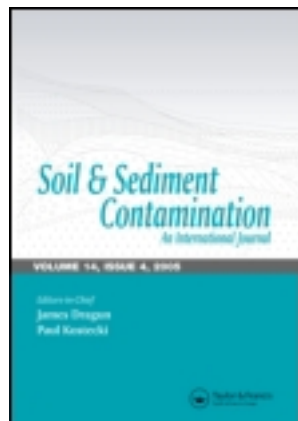


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Soil and Sediment Contamination: An International Journal

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/bssc20>

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Accepted author version posted online: 05 Oct 2012.

To cite this article: K. Tomchou Singh, G. N. Nayak & Lina L. Fernandes (2013): Geochemical Evidence of Anthropogenic Impacts in Sediment Cores from Mudflats of a Tropical Estuary, Central West Coast of India, *Soil and Sediment Contamination: An International Journal*, 22:3, 256-272

To link to this article: <http://dx.doi.org/10.1080/15320383.2013.726291>

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Geochemical Evidence of Anthropogenic Impacts in Sediment Cores from Mudflats of a Tropical Estuary, Central West Coast of India

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The concentration of trace metals (Co, Cr, Zn, Cu, and Pb), major elements (Al, Mn, Fe, Ca, Mg, and K), along with the percentage of sediment components (sand, silt, clay, and organic carbon), was determined in three sediment cores, collected from intertidal regions of the Zuari estuary (ZA and ZR) and Cumbharjua canal (CB). The Cores CB and ZR, collected from the upper middle estuarine environment, showed higher values of finer fractions and total organic carbon as well as metals (except of Ca) than Core ZA, which was sampled from the lower estuarine environment. The concentration of trace metals including Mn and Fe was found to be largely dependent on the proximity to mining areas, with Core ZR and Core CB representing the highest metal concentrations (Mn, Fe, Cr, and Zn). Absence of a significant early diagenetic remobilization might have preserved the metal loadings due to mining and industrial activities in Cores ZR and CB. In Core ZA, all the elements except Cu showed significant enrichment in the upper portion. Enrichment factor computed in all the cores was found to be above 2 for all the studied metals except Zn, which suggests a high degree of metal contamination. All these observations indicate that the present study area is under the strong influence of anthropogenic activities, especially in recent years.

Keywords Mudflats, metals, contamination, diagenesis, cores, Zuari estuary

Introduction

Industrial and urban expansion around estuaries in recent years has led to an increase in metal input, a fraction of which adsorbs onto fine-grained suspended material and subsequently gets deposited and buried in sub- and intertidal mudflats and saltmarshes. Diagenetic processes in the sediments can change and redistribute these contaminants between the solid and the dissolved phases, but most of the elemental contaminants are immobilized through sedimentation (Hanson *et al.*, 1993). The occurrence of elevated levels of trace metals, especially in the sediments, can be a good indicator of man-induced pollution. Further, high levels of heavy metals can often be attributed to anthropogenic influences, rather than natural enrichment of the sediment by geological weathering (Davies *et al.*, 1991; Lord and Thompson, 1988). Therefore, analysis of cores containing undisturbed

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sediments from these sub-environments may allow reconstruction of recent and historical inputs of metal contaminants, thereby allowing an assessment to be made of the scale of pollutant inputs from past industrial and urban developments (Valette-Silver, 1993; Croudace and Cundy, 1995; Cundy *et al.*, 1997).

In past years, tremendous efforts have been made to characterize the fate, loading, and distribution of heavy metals in sediments (Neumann and Leipe, 1998; Arambarri *et al.*, 2003; Glasby *et al.*, 2004) around the world. These studies have improved our understanding of heavy metal contamination in river and estuarine systems. However, in an Indian context, there is still a paucity of information about these highly sensitive and important areas of interface between the land and the sea. As witnessed from the available literature, only limited work has been carried out on estuarine tidal mudflats. Although a few studies on surface sediment contamination in some stretches of the Zuari estuary have been performed (Singh, 2000; Dessai and Nayak, 2009), systematic investigations in the subsurface sediments along the estuarine system have not been conducted so far. Therefore, in the present study an attempt has been made to understand the processes affecting the distribution and concentration of sediment components and metals, which will help to reconstruct the history of pollution in the region.

Study Area

The Mandovi and Zuari estuarine systems in Goa, confined between latitudes $15^{\circ} 09' N$ and $15^{\circ} 33' N$ and longitudes $73^{\circ} 45' E$ and $74^{\circ} 14' E$ (Figure 1), are amongst the largest estuarine ecosystems on the west coast of India. Both of the estuaries are micro- to meso-tidal, where tidal range is about 1.5 and 2.3 m during neap and spring tides, respectively.

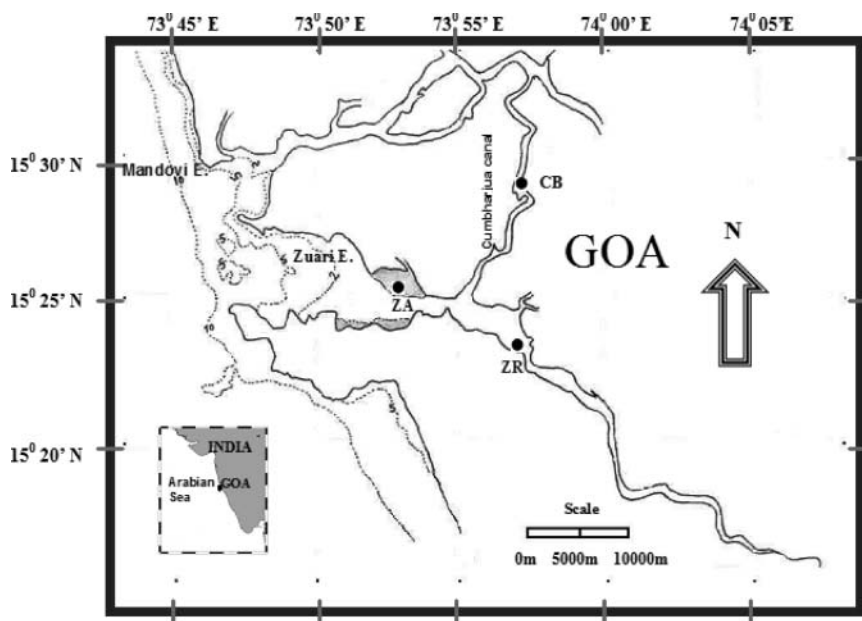


Figure 1. Study area showing location of cores: Zuari River (core ZR and core ZR) and Cumbharjua canal (core CB).

