.71	0.70	0.28	-0.55	-0.40	0.81	0.53	1.00				
Cu (ppm)	-0.97	-0.19	0.49	0.78	0.36	-0.52	0.33	-0.33	0.30	1.00			
Co (ppm)	-0.79	-0.19	0.43	0.95	0.42	-0.05	[illegible]	0.32	0.48	0.76	1.00		
Pb (ppm)	-0.80	0.31	0.00	0.85	0.50	-0.42	0.10	-0.36	0.00	0.87	0.69	1.00	
Al (%)	-0.61	-0.63	[illegible]	0.66	-0.07	-0.20	0.94	0.51	0.87	0.59	0.84	0.32	1.00

sediments can be related to various natural and anthropogenic activities. However, it is also important to understand the processes involved in the abundance and distribution of Fe and Mn within the estuaries in addition to the source.

Core collected towards the lower estuarine region showed low concentration of metals as compared to cores collected from both lower middle and upper middle regions. Lower estuarine region composed of small quantity of finer sediments as a result of violent hydrodynamic condition (Pearl, 2010). Except for Cu and Pb concentration of all the metals is noted to be lower than crustal average at this location. Dilution of Fe and associated trace metals by sand in the upper portion of core is noted. Enhancement of Fe in the upper portion of the core occurs at lower depths than Mn due to the greater sensitivity of Mn to redox change (McBride, 1994) which is clearly observed in this core. Most of the metals follow the trend of silt in lower estuary and Fe oxyhydroxides seems to have played crucial role in concentration of metals (Hamilton -Taylor et al., 1996).

In the core collected from lower and upper middle estuary, fine grained organic matter rich sediments facilitated suitable condition for metal trapping (Alongi et al., 2004). Total metal concentration is a function of organic matter, mineralogy and textural related qualities of the sediments (Willey and Fitzgerald, 1980). Concentration of all the metals is noted to be higher than crustal average except Ni, Al at lower middle estuary and except for Al, Ni, Zn and Cr at upper middle estuary. In addition, concentrations of Fe, Mn, Al, Cr, Zn and Ni is found to be higher in lower middle estuary than upper middle estuary indicating lower middle estuary as favorable location for higher metal concentration. Addition of Fe and Mn from mining related activities can be a strong possibility. However, river input during pre monsoon is considerably less and tidal influx controls the whole estuary. Distribution of metals is also controlled by post depositional processes. Reduced Mn concentration in the surface sediments might be due to dissolution and mobility of Mn ions which are easily removed from the pore water of sediments to the upper water column through active diffusion and advection processes (Janaki- Raman et al., 2007). Increase in Mn concentration in sub surface layers in pre monsoon can also be attributed to increased reduction of Mn oxyhydroxides which is microbially mediated (Lovley, 1995). Higher Pb in the upper portion of the core collected from upper middle estuary might be due to anthropogenic input from atmospheric source and gasoline additive used by mechanized boats. Higher concentration of Co observed agrees with higher concentrations of Co during pre-monsoon reported in Mandovi estuary by Alagarsamy (2006).

Correlation of sediment parameters and metals

Lower estuary (Betim): Sand fraction exhibits negative correlation with most of the metals except Cu with which it shows significant positive correlation ($r = 0.80$). Silt shows a significant positive correlation with most of the metals namely Fe ($r = 0.70$), Ni ($r = 0.71$), Zn ($r = 0.79$), Co ($r = 0.92$), Pb ($r = 0.92$), Al ($r = 0.87$) and to lesser extent with Mn ($r = 0.53$) (Table 1a). This indicates role of Fe oxyhydroxides in the distribution of trace metals associated with coarser size sediments. This is further supported by significant correlation of Fe with Ni (0.63), Zn (0.65) and Co ($r = 0.54$) and Mn with Pb ($r = 0.81$) and Co ($r = 0.51$). Both Mn and Fe oxyhydroxides are known to scavenge a variety of trace metals either by binding or by incorporation into the crystal structure (Burdige, 1993). Clay exhibits a significant correlation with Mn and Pb (Table 1a) indicating role of Mn in the distribution of Pb. Organic matter and Ni ($r = 0.74$) show a significant correlation in this core. Organic carbon also exhibits significant correlation with Al ($r = 0.51$) and Al exhibits significant correlation with Ni, Zn, Co and Pb indicating the role of clay along with the organic matter in binding these trace metals in addition to Fe - Mn oxyhydroxides. Significant correlation observed between Fe and Al indicates that Fe is also of lithogenic origin (Nath et al., 2000). Correlation obtained between different metals indicates that they are derived from common source, identical behavior during transport and post depositional processes.

