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Grain size, geochemistry, magnetic susceptibility: Proxies in identifying sources and factors controlling distribution of metals in a tropical estuary, India

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ABSTRACT

The aim of this study is to understand the various sources and factors controlling the abundance and distribution of the metals through the analyses of selected metals (iron, manganese, chromium, copper, zinc and cobalt), sand, silt, clay, organic carbon and magnetic susceptibility of the surface sediments of Zuari estuary in three different seasons. Total suspended matter (TSM) concentration and salinity of near surface and bottom waters were also measured. The study undertaken for three seasons, based on 18 selected stations all along the estuary, indicated that the concentration of most of the metals were comparatively higher during pre-monsoon than in monsoon and post-monsoon seasons. Further, along the length of the estuary, high concentrations were observed at lower middle and lower estuary and also at few stations at the upstream end. Salinity, distribution of TSM, size of the sediment, organic matter, geomorphological setup, fresh water input from land and release of industrial waste within the estuary played a role in distribution and concentration of metals. Magnetic measurements indicated the dominance of haematite like minerals and helped in understanding the source and depositional processes.

1. Introduction

River Zuari within the state of Goa is one of the dynamic tropical estuaries along the central west coast of India. It has been classified as tide dominated coastal plain estuary and geomorphollogically as drowned river valley estuary (Murty et al., 1976). The river is fed by monsoon precipitation and receives large volume of land runoff from the catchment area of 550 sq km of Zuari estuary basin. Kushawati, is one of the major tributary of Zuari river. River Zuari is 67 km in length, has wide mouth, approximately 5.5 km, maintains almost the same width up to about 12 km upstream, which narrows down to less than about 0.5 km further upstream, within its estuarine limits.

Geologically catchment area of Zuari is covered by rocks of the Dharwar Super Group of the Archaean Proterozoic age. The Dharwar rocks with NW-SE trend are represented by metamorphosed basic and acid volcanic rocks and sediments at the base, overlain by greywacke suite of rocks, which in turn, is followed by pyroclasts and tuffs with the associated chaemogenic precipitates of lime, manganese and iron and ultimately again overlain by greywacke suite of rocks. There are 10 large open cast mines along with many small-scale mines of manganese ore with associated lesser iron ores within the catchment area of Zuari river.

Many mining associated activities such as transportation of ore to platforms, ore loading, effluents from beneficiation plants and barge-building activity within the river basin do take place. All these activities associated with mining contribute large quantity of material into the Zuari estuary. The Mandovi estuary, which is connected to Zuari estuary through Cumbharjua canal (Fig. 1) also passes through extensive mining activities and adds substantial amounts of mining material to the Zuari estuary during monsoon and ebb tide.

Sediment composition within estuaries is mainly dependent on type and amount of material released from the catchment area of a river. The rivers within tropical climatic zones are bound to release higher quantity of material to the estuaries due to the humid climate. Within the estuaries, sediments are major repositories of metals (Jonathan et al., 2004; Simeonov et al., 2007). Once released into the aquatic environment, trace metals may interact with suspended matter, and subsequently be removed from the water column facilitating deposition. Metal concentration in sediments within estuaries can be influenced by factors such as salinity (Coakley et al., 1993), freshwater discharge (Forstner and Whittmann, 1981), flow rates (Schoellhamer, 1995) and geomorphological setup. Further, sediments composed of different geochemical

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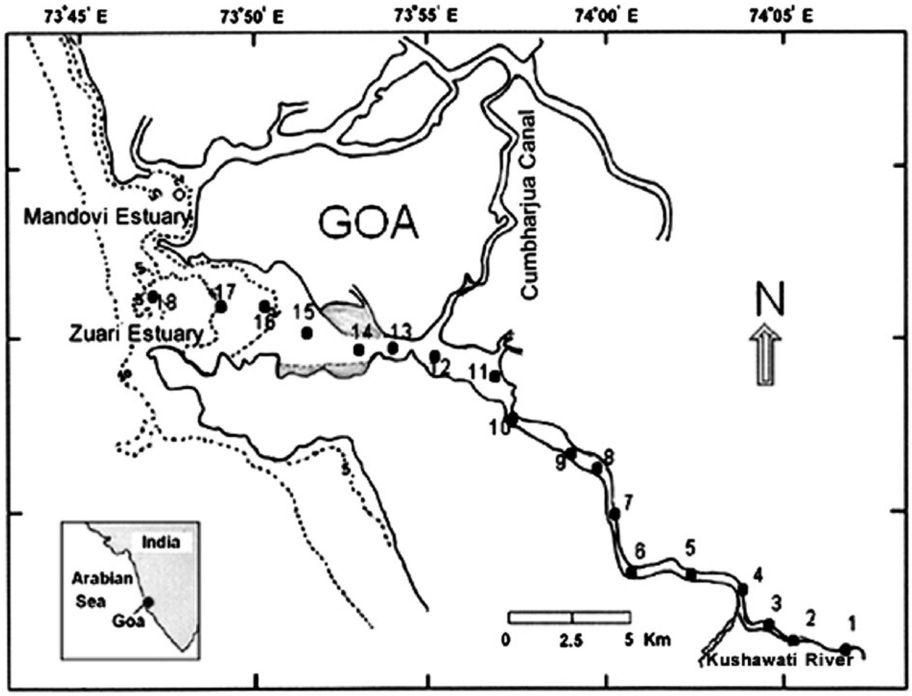

Fig. 1. Map showing the station locations of samples along the Zuari estuary.

phases such as clay, silt, sand, organic material, oxides of iron and manganese, carbonates and sulphide complexes, act as potential binding sites for metals entering an estuarine system (Jonathan et al., 2004). Metals are natural constituents, but anthropogenic activities can cause elevated levels of these metals in various parts of the system (El-Hassan and Jiries, 2001; Homady et al., 2002). Once the metal concentration exceeds the certain level, they may lead to severe environmental problems. Considering the importance of studying behaviour of metals in the estuarine system an attempt has been made in this paper to understand the various sources and factors controlling the distribution and abundance of selected metals within a tropical (Zuari) estuary.

2. Materials and methods

Surface sediment samples as well as near surface and near bottom water samples were collected from 18 selected stations in three different seasons, all along the length of the estuary onboard a fishing trawler. Water samples were collected by using Niskin sampler and sediment samples by using Van Veen grab. Water samples were transferred to pre-cleaned plastic bottles. From the grab sampler, upper 5 cm sediment was collected by using plastic spatula as a representative of surface sediment. Collected sediment samples were transferred to pre-cleaned polyethylene bags. Sediment samples were preserved in the deep freezer. The sampling locations are shown in Fig. 1.

Salinity of both surface and bottom waters was determined by Mohr-Knudsen method (Grasshoff, 1983). To obtain total suspended matter (TSM) concentration, 1 L of both surface and bottom water samples were vacuum filtered through 0.45 μm millipore membrane filter separately. The filter papers were oven dried at 60 °C and then weighed. TSM is expressed as mg/l.

Sediment samples collected were oven dried at 60 °C. For total metal analysis 0.2 g of finely ground sediment sample was digested with a mixture of 10 ml of HF, HNO_3 and $HClO_4$ (7:3:1) on the hot plate at 150 °C in Teflon beakers. The above solution after drying completely was mixed with 5 ml of the same acid mixture and dried on the hot plate for 1 h and then 2 ml of concentrated HCl was added again and dried completely. Final residue was then dissolved in 10 ml of 1:1 HNO_3; after ensuring complete digestion (clear solution) of the sediment sample, the contents from the Teflon beakers were transferred into the acid washed polypropylene volumetric flaks and the solution was made up to 50 ml with millique water. Metal concentration was later determined in the above solutions by an atomic absorption spectrophotometer (GBC 932AA model). The accuracy of the analytical method was analysed by the standard reference materials MAG-1 (Marine Sediment) and GR-1 (Green River Shale). The recoveries of all the metals were good which lie between 89% and 95% except for Cr, for which it was 80%. Another part of the sample was used to determine organic carbon, following Walkley Black method, adopted and modified by Jackson (1958). Yet another part of the sediment sample was used for granulometric analysis to obtain sand, silt and clay components (Folk, 1968).