The Zuari River is about 70 km long with a basin area of 973 km² and catchment area of around 550 km². For the major part of their length, both rivers, along with their respective tributaries, traverse through extensive open-cast mining activity zones. The Cumbharjua canal joins the two rivers within the estuarine reaches. Its length is around 17 km and is aligned roughly in a north-south direction. It joins the Mandovi and Zuari at distances of 14 and 11 km, respectively, from their mouths. These two estuaries constitute the backbone of Goa's economy. Mormugao port, one of the best natural harbors, is situated on the southern bank of the Zuari estuary near its mouth. More than 10 million tons of iron ore are exported annually through this port.

Geological Setting and Mining Background

Goa is largely covered by the rocks of the Goa group belonging to the Dharwar Super group of the Archaean proterozoic age, except for a narrow strip along the northern corner that is occupied by the Deccan traps of upper cretaceous to lower Eocene age. The Dharwarian rocks, which extend in a general NW-SE trend, are represented by metamorphosed basic and acidic volcanic rocks (Gokulam, 1972). The sediments at the base are overlain by greywacke suite of rocks, followed by pyroclasts and tuffs with the associated chaemogenic precipitation of lime, manganese and iron, and then by greywacke suit of rocks. The soil of Goa is mostly derived from laterites which are rich in ferric aluminium oxides and is reddish in color. Alluvial and loamy soils are found along the riverbanks and are rich in minerals and humus.

Mining began in Goa in the 1950s in order to meet the industrial demand that increased within a decade (Salgaonkar, 1991). In the 1980s and 1990s, mining became a highly sophisticated, capital-intensive industry. Based on the concentration of ore, the Goan mining area has been divided into three regions: the northern zone dominated by iron ore; the central zone comprising iron ore and ferruginous manganese ore deposits; and the southern zone, through which the Zuari estuary flows, comprised mostly of ferruginous manganese ore deposits. Of the total production, the majority of the ore is extracted from the northern zone. At present, there are around 108 and 127 industries along the Mandovi and Zuari river banks, which discharge around 8×10^5 m³ and 4.4×10^6 m³ of effluents per year into their respective rivers and tributaries. In addition, there are about 27 and 10 large mines in their respective basins which generate around 1500–6000 and 1000–4000 tonnes of rejects (waste material) per day per mine, a good amount of which can be expected to enter both rivers (NIO, 1979). Around 15 million tonnes of iron and manganese ore are transported annually along these rivers to the nearby Mormugao harbor (Satyanarayana and Sen Gupta, 1996). Mining in Goa consists of both manual and mechanical techniques employing an opencast method, which involves the systematic removal of overburden by performing the bench and slope method along hilltops and slopes, as iron ore deposits lie under a thick mantle of laterite. The iron ore is mined in the hinterland from where it is transported by trucks to the riverbanks in the upstream region, where it is stored for loading onto the barges. During the monsoons, the ore stacked at the river banks gets washed away with rain and the washings drain into the river, carrying along with them the sediments in suspension. The effects of mining activities on the suspended sediment load are clearly seen in the lower reaches of both the estuaries, wherein these estuaries are wide and shallow with large stretches of mudflats exposed during the low tide. Mining activities and the uncontrollable construction in major tourism centers within the catchment area of these estuaries have accelerated coastal pollution and erosion. Hence, it is of prime concern to

study the environmental status and the processes that are controlling the distribution of sediment components and metals in the region.

Materials and Methods

Three sediment cores, two from the Zuari estuary (ZR and ZA) and one from the Cumbharjua canal (CB) (Figure 1), were collected from the mudflats during low tide using a hand-driven PVC coring tube. The ZR and ZA cores were collected at a distance of about 17 and 11 km from the river mouth while core CB was sampled 10 km from the Cumbharjua canal mouth. The cores were sub-sampled at 2 cm intervals with a plastic spatula to avoid metal contamination, transferred to clean polyethylene bags, stored in an icebox, and transported to the laboratory. The subsamples were later dried at 60°C. Sediment component (sand, silt, clay) analysis was carried out by Pipette method (Folk, 1968). Total Organic Carbon (TOC) was estimated by a wet oxidation method (Gaudette *et al.*, 1974), in which exothermic heating and oxidation with $K_2Cr_2O_7$ and concentrated H_2SO_4 was followed by titration of excess dichromate with 0.5 N $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. Sediment samples for major and trace metal analysis were digested using an $HF-HClO_4-HNO_3$ mixture in Teflon beakers and heated until completely dried. After the samples were cooled at room temperature, the same acid mixture was added and heated again, followed by addition of conc. HCl and 50% HNO_3 . The final solution was diluted with deionized water and then analyzed for elements such as Al, K, Mg, Ca, Fe, Mn, Co, Cr, Pb, Zn, and Cu using an atomic absorption spectrophotometer (GBC 932 AA, GBC Scientific Equipment Pvt Ltd., Australia). The instrument was calibrated by running blank and standard solutions prior to each element analysis. Recalibration check was performed at regular intervals. Precision was monitored by analyzing triplicate samples of some selected samples and was generally found to be < 6% standard deviation (% SD) for the major and trace elements. Accuracy of the method was determined by comparing the certified sediment standard from the Geological Society of Japan (GSJ-JSd-1) with observed values and was $\pm 3\%$ for Zn; $\pm 6\%$ for Fe and Mg; $\pm 10\%$ for Mn, Al, Ca, K; $\pm 15\%$ for Cu, Pb and $\pm 30\%$ for Co and Cr of the working values quoted.

To ensure comparability of data from a variety of materials (e.g., soils, fluvial, and estuarine sediments) (Birch, 2003; Birch *et al.*, 2004) and to reduce variance caused by variable grain-size distributions (Forstner and Wittman, 1979; Loring, 1991), the metal concentrations of all the cores were normalized against aluminum. Further, to evaluate the anthropogenic influences of heavy metals in sediments, an enrichment factor (EF) has been used as an index, which is the observed metal to aluminum ratio in the sample of interest divided by the background metal/aluminum ratio. It is expressed mathematically as

$$EF = (Me/Al)_{\text{Sample}} / (Me/Al)_{\text{Background}}$$

where $(Me/Al)_{\text{Sample}}$ is the metal to Al ratio in the samples of interest, and $(Me/Al)_{\text{Background}}$ is the natural background value of metal to Al ratio (Zhang and Liu, 2002). The concentration of Post-Archean Average Shale (PAAS) given by Turekian and Wedepohl (1961) was adopted as the background for this study.