Lower middle estuary (Karyabhat): In the core collected from lower middle estuarine region, the sediments largely consist of finer sediment components deposited in calmer hydrodynamic conditions. Sand shows a significant correlation only with Ni ($r = 0.70$). Silt shows a significant correlation with Fe ($r = 0.57$), Mn ($r = 0.74$), Cr ($r = 0.77$) and Cu ($r = 0.96$) (Table 1b). Clay exhibited significant correlation with Ni ($r = 0.85$), Zn ($r = 0.55$) and Pb ($r = 0.75$). Organic matter shows a good correlation with Zn ($r = 0.69$) and Cr ($r = 0.78$). Wang et al. (2008) stated that in the area with weak hydrodynamics, finer sediments dominate and the aggregation of trace metals is obvious. Further it is known fact that finer sediments have high specific surface area and also can act as a substrate for organic matter flocculation (Keil et al., 1994) that in turn helps in binding metals. Fe and Mn show significant correlation with Cu ($r = 0.73$); ($r = 0.76$) respectively and Mn exhibits significant correlation with Fe ($r = 0.87$), thus indicating redox sensitive elements namely Fe and Mn mainly control the distribution of Cu (Achyuthan et al., 2002). Observed correlation between Zn and Pb ($r = 0.70$); Cr and Cu ($r = 0.74$) Ni and Pb (0.68) (Table 1b) indicate that they are derived from similar source or similar mechanism of transport and deposition in sediments. Nguyen et al. (2009) has stated that metals belonging to the same group show strong correlation among them and suggest their common origin, similar behaviour during accumulation.

Upper middle estuary (Ribander): In upper middle estuary, sand and silt show negative correlation with most of the metals and also with organic carbon. Organic matter and clay fraction show significant correlation with most of the metals (Table 1c). The role of organic matter and sediment grain size in relation to the accumulation of metals in the sediments has been well emphasized (Davies et al., 1991, Sakai et al., 1986, Thorne and Nickless, 1981). Large amounts of trace metals are bound in the fine-grained fraction of the sediment, mainly because of its high surface area-to-grain size ratio and humic substance contents (Horowitz and Elrick, 1987; *Moore et al., 1989). Redox sensitive elements viz. Fe and* Mn have shown good correlation between themselves but poor correlation with metals except Mn with Pb. Metal – metal correlation is significant in many cases (Table 1c) indicating that they have similar geochemical behaviour. The absence of strong correlation among some of the metals suggests that the concentrations of these metals are not controlled by a single factor, but a combination of geochemical support phases and their mixed associations (Jain et al., 2005).

Metal enrichment locations

Further, Isocon diagrams (Fig 6) has been employed in the study where average values of all the variables are used in order to understand variability in depositional processes between three locations, i.e. from lower estuarine region (Betim) to middle estuarine regions (Karyabhat and Ribander). The data was plotted on the Isocon diagram described by Grant (1986) and applied earlier by Cundy et al. (1997) and Singh and Nayak (2009).