Magnetic susceptibility measurements of sediments were carried out using Bartington MS2 system. Both the high (4.7 kHz) and low (0.47 kHz) frequency measurements were performed using a dual frequency Bartington MS2 susceptibility meter. Magnetic susceptibility (χ) measurements of very weak samples were carried out employing the more sensitive Agico's Kappabridge KLY-4S instrument. Frequency dependent susceptibility (χ_{fd}%) was calculated using the formula $(\chi_{LF} - \chi_{HF})/\chi_{HF} \times 100$ where χ_{LF} is magnetic susceptibility at low frequency and χ_{HF} is susceptibility at high frequency. Further, anhysteretic remanence magnetisation (ARM) was imparted in a steady 0.05 mT field superimposed over decreasing alternating field (A.F.) from 100 mT to 0 mT using a Molspin A.F. demagnetizer. ARM created within the sample was then measured using Molspin spinner magnetometer. Isothermal remnant magnetisation (IRM) was acquired by first exposing the samples to series of successively larger fields along one direction and then in the opposite direction (backfields, −20 mT, −30 mT, −40 mT, −100 mT, −200 mT and −300 mT) using a Pulse magnetizer (Magnetic measurements Ltd.). After each forward and reverse field (DC demagnetization), samples were measured using the Molspin spinner magnetometer. The IRM achieved at 2 *T* is referred as the saturation isothermal remnant magnetisation (SIRM). Various other parameters were evaluated in terms of magnetic concentration, mineralogy and grain size as summarized by Thompson and Oldfield (1986) and Oldfield (1999).

3. Results and discussion

3.1. Salinity and total suspended matter (TSM)

The salinity remains almost negligible during monsoon from head of the estuary up to the station 12, further downstream it shows an increasing trend in both surface and bottom waters with variations in between (Fig. 2a). River receives considerable volume of freshwater during this season, in the form of runoff from catchment area and monsoon precipitation. Salinity shows a general increasing trend from head to the mouth of the estuary during post-monsoon and pre-monsoon (Fig. 2a). Little difference in salinity was observed between surface and bottom waters during post and pre-monsoon. However, at most of the stations, bottom water shows slightly higher salinity than the surface waters in all the three seasons. Average salinity obtained for different seasons in bottom waters was also observed to be higher than the respective surface waters. The quantity of freshwater discharge from river Zuari during pre-monsoon and post-monsoon period is negligible i.e. about 0.03 cu. km per year (Wagle et al., 1988) and the flow within the estuary during these seasons is regulated largely by tides of semidiurnal nature. Thus estuary remains well mixed during pre-monsoon and partially mixed during post-monsoon.

Concentration of TSM varies from 6.4 to 32.4 mg/l and 7.6 to 117.4 mg/l in surface and bottom waters respectively for 18 stations during monsoon. While, during post-monsoon it varies from 5.7 to 60.0 mg/l and 7.9 to 224.9 mg/l in surface and bottom waters respectively. Surface TSM concentration varies from 8.8 to 28.6 mg/l and bottom TSM from 11.6 to 100.9 mg/l during pre-monsoon. Bottom waters showed comparatively higher concentration of TSM than the surface water in all the three seasons (Fig. 2b). The higher TSM values are observed in the zone of higher salinity in all the three seasons with some exceptions. In general, concentration of TSM is found to be less in the upstream/head region and higher in the downstream/lower estuarine regions. Decrease in TSM content from mouth of the Zuari estuary towards upstream during pre-monsoon and post-monsoon was earlier reported by Nayak and Bukhari (1992).

3.2. Sand, silt, clay and organic carbon

The sand contents during monsoon, post-monsoon and pre-monsoon vary from 2.3 to 94.8%, 28.8 to 95.4% and 2.5 to 98.4% respectively. Higher sand content is observed in the upper estuarine region with few peaks in the lower estuary. At the mouth i.e. station 18, higher values have been recorded in all the three seasons (Fig. 2c). Silt contents vary from 1.7 to 64.4%, 1.0 to 25.3% and 0.1 to 30.6% respectively during monsoon, post-monsoon and pre-monsoon. Generally higher values of silt are noted in the lower half of the estuary in all the three seasons. Clay content varies from 2.4 to 57.4%, 1.2 to 63.7% and 1.6 to 68.5% during monsoon, post-monsoon and pre-monsoon respectively for the 18 stations analysed. Comparatively higher values are obtained for the lower half of the estuary but values decrease near the mouth region. Organic carbon in surface sediments of Zuari estuary varies from 0.03 to 2.4% (Avg. 0.7), 0.1 to 2.3% (Avg. 0.9) and 0.2 to 2.6% (Avg. 1.0) during monsoon, post-monsoon and pre-monsoon seasons respectively. Average (Avg.) organic carbon values are comparatively higher during pre-monsoon season followed by post-monsoon and then monsoon season. It is clear from the distribution of results that organic carbon, silt and clay are enriched in the lower estuary whereas sand is dominating in the upper estuarine region (Fig. 2c, d, e, f). In general higher values of organic carbon are observed wherever clay and silt content is high and sand is low, which is supported by the significant average positive correlation obtained between organic carbon with silt ($r = 0.63$) and clay ($r = 0.87$) and significant negative correlation with sand ($r = -0.85$).

3.3. Geochemistry of metals

Iron (Fe): Concentration of Fe in surface sediments of Zuari estuary varies from 3.0 to 13.2%, 1.1 to 13.5% and 4.0 to 16.8% during monsoon, post-monsoon and pre-monsoon season respectively for 18 stations analysed. When the distribution of Fe concentration is considered for whole estuary from upstream to the mouth, the highest concentrations have been recorded between stations 10 and14 and also at stations 3 and 4 (Fig. 3a). Moreover, when the average values of three seasons are compared pre-monsoon showed relatively higher concentration (Avg. 8.7%) followed by monsoon (Avg. 8.4%) and then post-monsoon (Avg. 7.6%).

Manganese (Mn): Mn content ranges from 612.5 to 5275.0 μg/g in monsoon, 462.5 to 5362.5 μg/g in post-monsoon and from 800.0 to 5937.5 μg/g in pre-monsoon. When the whole estuary is considered the higher concentration of Mn is available within the surface sediments between stations 7 and 14 (Fig. 3b). The distribution trend of the average Mn (μg/g) values is similar as that of Fe, maintaining higher concentration during pre-monsoon (Avg. 3099.3) followed by monsoon (Avg. 3069.2) and then the post-monsoon (Avg. 2936.7).