R-mode factor analysis was also applied to the whole dataset to understand the degree of geochemical association between sediment components and metals of all three cores. The analysis helps to better elucidate the factors governing the metal distribution and grain size variations in the intertidal zone (Meglen, 1992).

Results

Core ZR: The sediment component data include 0.09–2.03% sand, 27.03–62.24% silt and 47.6–71.30% clay. Sand percentage is found to decrease from the bottom to surface of the core while silt and clay show trends opposite to each other (Figure 2A). TOC remains nearly constant throughout the core with high and low peaks ranging from 1.27 to 3.72%. The metals range from 1.02–1.32, 1.03–1.75, 5.94–7.89, 0.02–0.09, 10.49–12.83% for K,

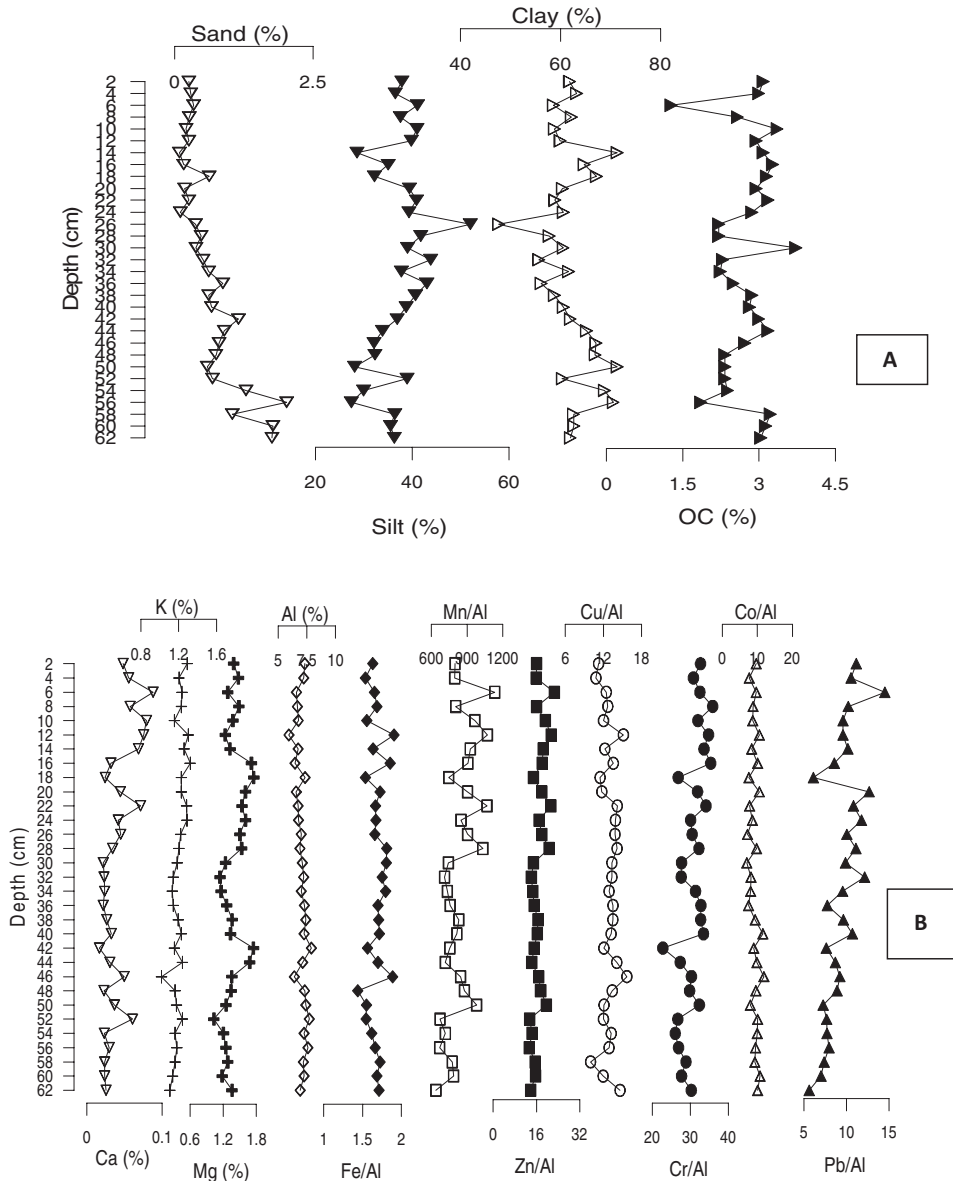


Figure 2. Vertical depth profiles in sediment core of Zuari River (core ZR): A- Sediment components (sand, silt, clay, and TOC); B- Metals (Ca, K, Mg, Al, Fe, Mn, Zn, Cu, Cr, Co, and Pb).

Mg, Al, Ca and Fe, while the range is 4412–7475 $\mu\text{g/g}$ for Mn, 96–149 $\mu\text{g/g}$ for Zn, 72–101 $\mu\text{g/g}$ for Cu, 180–243 $\mu\text{g/g}$ for Cr, 50–84 $\mu\text{g/g}$ for Co and 39–96 $\mu\text{g/g}$ for Pb. The metals can be divided into two groups of markedly different distribution profiles (Figure 2B). Vertical distribution of Mn, Zn, Cr, Pb, and Ca exhibit somewhat similar trends, indicating that they may be derived from the same source and/or have undergone similar post-depositional processes. On the other hand, Fe, Co, and Cu show more or less similar downcore distributions. For K, Mg, and Al, different profiles are seen with depth but overall a constant trend is maintained.