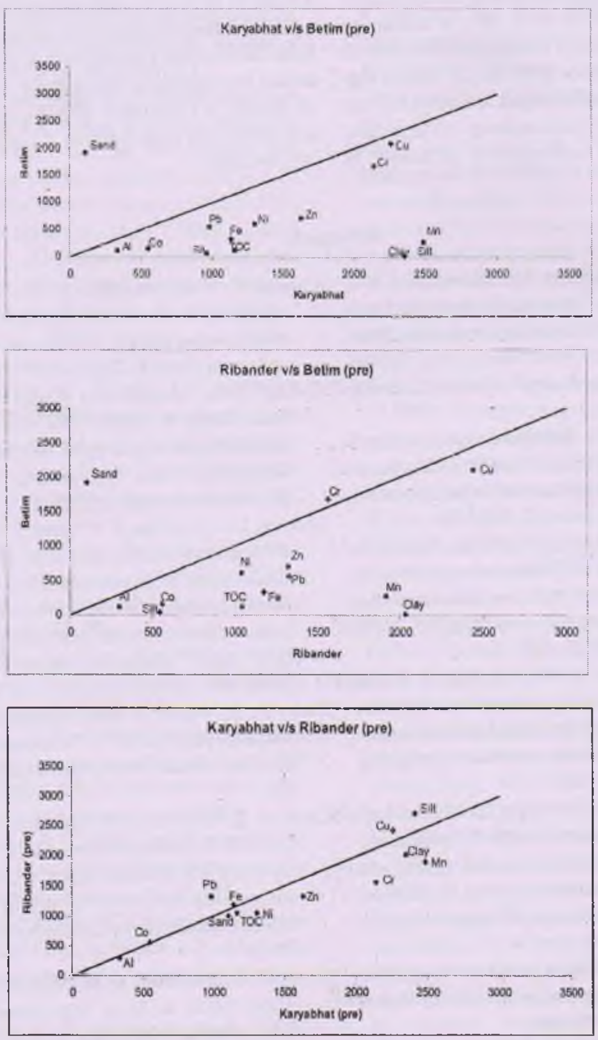

Fig. 6. Isocon diagam (Grant, 1986) individual points represent average value of sediment component and element in each core.

The diagram reveals significant difference among the three sampling sites. When the core sediments from lower estuarine region (Betim) and lower middle (Karyabhat) region of the estuary are compared; it is observed that Al and Cu lie close to Isocon line indicating no much variation in their concentration between two locations. Majority of elements along with organic carbon, finer sediment fractions show enrichment in Karyabhat and coarser sediments are more pronounced in Betim. When comparison is made between Ribander and Betim it is observed that Cr along with Al didn't show much variation in both the areas. Sand is dominant in Betim whereas, Zn, Pb, Fe, Mn, Co is enriched in Ribander in association with organic matter and finer sediment fraction. Thus, revealing the role played by organic matter and Fe-Mn oxy hydroxides in binding of metals. When the two cores from middle estuarine region are compared it is seen that Fe, Co, Al, Sand and organic matter lie on or close to Isocon line indicating not much variation in these parameters in both the areas. The concentration of Ni, Zn, Cr, Mn and clay are more pronounced in Karyabhat indicating the role played by finer sediment fractions along with associated Mn oxyhydroxides in concentration of metals. In Ribander, the concentrations of Cu and Pb along with silt are dominant. Being a part of main estuarine channel, transportation of Fe- Mn ores from hinterland to harbor and sand mining towards upper middle estuary might be a reason for retaining higher silt fraction in the sediments here.

CONCLUSIONS

From the study carried out on estuarine mudflats, it is clear that size of the sediment indicate prevailing energy conditions. Deposition of coarser and finer sediments towards the lower and middle regions of the estuary represent high and low energy environment respectively at these stations. Distribution of trace metals is regulated by sediment grain size, organic matter and Fe - Mn oxyhydroxides present in the sediments. Among the three cores collected from different mudflats within the Mandovi estuary, the one which was collected from sub-channel (Karyabhat) in the lower middle estuary has enriched with metals. The enrichment of metals is facilitated by the presence of finer sediments and high content of organic matter at this location.

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