As mentioned earlier, the catchment area of Zuari estuary is known for considerable anthropogenic activity especially open cast mining of Mn and Fe ores. The concentration of Fe and Mn within the estuarine sediments can be related to various natural and anthropogenic activities. It is also important to understand the processes involved in the distribution and concentration of Fe and Mn within the estuarine system in addition to the source from where they have been received. The behavior of Mn with reference to salinity within the estuary is quite different from that of Fe. It is well established that the Mn remains in solution phase in the lower salinity up to 10 (Kerdijk and Salomons, 1981). Further, downstream as the salinity increases Mn slowly flocculates and finally it precipitates (Balachandran et al., 2005) at around 18 salinity and gets incorporated in the surface sediments. Fe, however, gets precipitated at low salinity. In Zuari estuary higher salinity is maintained from the mouth of estuary up to slightly upstream end of the mouth Cumbharjua canal. Higher concentration of Mn obtained between stations 7 and 14 must be due to the availability of higher salinity in this part of the estuary. River input is considerably less and tidal influx controls the whole estuary during pre monsoon, the salinity in the upstream is high which favours the precipitation of Mn in the upstream and therefore during this season higher values have been recorded within the sediments of upstream. The distribution of Fe and Mn can be better explained considering additional input from Cumbharjua canal in addition to the input of these elements from the catchment area of Zuari estuary. It is a known fact that the catchment area of river Mandovi has large iron ores mines (27 major mines with lesser Mn ores). The fresh water during monsoon flows from Mandovi to Zuari through Cumbharjua canal, which is expected to carry considerable amount of Fe and once it reaches the Zuari estuary due to the salinity it gets precipitated and possibly gets remobilized between stations 10 and 14. Fe and Mn show significant correlation with

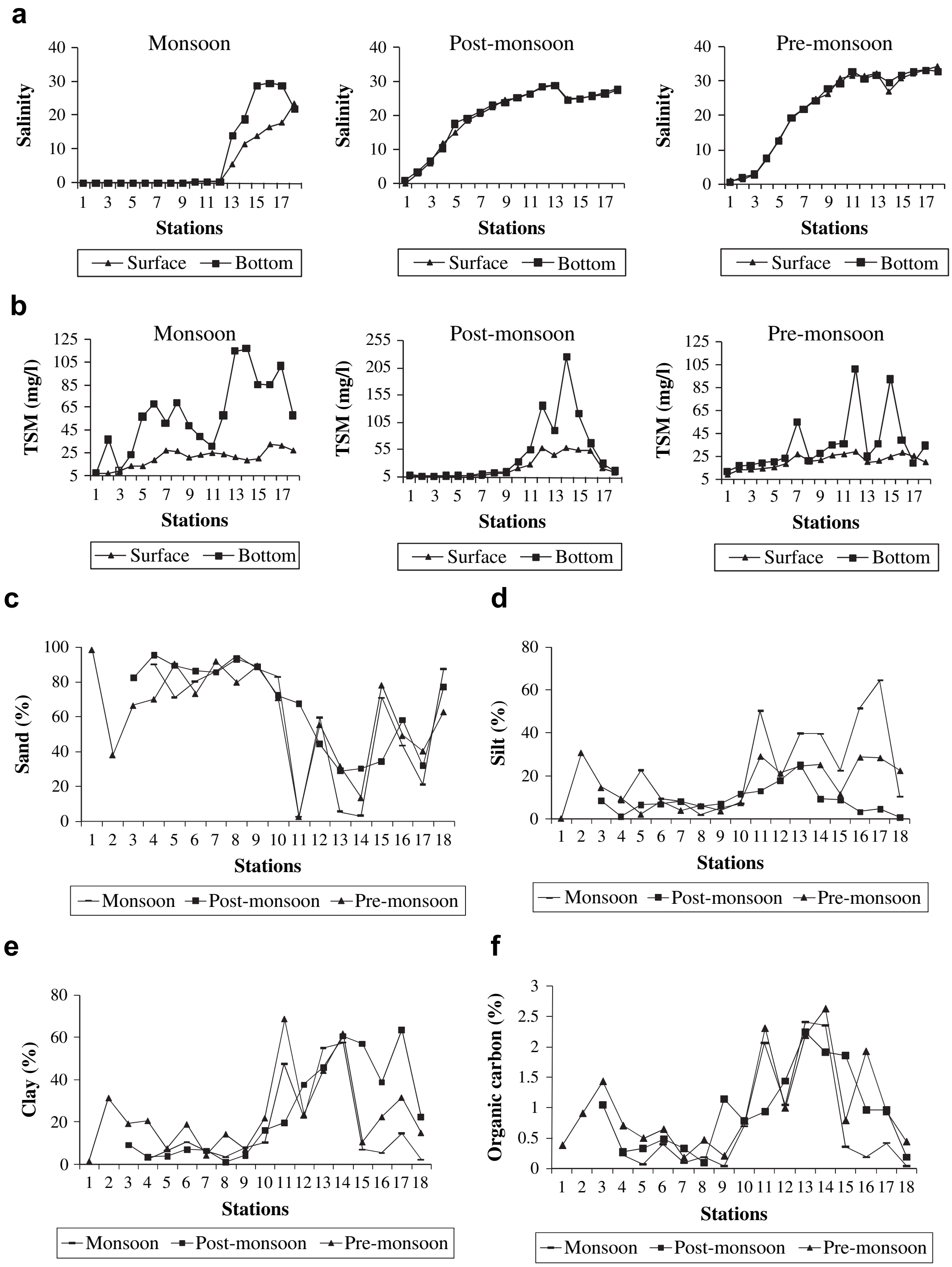

Fig. 2. Spatial variation of salinity (a) total suspended matter (TSM) (b) sand (c) silt (d) clay (e) in Zuari estuary.

finer size sediments during monsoon and post-monsoon season (Table 1 a & b). However, they do not show any significant relationship with clay and silt during pre-monsoon season (Table 1c). This may be due to decline of adsorption potential in finer sediment grades that results from the tendency of these particles to flocculate in saline waters (Knox, 1986), forming large particle-aggregates with a correspondingly low total surface-area-to-volume ratio. Organic carbon present in the sediments acts as a trap for Fe and Mn in this region, which is supported by the significant correlation values obtained for Fe and Mn with organic carbon for monsoon and post-monsoon season.

Chromium (Cr): Concentration of Cr ranges from 22.8 to 242.0 μg/g, 70.3 to 279.5 μg/g and 143.0 to 502.0 μg/g during monsoon, post-monsoon and pre-monsoon seasons respectively. The average Cr (μg/g) values of three seasons shows relatively higher concentration during pre-monsoon (267.4) followed by post-monsoon (178.9) and then monsoon (113.5). Except for the monsoon, the distribution of Cr within the surface sediments of Zuari estuary largely follows the trend of that of Fe and Mn (Fig. 3c), which is also supported by the significant correlation values obtained for these metals during post-monsoon and pre-monsoon. Association of Cr with Fe ores has been reported (Bukhari, 1994)