Core ZA: The sediment component data show varied downcore distribution (Figure 3A) with 1.37–76.26% sand, 11.48–62.24% silt, and 9.16–64.08% clay. On the whole, from the bottom to the surface, sand increases while silt, clay, and TOC decrease. TOC ranges from 0.57–3.51%. In the case of major elements, K, Mg, and Al vary from 0.48–1.24%, 1.33–2.16%, and 2.30–8.37%, respectively. These elements show a decreasing trend from the bottom to the surface of the core and are observed to be broadly similar to silt and clay profiles. The distribution profiles of Fe and Mn vary from 5.91–12.67% and 1075–6275 $\mu\text{g/g}$ and are observed to be very similar, although Fe shows larger variations than Mn, indicating a common source of local origin and/or similar post depositional behavior (Figure 3B). Both show a constant trend from the bottom to 48 cm wherein an increase is observed followed by a decrease in the upper portion (0–8 cm). In contrast, Ca ranges from 0.04–0.30% and after maintaining a nearly constant trend downcore, increases in the upper portion (0–48 cm). The high Ca values in the upper portion can be attributed to the higher sand associated shell contents. Zn (69–159 $\mu\text{g/g}$), Cr (153–367 $\mu\text{g/g}$), Cu (39–106 $\mu\text{g/g}$), Co (26–68 $\mu\text{g/g}$), and Pb (26–64 $\mu\text{g/g}$) show similar trends with lower values downcore and enriched values in the upper portion of the core.

Core CB: The sediment components include 1.69–36.99% sand, 11.34–37.56% silt, and 40.08–78.56% clay. The distribution of sand (Figure 4A) and clay is observed to be opposite with sand decreasing and clay increasing from the bottom to the surface of the core. Silt, after an initial fluctuation, shows an increase from the bottom to 56 cm and then a gradual decrease up to the surface. TOC ranges from 1.52–3.10% and shows more or less constant trend with depth. Mn and Pb (Figure 4B), ranging from 3187–12050 and 29–61 $\mu\text{g/g}$, increase from the bottom to surface while K (0.89–1.53%) with Mg (0.45–1.19%) and Al (5.48–10.23%), and Cr (163–361 $\mu\text{g/g}$) with Co (101–130 $\mu\text{g/g}$), show similar trends. Zn (72–112 $\mu\text{g/g}$) and Cu (62–102 $\mu\text{g/g}$) between 64–38 and 30–14 cm depths show similar increasing and decreasing trends while Fe (14.59–30.69%) shows a large fluctuating trend with an overall increasing pattern towards the surface.

Discussion

Vertical Variations

The geochemical trends identified in Cores ZR and CB reflect different processes. First, heavy metals are generally adsorbed onto clays and thus metal trends could reflect a grain size trend (Grant and Middleton, 1990). However, in the present study heavy metals show poor correlations with clay in core ZR and also in core CB. Second, metals could also associate with the organic matter (De Groot *et al.*, 1976; Fletcher *et al.*, 1994; Williams *et al.*, 1994). In the present cores, metal contents varied independently with variations in the total organic carbon content. So, both the finer grain size and total organic carbon as dominant factors controlling the metal distribution can be ruled out. Thus it is more probable that the observed distributions are related to changes in the source function or/and

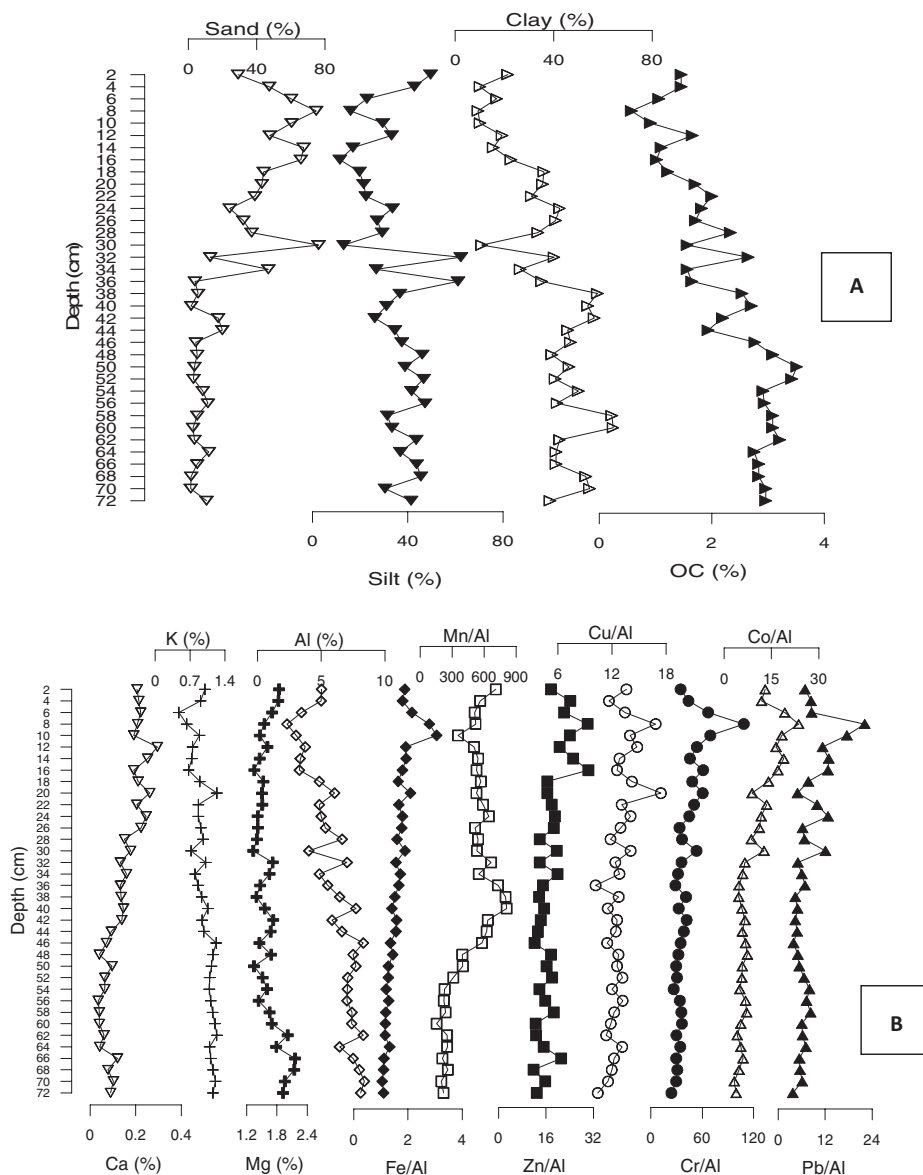


Figure 3. Vertical depth profiles in sediment core of Zuari River (core ZA): A- Sediment components (sand, silt, clay, and TOC); B- Metals (Ca, K, Mg, Al, Fe, Mn, Zn, Cu, Cr, Co, and Pb).