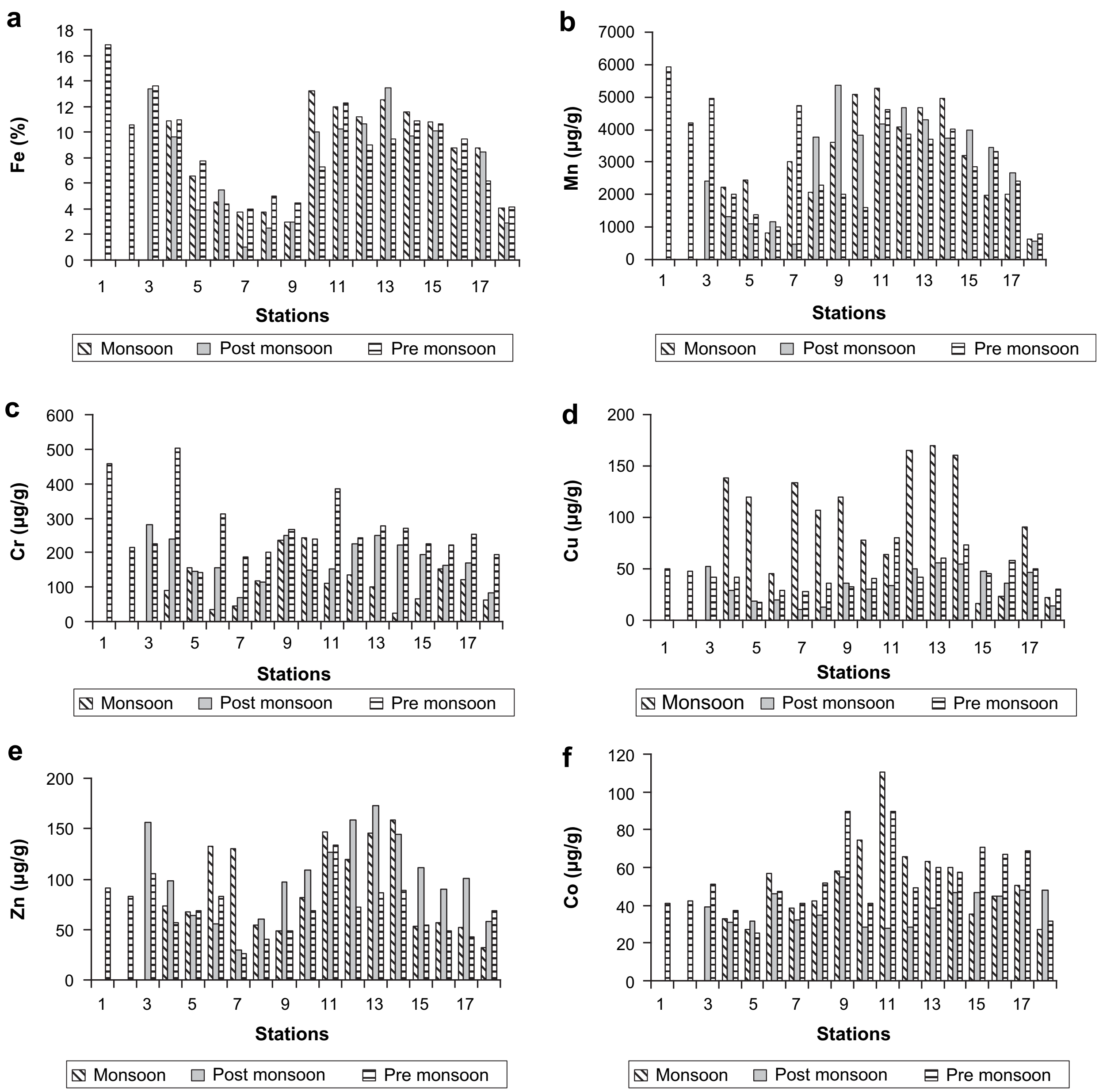

Fig. 3. Distribution and abundance of Fe, Mn, Cr, Cu, Zn and Co in surface sediments of Zuari estuary.

within the catchment of Mandovi estuary. All along the banks of especially Mandovi estuary, ore processing units to enrich the percent of iron ore are operating and it is expected that these industries are forced to release associated elements to the waters of the estuary. In addition the loading jetties in the upstream of Zuari estuary are also expected to release considerable amount of Fe, Mn and Cr. As the river current is considerably low during pre-monsoon Cr gets incorporated into the sediments to a large extent during this season. Cr exhibits significant correlation with organic carbon, Cu and Zn during post-monsoon season (Table 1b), indicating the role of organic matter in the distribution of Cr, Cu and Zn.

Copper (Cu): Cu content ranges from 16.5 to 169.5 µg/g, 10.5 to 56.0 µg/g and 17.3 to 80.8 µg/g during monsoon, post-monsoon and pre-monsoon respectively. The concentration of Cu remained very low during pre-monsoon and post-monsoon compared to monsoon season, however, maintaining the trend similar to Fe and other elements (Fig. 3d). No significant relation between Cu concentrations in waters with salinity was reported earlier in Zuari estuary (Sankaranarayanan and Reddy, 1973). The higher concentration obtained during monsoon can be directly related to the material input from the catchment area brought by the tributaries as well as input from Cumbharjua canal. Foster and Morris (1971) have made similar observations elsewhere. Cu exhibits significant correlation ($p \leq 0.01$ or $p \leq 0.05$) with Fe, Mn, Zn, organic carbon, clay and silt during post-monsoon and pre-monsoon seasons. Cu shows significant correlation with Zn and Mn during monsoon (Table 1 a, b & c).

Zinc (Zn): Zn concentration varies from 32.3 to 158.8 µg/g, 29.5 to 172.3 µg/g, 26.3 to 133.5 µg/g during monsoon, post-monsoon and pre-monsoon seasons respectively. The distribution of Zn follows the trend of Fe with the values decreasing from station 1 to 7 and maintaining highest values between stations 11 and 14 especially during post-monsoon season (Fig. 3e). In case of other two seasons higher values of Zn are seen in the upper estuary at

Table 1
Correlation matrix for metals, sand, silt, clay, organic carbon (OC) and magnetic parameters of surface sediments of Zuari estuary for a) monsoon season, b) post-monsoon and c) pre-monsoon. ** – correlation is significant at 0.01 level, * – correlation is significant at 0.05 level.

	Fe	Mn	Cr	Cu	Zn	Co	OC	Sand	Silt	Clay
a)										
Fe	1.00									
Mn	0.67**	1.00								
Cr	0.08	0.28	1.00							
Cu	0.18	0.46*	0.03	1.00						
Zn	0.38	0.56*	−0.41	0.48*	1.00					
Co	0.49*	0.71**	0.23	0.10	0.58*	1.00				
OC	0.67**	0.74**	−0.22	0.41	0.78**	0.67**	1.00			
Sand	−0.60**	−0.52*	0.18	−0.20	−0.55*	−0.56*	−0.84**	1.00		
Silt	0.47*	0.22	−0.08	−0.07	0.20	0.34	0.49*	−0.88**	1.00	
Clay	0.57*	0.70**	−0.24	0.44	0.78**	0.65**	0.99**	−0.87**	0.53*	1.00
χ_{ARM}	0.82**	0.73**	−0.09	0.43	0.72**	0.68**	0.91**	−0.77**	0.49*	0.87**
χ_{ARM}/SIRM	0.24	0.58*	−0.24	0.26	0.69**	0.69**	0.82**	−0.70**	0.37	0.87**
χ_{Arm}/χ	0.20	0.50*	−0.30	0.24	0.70**	0.66**	0.81**	−0.72**	0.40	0.86**
χ_{fd}	0.12	0.51*	−0.23	0.23	0.67**	0.67**	0.72**	−0.61**	0.31	0.77**
X	0.64**	0.28	0.38	0.20	−0.03	0.06	0.01	0.12	−0.10	−0.10
b)										
Fe	1.00									
Mn	0.42	1.00								
Cr	0.71**	0.50*	1.00							
Cu	0.84**	0.61**	0.80**	1.00						
Zn	0.90**	0.65**	0.80**	0.92**	1.00					
Co	−0.20	0.08	0.15	0.20	−0.09	1.00				
OC	0.68**	0.66**	0.63**	0.89**	0.81**	0.25	1.00			
Sand	−0.57*	−0.46*	−0.29	−0.78**	−0.62**	−0.23	−0.84**	1.00		
Silt	0.55*	0.54*	0.37	0.53*	0.68**	−0.32	0.68**	−0.50*	1.00	
Clay	0.48*	0.36	0.22	0.71**	0.50*	0.35	0.74**	−0.97**	0.28	1.00
χ_{ARM}	0.91**	0.52*	0.78**	0.92**	0.92**	−0.04	0.84**	−0.66**	0.72**	0.53*
χ_{ARM}/SIRM	0.02	0.27	−0.02	0.34	0.14	0.21	0.48*	−0.57*	0.07	0.62**
χ_{Arm}/χ	0.00	0.31	0.00	0.37	0.15	0.28	0.50*	−0.61**	0.05	0.66**
χ_{fd}	0.24	0.33	0.16	0.49	0.29	0.08	0.58*	−0.63**	0.18	0.65**
X	0.77**	0.22	0.63**	0.53*	0.66**	−0.25	0.38	−0.15	0.53*	0.02
c)										
Fe	1.00									
Mn	0.70**	1.00								
Cr	0.53*	0.24	1.00							
Cu	0.56**	0.54*	0.39	1.00						
Zn	0.62**	0.38	0.36	0.54*	1.00					
Co	0.05	0.18	0.13	0.57**	0.13	1.00				
OC	0.43*	0.36	0.11	0.86**	0.56**	0.42*	1.00			
Sand	0.23	0.23	−0.10	−0.83**	−0.52*	−0.42*	−0.87**	1.00		
Silt	0.15	0.18	−0.09	0.67**	0.32	0.34	0.71**	−0.89**	1.00	
Clay	0.26	0.23	0.20	0.84**	0.59**	0.43*	0.88**	−0.96**	0.739**	1.00
χ_{ARM}	0.86**	0.70**	0.39	0.66**	0.76**	0.06	0.63**	−0.49*	0.36	0.51*
χ_{ARM}/SIRM	−0.05	−0.02	0.23	0.57*	0.34	0.58*	0.48*	−0.63	0.43	0.69**
χ_{Arm}/χ	−0.11	−0.09	0.21	0.55*	0.23	0.55*	0.48*	−0.63	0.47*	0.67**
χ_{fd}	−0.05	−0.05	0.28	0.58*	0.30	0.58*	0.49*	−0.65	0.48*	0.69**
X	0.71**	0.61**	0.18	0.17	0.50*	−0.19	0.18	0.01	0.01	−0.02