early diagenetic modifications. The diagenesis in marine sediments may be recognized by studying the concentration profiles of redox-sensitive metals in sediment cores. Fe and Mn are dominant participants in bacterially driven aquatic redox processes (Stumm and Morgan, 1981), and the presence of a strong Fe or Mn peak may indicate redox mobilization of Fe, Mn, and trace metals originally associated with Mn/Fe substrates. Early diagenesis has an important control on heavy metal distribution in some estuaries, wherein dissolution of iron/manganese oxides at depths results in their migration upwards by diffusion and

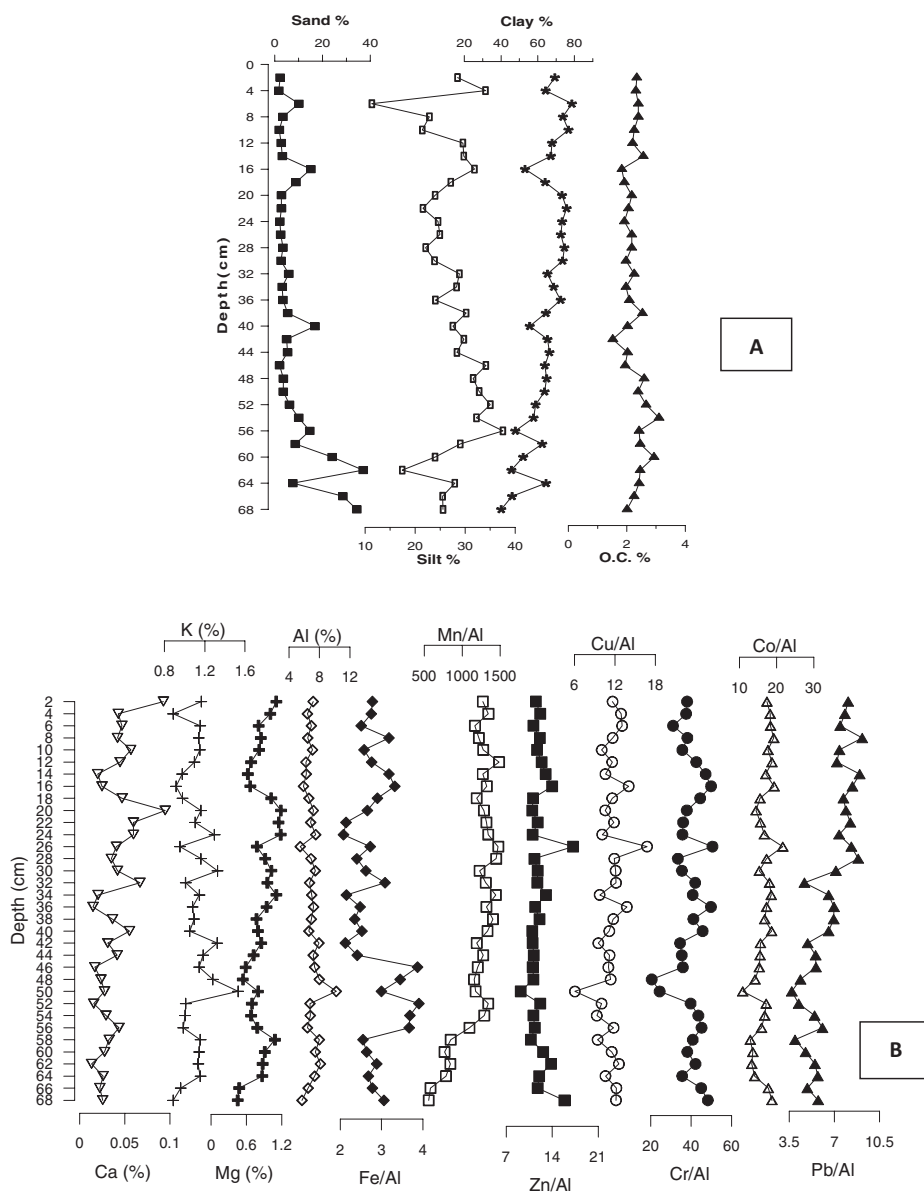


Figure 4. Vertical depth profiles in sediment core of Cumbharjua canal (core CB): A- Sediment components (sand, silt, clay and TOC); B- Metals (Ca, K, Mg, Al, Fe, Mn, Zn, Cu, Cr, Co, and Pb).

then reprecipitation in well oxygenated conditions at the surface (Zwolsman *et al.*, 1993; Croudace and Cundy, 1995). The similarity between Mn, Zn, Cr, and Pb profiles in core ZR indicates that either these elements have undergone similar early diagenetic remobilization and reprecipitation around redox boundaries, or that all these elements are derived from the same source (Fe, Cu, and Co). However, there is little evidence to support the early diagenetic modification, as redox-sensitive elements Fe and Mn show no significant enrichment and associations with the heavy metals in the upper and/or lower portions of the core as

found elsewhere (Klinkhammer, 1980; Allen *et al.*, 1990; Shaw *et al.*, 1990; Zwolsman *et al.*, 1993). Higher concentration of Fe in the lower portion of the core ZR (30–64 cm) is accompanied by high Cu and Co. On the other hand, when the input of Mn is high in the upper portion (0–30 cm), the concentrations of Zn, Cr, and Pb are also observed to be high. Both these observations point to a common anthropogenic source. Concentrations of certain metals (Fe, Mn) are significantly higher in areas where mining activities occur (Rowlatt and Lovell, 1994; Nieto *et al.*, 2007). The anthropogenic inputs of Fe and Mn, through mining and associated activities in this estuarine system, are well known, which might have controlled the distribution of the heavy metals. All these observations support the fact that the early diagenetic remobilization has not significantly affected the vertical distribution of heavy metals. Instead, they are probably due to contaminant inputs. Similar phenomena were also observed elsewhere (e.g., Allen and Rae, 1986; Cundy and Croudace, 1996; Cundy *et al.*, 1997).

Similarly, in core CB there is little evidence to support the diagenetic modifications of the heavy metals. The enrichment of Fe, Zn, Cr, and Cu in the lower portion of the core with pronounced peaks at 62 cm depth coincides with sand peak. This signifies the probability of their association with coarser fractions or the presence of detrital particles (i.e., mining and smelt products) rich in metals. Similar enrichment of heavy metals in the coarse particles has been observed in other estuaries subjected to mining and smelting wastes (Hughes, 1999; Cundy *et al.*, 2003). The enrichment of Co, Pb, Cu and, to some extent, Fe in the upper portion of the core may be due to anthropogenic input. Hence, these two cores seem to preserve the general metal loadings of mining and industrial activities in their respective drainage basins.