some places and also between stations 11 and 14. The distribution of Zn within the estuary is controlled by variation in salinity. It is reported (Kerdijk and Salomons, 1981) that the Zn gets incorporated into the surface sediments at zero salinity as well at higher salinity of around 28. High values obtained at the upstream and middle lower estuary between stations 11 and 14 can be very well explained with help of role of salinity in the deposition of Zn. The source for the Zn in the aquatic environment can be industrial as well as sewage effluents (Alagarsamy, 2006) in addition to land runoff. Organic carbon holding Zn within the sediment is well known. The significant correlation ($p \leq 0.01$) obtained between Zn and organic carbon for the surface sediments of Zuari estuary strongly supports the retention of Zn in the sediments by the organic carbon.

Cobalt (Co): Co concentration ranges from 27.0 to 110.8 μg/g, 27.8 to 55.0 μg/g and 25.5 to 90.0 μg/g during monsoon, post-monsoon and pre-monsoon respectively. Co concentrations are observed to be relatively higher during pre-monsoon followed by monsoon and then post-monsoon. The higher concentrations of Co during pre-monsoon have also been reported in the adjacent Mandovi estuary by Alagarsamy (2006). The distribution of Co during monsoon and pre-monsoon are comparable with that of other elements described above. Concentration remains almost constant during post-monsoon, with minor fluctuations and without any particular trend. However, slightly higher values have been recorded between stations 13 and 18 and also at stations 3, 6 and 9 (Fig. 3f). Co displays significant correlation ($p \leq 0.01$ or $p \leq 0.05$) with Fe, Mn, Zn, organic carbon and clay during monsoon while it exhibits significant correlation with Cu along with organic carbon and clay to some extent during pre-monsoon.

The distribution pattern of elements except for few recorded variations depict that all the elements tend to decrease from the upstream (station 1) to the middle of the estuary (station 6/9) that is up to slightly upstream end of around the mouth of the Cumbharjua canal in Zuari estuary and further downstream maintain higher concentration (especially between stations 10 and 14) with gradual decrease towards the mouth. The distribution of various elements detailed above based on present study in the Zuari estuary, reveals that in the upstream end, mining and its associated activities are largely responsible for the concentration and distribution of Fe and Mn and to some extent also of Cr. Kushawati tributary which joins the Zuari estuary between stations 3 and 4, also contributes to the increase in metal concentrations at these stations. In the lower half of the estuary between stations 10 and 14 almost all the elements studied except for Cr, during monsoon, maintain higher concentrations. Finer sediments (silt + clay) and organic carbon also maintains relatively higher concentration in this region, supporting that the organic carbon acts as a trap for most of the metals within the estuarine region. It is a known fact that the organic matter decides the site of deposition of metals due to its ability of complexation and adsorption, which leads to strong correlation between it and metal elements (Gonzalez et al., 1991; Ergin et al., 1996). Strong correlation obtained between most of the metals with organic carbon and finer size sediments especially during monsoon and post-monsoon seasons signifies the vital role played by organic carbon and finer size sediments in the distribution of metals in the sediments of Zuari estuary. Major role of organic carbon and finer size sediments in the distribution of metals have also been recently established by Du Laing et al. (2007) in the Scheldt river. The Zuari estuary maintains strongly lower estuarine/marine conditions up to slightly upstream end of the mouth of the Cumbharjua canal in Zuari. Further upstream it acts as a river (fresh water) during monsoon and also to lesser extent during early post-monsoon season providing different environment compared to lower half of the estuary. Lower half of the estuary being wider and receives additional inputs of both water and sediment from the Cumbharjua canal, it will be appropriate to look for various possible factors for the higher concentration of the metals obtained for this part of the estuary. Factors like, TSM, tide and tidal currents, geomorphological set up, Cumbharjua canal and lower estuarine/marine nature of the estuary, may be playing a major role in enrichment of metals in this region. TSM has been considered as one of the major carrier of trace metals into the estuary which transfers the metals finally into the sediments. Higher TSM values obtained in the lower estuarine region especially in bottom waters can be due to presence of higher salinity which must be facilitating settlement of part of the finer sediments resulting higher concentration of silt and clay along with the adsorbed metals in the lower estuarine region. The zone of higher TSM was reported by (Nayak and Bukhari, 1992) near the Cumbharjua mouth and was related to resuspension by the tidal surge. It is also important to note that the width of the river gets reduced to less than half at this place and therefore causing tidal turbulence and resulting resuspension. Higher concentration of metals, observed in the present study, along this region can therefore be explained with reference to geomorphology as well as tidal surge. Metals brought by high velocity river currents, on settling within the estuary, get incorporated in the sediments. Resuspension of bed load sediments due to tidal surge and geomorphological constriction involves drag and lift force resulting removal of less denser material from the surface sediments, which in turn helps in concentration of denser particles as well as the particles with adsorbed metals and therefore responsible for higher concentration of the studied metals along this region.

3.3.1. Factor analysis

R-mode factor analysis with Varimax-normalized rotation by means of the principal components extraction method was attempted to identify common sedimentological and geochemical characteristic of the original data. Factor analysis has extracted three common factors viz. Factor 1 (F1), Factor 2 (F2) and Factor 3 (F3) with significant loadings within each factor for all the three seasons that are presented in the figure (Fig. 4).

First factor (F1) during monsoon accounts for 55.0% of total variance. High positive loading of elements such as Fe and Co with silt, clay and organic carbon indicates general association of these elements with finer fraction of the sediment and organic matter. Also strong negative effect of sand with the metals supports association of the metals with finer fractions. The second factor (F2) accounts for 14.9% of total variance. The strong loading of Cr alone in this factor indicates that other metals are not associated with Cr in this season. The third factor (F3) accounts for 13.9% of total variance. The strong association of Cu and Zn with Mn, clay and organic carbon in F3 is an indication of association of these metals with Mn oxides, finer size sediments and organic matter.

First factor (F1) during post-monsoon accounts for 61.1% of total variance. High positive loading of Fe, Mn, Cr, Cu, Zn and organic

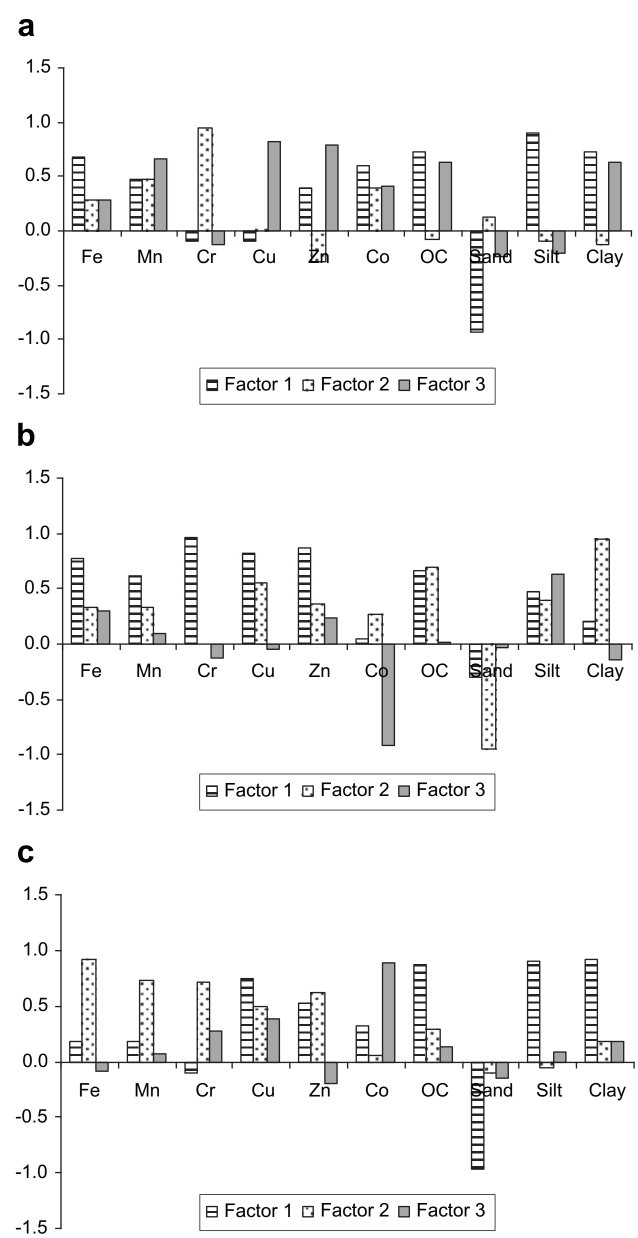

Fig. 4. R-mode factors computed for surface sediments of Zuari Estuary for monsoon (a) post-monsoon (b) and pre-monsoon (c).

carbon and moderate loading of silt indicates role of Fe-Mn oxyhydroxides and organic matter in accumulation and incorporation of these metals into the sediments. Conversion of iron into complex hydroxy compounds which leads to precipitation (Riley and Chester, 1971) and helps in co-precipitation of other metals in the water is responsible for increase in concentration of these metals in the sediments. The second factor (F2) accounts for 16.2% of total variance. Association of clay, organic carbon and Cu indicates adsorption of Cu to finer fraction and to humic substances. The third factor (F3) accounts for 10.2% of total variance. The high negative loading of Co alone in F3 indicates that other metals are not associated with Co.

First factor (F1) during pre-monsoon, accounts for 53.8% of total variance. The high loading of Cu, Zn, organic carbon, clay and silt is observed in this factor. Cu can easily form complex with organic matter because of the high formation constants of organic-Cu compounds (Stumm and Morgan, 1981). The second factor (F2) accounts for 20.0% of total variance. High loading of Fe, Mn, Cr, Zn and moderate association of Cu is observed in this factor. Fe-Mn oxyhydroxides may be the controlling factors here. The third factor (F3) accounts for 9.0% of total variance. The high positive loading of Co alone, in F3 indicates that it is not associated with other metals in this season, as observed in post-monsoon season.

Factor analysis indicated role of organic carbon, grain size and Fe-Mn oxides in the distribution of metals in the different seasons.

Percentage of clay displayed significant positive correlation with bottom TSM during post-monsoon season ($r = 0.90$, $p \leq 0.01$) and weak correlation during monsoon and pre-monsoon season. Further, significant positive correlation ($r = 0.90$, $p \leq 0.01$) is observed between Fe and bottom TSM during monsoon while other metals exhibits weak positive correlation (Fig. 5a). Most of the metals in surface sediments display significant correlation with bottom TSM concentration in post-monsoon season (Fig. 5b). No correlation is observed between metals and bottom TSM during pre-monsoon (Fig. 5c). This suggests that metals are entering into the estuary during monsoon season due to heavy land runoff in the form of adsorbed particles onto clay and or free ions. Low salinity condition available in the estuary must be facilitating them to stay in adsorbed form for longer time in suspension i.e. up to post-monsoon season. However, much before pre-monsoon season, desorption of metals takes from TSM and finally metals gets deposited and incorporated into the surface sediments. Relatively higher concentration of most of the metals in the surface sediments observed during pre-monsoon season is the testimony of this process.

In general, most of the studied elements (Fe, Mn, Cr and Co) showed higher concentration during pre-monsoon indicating favorable conditions for incorporations of the metals in the sediments during this season. During this season, estuary is largely controlled by saline water influx and therefore salinity largely facilitates the deposition of metals. The deposited metals get incorporated into the sediments and remain in the sediments depending on the availability of organic matter as well as the sediment size. During monsoon, considerable quantity of fresh water is added to the estuary from the catchment area of Zuari, which is responsible for diluting the salinity in the upstream end providing different environment for deposition compared to pre-monsoon. Post-monsoon facilitates deposition for metals largely similar to pre-monsoon.

3.4. Magnetic susceptibility

To understand the source and the factors governing the distribution and abundance of metals, magnetic parameters like magnetic concentration, mineralogy and grain size were studied. The magnetic parameters which depend on the concentration of magnetic minerals are magnetic susceptibility (χ), saturation isothermal remnant magnetisation (SIRM) and susceptibility of anhysteretic remnant magnetisation (χ_{ARM}). These parameters increase in value as the concentration of magnetic material in sediment increases. Although these parameters are concentration based, they also depend on the magnetic grain size. SIRM is also dependent on the magnetic mineralogy, for example the minerals having larger magnetisation contribute to larger SIRM values.

Mineral dependent parameters are hard isothermal remnant magnetisation (HIRM), soft isothermal remnant magnetisation (IRM_S) and S-ratio. The HIRM parameter is a measure of concentration of high coercivity magnetic minerals (e.g. haematite and goethite) and it varies directly with the concentration of high coercivity minerals while IRM_S reflects low coercivity magnetic minerals (e.g. magnetite). The values of S-ratio about 100%, indicate a high proportion of magnetite, whereas lower values indicate an increasing proportion of haematite and goethite (Thompson and Oldfield, 1986; Robinson, 1986; King and Channell, 1991). Magnetic grain size is indicated by frequency dependent susceptibility (χ_{fd}), χ_{ARM}/χ and χ_{ARM}/SIRM. Increase in values of these parameters indicates the increase in fine grained magnetic minerals (single domain).

Relatively high magnetic concentrations are observed during monsoon, in the upper estuarine region in Zuari estuary i.e. at stations 4 and 5 and also in the lower half of the estuary which includes stations 10 and 12 (Fig. 6). Further, magnetic grain size parameters show lower values at these stations indicating association of higher concentrations of mineral with the coarser grains, suggesting that the control is detrital as well as authigenic components (Sangode et al., 2001). Concentration dependent parameters such as χ, SIRM and χ_{ARM} are significantly correlated with Fe indicating anthropogenic origin and its association with coarser magnetic grains (Table 1a). χ_{fd}, χ_{ARM}/χ and χ_{ARM}/SIRM along with χ_{ARM} show significant correlations with Mn, Zn, Co and clay content indicating the role of both magnetic concentration and grain size in their association. HIRM and IRM_s show similar distribution pattern and follows the trend of χ indicating that both soft (magnetite like phase) and hard (haematite like phase) minerals are contributing to the sediment. The changes in S-ratio indicated that high coercivity minerals such as haematite like minerals phases were dominating in the upper estuarine region i.e. between stations 1 to 8 and also between stations 11 and 14. Less haematite like minerals are dominating in other stations of lower estuarine region and also at station 9.