On the other hand, in core ZA the good correlation of Fe with Mn (0.64, $p < 0.05$) and Cu (0.69, $p < 0.05$) may indicate readsorption by Fe and Mn oxyhydroxides (Tessier *et al.*, 1985; Finney and Huh, 1989). Though diagenetic processes may have modified the original trace metal distribution, the profiles of Fe, Mn, Pb, and Cu in the upper portion seem to reflect the input of recent past. In this core, in addition to clay, Al is moderately to strongly correlated to metals ($p < 0.05$; $R = 0.61$ with Fe, 0.65 with Zn, 0.93 with Cu), indicating that the variations in metal concentrations are an artifact of varying grain size. Since Mn and Fe have positive correlations with Al, the diagenetic mobility of Fe and Mn, as a result of pH and redox changes, does not appear to be significant (Mil-Homens *et al.*, 2006). The Mn profile, however, seems to reflect diagenetic modifications to some extent. The sudden enrichment of Mn from 48 cm depth to top of the core may suggest the line of oxic-anoxic interface which is, however, not pronounced in the Fe profile. All of the heavy metals (Zn, Cu, Cr, and Pb) show low values at the bottom, with enrichment in the upper portion of the core (0–36 cm depths). The diagenetic signal is probably masked by the high input of Fe and Mn in this particular area. In reservoirs with rapid sedimentation rates, sedimentary diagenesis can be disrupted. This occurs because sediment particles are unable to equilibrate in a sediment layer before being buried by an overlying sediment layer (Callender, 2000). Therefore, Fe and Mn profiles reflect the anthropogenic input rather than post-depositional modifications. It is clearly seen that the heavy metals, including Fe and Mn, are enriching steadily towards the top of the core, highlighting the increasing anthropogenic impact in the recent past.

Intercore Variations

Geochemical data of surface sediments and cores frequently show variations due to one or more factors. These may be due to mineral variations (change in clay, sand, carbonate

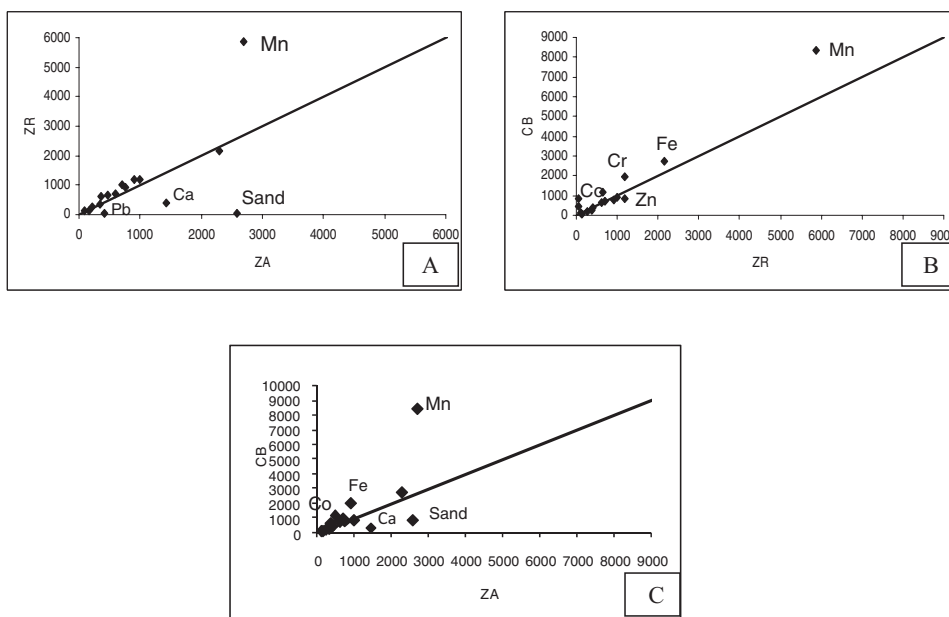


Figure 5. Isocon diagrams for Cores ZR, ZA, and CB. Individual points represent average concentrations of element in each core. To ensure all elements plot on the same scale, major elements (%): Al, K, Mg and Fe are multiplied by 50; Ca and Mn (ppm) by 1; trace elements (ppm): Zn, Cu, and Pb by 10. Only those elements that plot significantly off the line of equal concentration are labeled.

or particulate organic matter inputs), redox-controlled element migrations or pollution (Cearreta *et al.*, 2000). A distinct difference is seen between the sediment components, total organic carbon, and metal distributions among the three cores. The two upstream cores (ZA and CB) show higher values and also good correlation between finer fractions and TOC when compared to core ZA sampled from the downstream region. In addition, the concentration of the metals, except of Ca, is also found to be higher in these two cores. The observed differences in metal concentration between core ZR and core CB, even though their sediment compositions as well as total organic carbon contents are similar, could be attributed to differences in source material and depositing site. These variations are clearly seen through the isocon diagrams (Figure 5). The isocon diagram is a simple yet effective way of showing how concentrations vary between different cores (Grant, 1986; Cundy *et al.*, 1997). It allows for a simple visual comparison of the average composition of sediments at each site (Rosales-Hoz *et al.*, 2003). The isocon diagrams show little difference among the major elements (Al, K, and Mg), which fall on or near the isocon line in all the cases, indicating little variations in bulk sediment composition. The differences are most apparent for Mn, Cr, and Ca and to a lesser extent for Co, Fe, and Zn, which are likely to have local anthropogenic inputs.

When cores ZR and ZA, from the same estuary, are compared, core ZR shows a significantly higher concentration of Mn while Ca is found to be much higher in core ZA (Figure 5A). This is in agreement with the study carried out on surface sediments by Singh (2000), wherein increasing concentrations of Fe and Mn were observed from the mouth to the head region in the Mandovi and Zuari estuaries. Further, the relatively higher concentrations of Fe and Mn, seen in cores collected near mining and industrial areas in the

upper reaches of the estuaries, indicated a significant impact of these materials. When core CB, collected from the Cumbhurjua canal, which connects the Mandovi estuary to Zuari estuary, is compared with cores of Zuari (Figures 5B and C), higher values of Mn and Fe are seen in core CB while the Zuari core (core ZR) shows higher values of Zn. Singh (2000) reported higher concentrations of Fe, Mn, Cr, and Cd in Mandovi estuarine sediments while the Zuari estuary exhibited higher Zn values. Nayak (1993) reported higher concentrations of Zn, Cr, and Cu followed by Co and Pb in estuaries and adjoining coastal waters and sediments of Goa. In general, the highest concentrations of heavy metals are found in cores ZR and CB, which were collected near mining and heavily industrialized areas. These high concentrations, to a large extent, are considered to be the effect of the nearby mining zone and ore transportation by barges in these watercourses.

Enrichment Factor (EF)

The computed EF for all the metals, except Zn, in all the cores is observed to be above 2 (Figure 6). Although Fe has the highest concentration, Mn is found to show the highest EF in the three cores. Based on the observed EF values, the elements measured can be separated into three groups (Borrego *et al.*, 2004):

1. Depleted elements ($EF < 1$): Zn in Core CB.
2. Enriched elements ($1 < EF < 2$): Zn in Cores ZA and ZR.
3. Highly enriched elements ($EF > 2$): Mn, Co, Cr, Pb, Cu, and Fe in all the cores.

In cores ZR and CB, the vertical distributions of EF of the studied elements show broad similarity (Figures 6A and C). All the metals, except Mn and Pb, maintain EF values without significant variations throughout the cores. Mn values are low at lower portions (52–62 cm depth), then increase and maintain almost constant trend in the upper portions of the cores. Pb exhibits downcore depletion. The order of abundance of EF for different elements in core CB is $Mn > Co > Fe > Cr > Pb > Cu > Zn$, while in core ZR the order is $Mn > Pb > Co > Fe > Cr > Cu > Zn$. However, in core ZA, the profiles are different, showing some variations at different depths (Figure 6B). From the vertical profiles of EF, three different levels were identified for this core and are given below:

- Level 1: From 0–32 cm depth, highest enrichment factors are seen for all the metals except for Mn;
- Level 2: Between 32–52 cm depth, EF of Zn, Cu, Cr, and Pb maintains almost constant value while Mn shows highest enrichment and decreases with increasing depth;
- Level 3: From 52 to 72 cm depth, all the elements show comparatively low and constant EF values, indicating a less polluted zone.

In general, Cu doesn't show significant variations throughout the core, while the rest of the elements show a significant enrichment in the recent past with an order of EF as $Mn > Co > Cr > Pb > Fe > Cu > Zn$. The high metal concentration clearly points to the inputs from mining and other anthropogenic activities.

Relationship Between Variables

In core ZR, three factors representing 58.82% of total variance in the samples are identified with the loadings of the variables (Table 1). Factor 1 accounts for 32.04% of the total variance and is characterized by high negative loadings (>0.5) for Mn, Zn, and

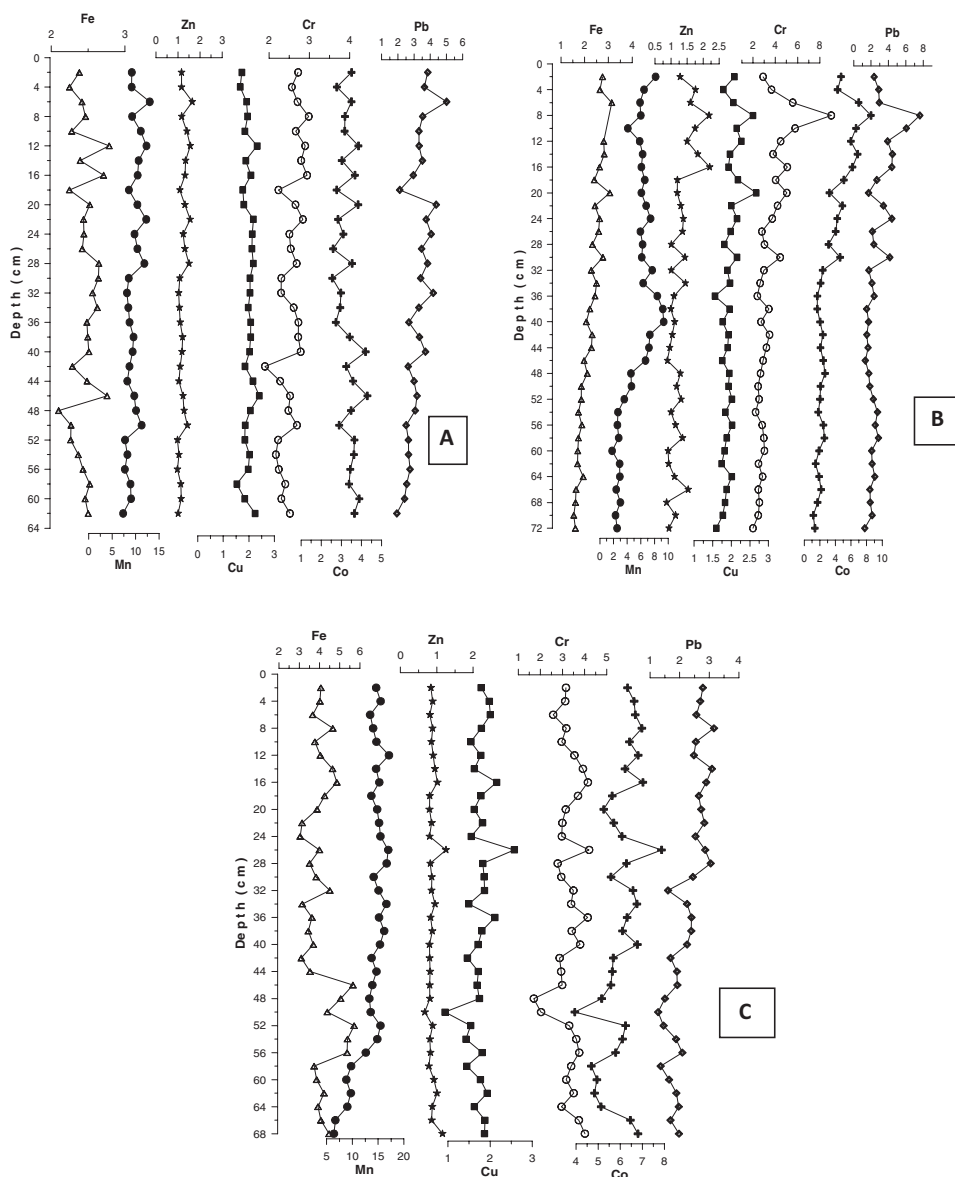


Figure 6. Downcore trends in metal enrichment factors (EF): A - core ZR; B - core ZA; C - core CB.