Magnetic susceptibility during post-monsoon is observed to be lower wherever granulometric parameters are higher indicating its association with coarser magnetic grains (Fig. 6). The values of S-ratios are between 86 and 92% indicating the presence of both haematite and magnetite like minerals. Concentration dependent parameters show significant correlation with Fe, Cr, Cu, and Zn. One of the concentration dependent parameter i.e. χ_{ARM} also exhibits significant correlation with Mn, silt and clay. Grain size parameters such as χ_{fd}, χ_{ARM}/χ and χ_{ARM}/SIRM do not show significant correlation with the metal concentrations indicating association of metals towards the coarser magnetic grains (Table 1b).

In case of pre-monsoon, relatively higher magnetic concentration is observed in the upper end of the estuary at stations 1, 2 and 3 and it seems to be due to anthropogenic input. But excluding the first three stations, when the upper estuary is compared with lower estuary, higher concentrations are also observed in the lower half of the estuary especially between stations 10 and 14 (Fig. 6). S-ratio indicates relatively higher concentrations of haematite like minerals in the upstream end of the estuary and also between station 11 and 14. The distribution of granulometric parameters

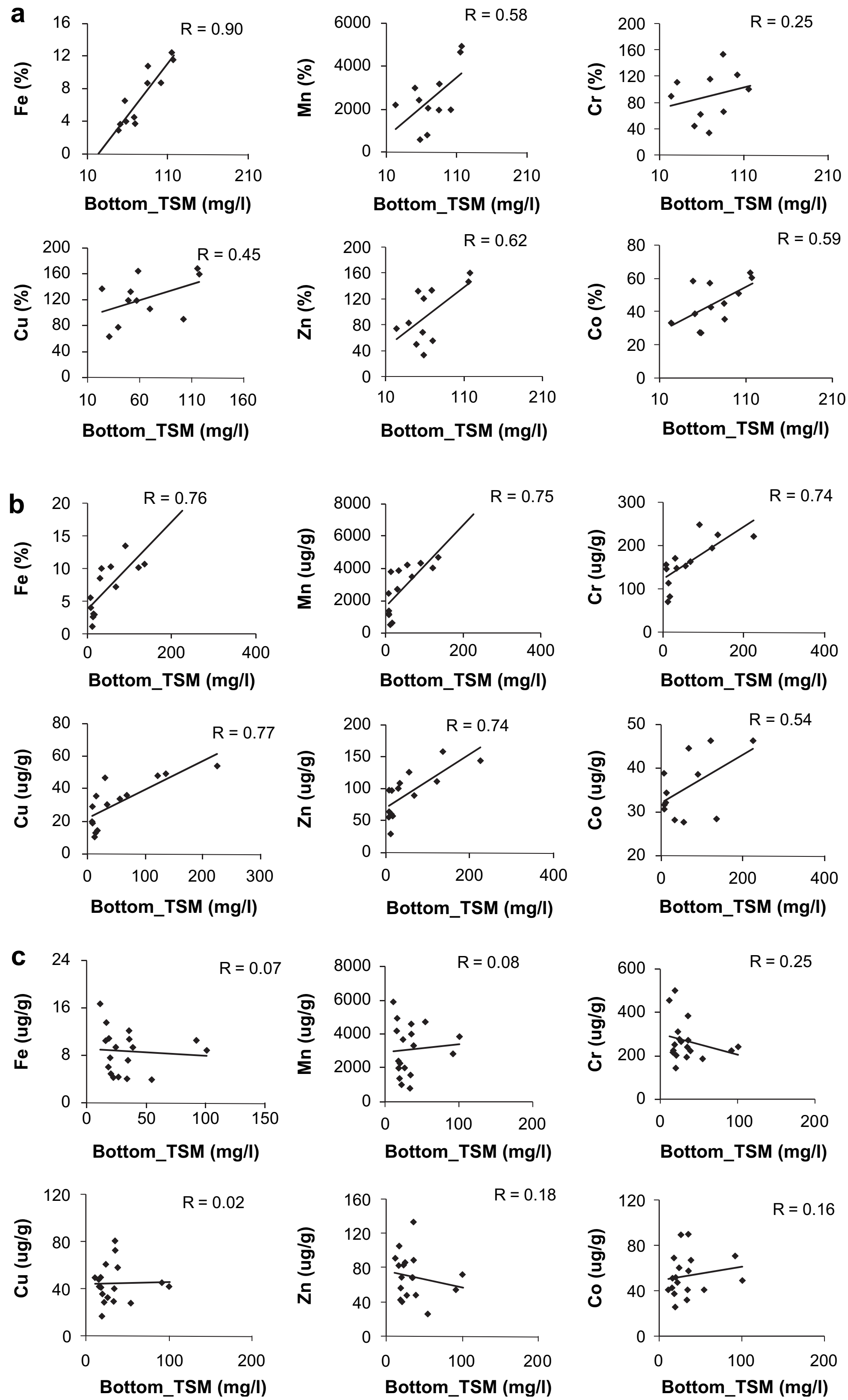

Fig. 5. Correlation between metals in surface sediments and total suspended matter (TSM): a) monsoon b) post-monsoon and c) pre-monsoon.

shows that finer grains are dominating in the lower half of the estuary with fluctuating trend. Fe, Mn and Zn show significant correlation with χ, SIRM and χ_{ARM}. χ_{ARM} also shows significant correlation with Cu and clay. Granulometric parameters show significant correlation with clay and silt and also with Cu and Co (Table 1c).