Ca and positive loadings for Fe. The elements in this group do not correlate with the finer fraction, which indicates that the dynamic environmental conditions exert no significant control over them (Borrego *et al.*, 2004). The negative correlations of heavy metals with Fe indicate the possibility of the absence of Fe-oxides as the main controller in the geochemistry of estuarine sediments. Thus, this factor probably reflects an anthropogenic source. Factor 2 accounts for 15% of the total variance and is dominated by high positive loadings for Pb, to a lesser extent on silt, and negative loadings on clay. This factor probably reflects a detrital source controlled by the silt and clay fractions.

Table 1
Factor analysis matrix after varimax rotation showing correlations with principal components; bold type indicates loadings > 0.70

Variance(%)	CORE ZR			CORE ZA			CORE CB		
	Factor 1 (32.04%)	Factor 2 (15.00%)	Factor 3 (11.78%)	Factor 1 (51.57%)	Factor 2 (14.13%)	Factor 3 (9.21%)	Factor 1 (29.02%)	Factor 2 (18.54%)	Factor 3 (14.31%)
Fe	0.69	0.25	0.29	0.54	0.65	0.33	-0.18	0.54	-0.66
Mn	- 0.86	0.12	0.14	0.12	0.89	0.12	0.80	0.37	-0.09
Zn	- 0.85	0.12	0.14	0.70	-0.20	0.04	-0.45	0.65	0.31
Cu	0.42	0.19	0.40	0.93	0.17	0.23	-0.20	0.17	0.65
Cr	-0.48	0.17	0.09	0.38	0.20	0.76	-0.44	-0.13	0.21
Co	0.24	-0.36	0.41	-0.58	-0.9	0.50	0.48	-0.08	0.25
Pb	-0.48	0.54	0.13	0.12	- 0.77	0.19	0.57	-0.16	0.53
Ca	- 0.78	0.06	-0.14	- 0.83	0.14	0.18	0.56	-0.24	0.25
K	-0.48	0.15	-0.45	0.92	0.05	0.16	0.40	0.84	0.05
Mg	-0.06	0.04	-0.62	0.44	-0.17	-0.41	0.49	0.15	0.50
Al	0.44	-0.12	0.40	0.97	0.15	0.01	0.11	0.93	-0.9
Sand	0.64	-0.40	0.47	- 0.93	-0.19	0.16	- 0.91	0.06	0.15
Silt	0.60	0.26	-0.48	0.02	-0.08	- 0.84	-0.08	0.96	-0.03
Clay	0.02	- 0.95	-0.02	0.82	0.15	0.10	0.87	0.10	0.31
TOC	0.26	-0.10	- 0.77	0.95	-0.04	-0.01	-0.26	0.16	-0.35

The opposite relationship between clay and silt within this group allows us to distinguish two mutually exclusive groups, as there is a factor of physical control that selects the sediment according to its size. Factor 3 accounts for 11.78% of the total variance and is dominated by high negative loadings for total organic carbon and Mg, reflecting their associations.

In core ZA, three factors represent 74.91% of the total variance, accounting for 51.57% factor 1, 14.13% factor 2, and 9.21% factor 3 of the total variance (Table 1). Factor 1 is characterized by high positive loadings on Fe, Zn, Cu, K, Al, clay, TOC, and negative loadings on Co, Ca, and sand, which reflects the association of metals with detrital components of sediments and total organic carbon. This factor includes Ca that is related to biogenic components. Mg is also present in this factor and is probably included in the shell fragments as magnesium calcite or aragonite (Mil-Homens *et al.*, 2006). This factor represents the distinction of two lithological groups: on the one hand, terrigenous origin, basically phyllosilicates and heavy metals; and on the other hand, marine origin, basically of Ca along with sand. Factor 2 is characterized by high positive loadings on Fe and Mn that supports the presence of diagenetic effects. Factor 3 is characterized by high positive loadings on Cr and moderate loadings on Fe and Co, which probably indicates anthropogenic origin.

In core CB, three factors represent 61.87% of the total variance and account for 29.02% factor 1, 18.54% factor 2, and 14.31% factor 3 of the total variance (Table 1). Factor 1 is characterized by high positive loadings for Mn, Pb, Ca, clay and high negative loadings on sand, suggesting their association with detrital components of the sediments. Within this factor, two mutually exclusive groups of metals are distinguished, which are associated with clay (Mn, Co, Pb, Ca, K, Mg, and Al) and sand (Fe, Zn, Cr, and Cu). This strengthened the possible association of the latter group with coarser fractions or presence of detrital mining particles, as discussed earlier. Factor 2 represents high positive loadings for Fe, Zn, K, and Al with moderate loadings for Mn, suggesting a common contamination source derived from inland areas. Factor 3 is characterized by high loadings for Cu and Pb and moderate loadings for Zn and Co with high negative loadings for Fe and silt, reflecting the possibility of a different anthropogenic origin, such as industrial units.

Conclusion

This study represents variation in sediment components and metal distributions between three cores collected from three different regions of the Zuari estuary. Cores CB and ZR, which were collected from upper middle estuarine mudflats, show higher values of finer fractions, TOC and metals, except of Ca in comparison with core ZA, which was collected relatively nearer to the river mouth. The differences are most apparent with Mn, Ca, and to some extent with Fe and Zn, which are likely to have local anthropogenic inputs. Overall, the highest concentrations of heavy metals are found in cores ZR and CB and could be attributed to the nearby mining zone and ore transportation by barges in these watercourses. In the case of core ZA, the diagenetic signal is probably masked by the high input of Fe and Mn in this particular area. Enrichment factors of all the metals, except Zn, in all the cores are above 2, revealing a high degree of contamination. Factor analysis grouped the samples from each core according to the main component that affects or dominates the sediment composition. In cores ZR and CB, the anthropogenic component was the dominant factor, reflecting mining and other industrial sources.

Acknowledgment

Critical comments given by reviewers have helped in improving the quality of the paper. The authors thank Dr. Rajeev Saraswat (Scientist, NIO) for the valuable suggestions made on the manuscript. Research funding received from the Ministry of Earth Sciences, Govt. of India, is appreciated.

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