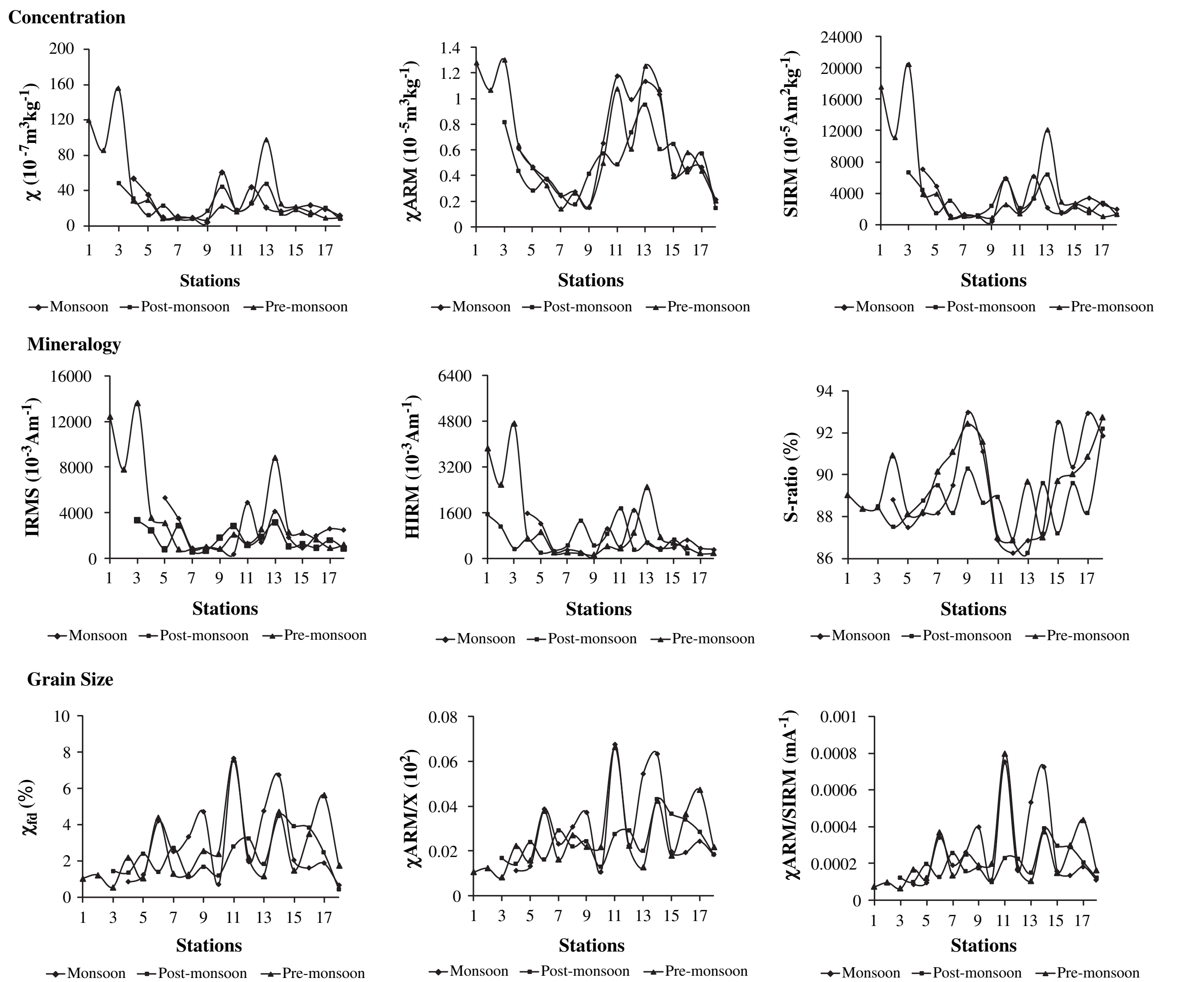

Fig. 6. Variation in magnetic concentration, minerals and grain size of surface sediments from Zuari estuary during monsoon, post-monsoon and pre-monsoon seasons.

Changes in magnetic properties under conditions of varying temperatures or magnetic fields provide information on type of minerals present and on their particle size (Deng et al., 2000; Laj et al., 2000). The thermal demagnetization plots obtained for two selected sediment samples for pre-monsoon season show similar curves, wherein the IRM undergoes a monotonic decay until their unblocking at $\sim$ 680 °C that is indicative of the presence of haematite (Fig. 7a). Also, curve of temperature dependence of magnetic susceptibility confirmed that haematite like minerals are dominating in the estuary (Fig. 7b).

In general, most of the studied metals display significant positive correlation with χ_{ARM} in all the three seasons. χ_{ARM} in turn shows significant correlation with χ during post-monsoon and pre-monsoon seasons and to some extent during monsoon season. χ_{ARM} is sensitive to single domain (*SD*, $\sim$0.03–0.07 μm) ferromagnetic minerals (Maher, 1988). More recently Zhang et al. (2001) and Booth et al. (2005) suggested that χ_{ARM} can be a proxy for clay content. Further, Zhang et al. (2007) had used χ_{ARM} to normalize heavy metal concentrations for particle size effects. Significant correlation obtained between χ_{ARM} and fine sediments (clay) suggest that χ_{ARM} can be used as grain size proxy for clay content in Zuari estuary. It is well established that the metals are in association with the iron oxides in the environment and the reduction of iron oxides have direct influence on the recycling of metals (Burdige, 1993). The strong correlation between χ_{ARM} and metals in most of the cases indicates the role of particle size and iron oxide played in the distribution of metals. Fine grains due to their high surface to volume ratio are more sensitive to the active portion of iron oxides. The grain size and hence the surface area, rather than degree of iron oxide crystallinity or structural form, impose a great influence on the kinetics and extent of iron oxide dissolution (Roden and Zachara, 1996; Haese et al., 1997). The finer grain is dissolved first due to high surface to volume ratio, which results in reduction of magnetic intensity as well as a shift in grain size towards the coarser end (Karlin and Levi, 1983). This is true at some stations which can be seen from magnetic susceptibility plots where lower values of susceptibility coincide with increase in grain size. The strong magnetic layer observed in all three seasons in the upper estuarine region could be due to moderate iron reduction with the generation of fine-grained magnetite (Karlin et al., 1987). The distribution of most of the metals in the present study follows largely the pattern of Fe in the sediments, thus Fe oxides and can be one of the factors in the distribution of metals in the sediment.

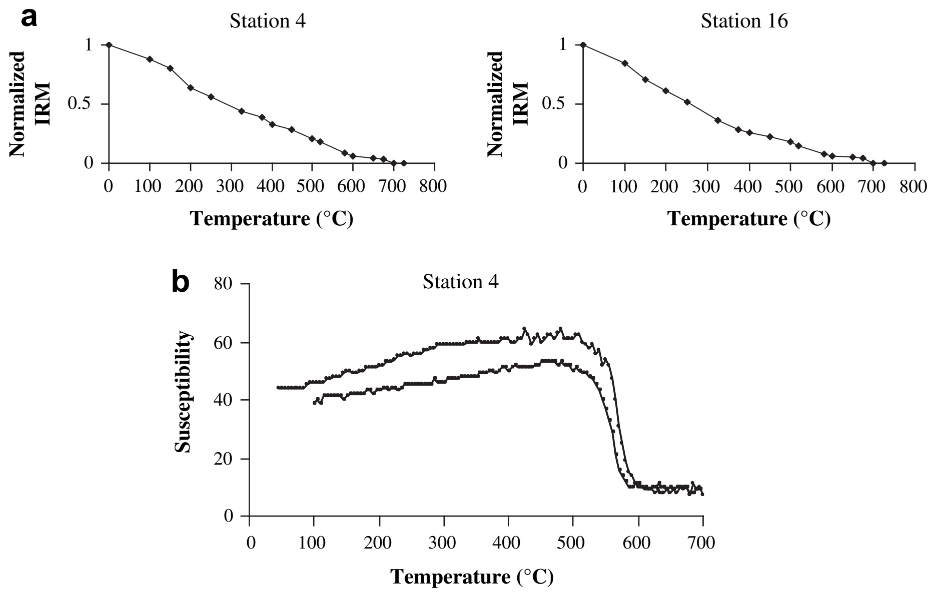

Fig. 7. Thermal demagnetization curves (a) and temperature dependence of magnetic susceptibility curve (b) for pre-monsoon season.

The increase in χ and SIRM and decrease in grain size parameters such as χ_{fd}, χ_{ARM}/χ and χ_{ARM}/SIRM reflects an increase in both total magnetic mineral concentrations and the relative importance of coarser magnetic grain size, i.e. pseudo-single domain (0.1 μm) and multidomain (> 1.0 μm) especially during post-monsoon and pre-monsoon seasons as compared to monsoon season. In general, during monsoon, most of the studied metals show significant and/or weak positive correlation with the magnetic grain size parameters and these in turn show significant correlation with the clay content, indicating the role of finer sediments in the distribution of metals in this season. In case of post-monsoon season, although the metals exhibit significant correlation with the clay content, they did not show significant correlation with magnetic grain size. Moreover during pre-monsoon season, most of the metals did not show significant correlation with the finer size of the sediment indicating shift of minerals towards the coarser grains in these two seasons. This indicates that hydrodynamic conditions prevailing during these two seasons facilitates shift of minerals towards coarser size due to dissolution of finer size minerals. It is important to note here that during these seasons geochemical changes leading to remobilization and concentration of metals has taken place. Similar distribution pattern of magnetic minerals (magnetite like phase and haematite like phase) in all the three seasons suggest that they are from the same source, probably of anthropogenic origin.

4. Conclusion

River runoff brought in large amount of material during monsoon season and this has settled and incorporated into the sediments much before pre-monsoon season. Geomorphological constriction and tidal surge also played an important role in distribution of metals in the lower half of the estuary. Metals showed affinity towards the organic matter, iron oxides and finer size of the sediment (clay) indicating their role in binding metals in the sediments. Relatively higher magnetic susceptibility and higher concentrations of metals in the upper estuarine region indicated anthropogenic input from the catchment area. The proxies geochemistry, magnetic susceptibility and grain size have helped in understanding the processes/factors responsible for the distribution and enrichment of metals in the Zuari estuarine sediments.

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