

Distribution and speciation of selected metals in surface sediments, from the tropical Zuari estuary, central west coast of India

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Abstract Estuarine sediments are major reservoirs for the metals. Distribution and mobility of metals within estuaries depends strongly on their specific chemical form. In the present study, surface sediments from Zuari estuary, Goa were analysed by a sequential procedure for Fe, Mn, Cu, Zn, Cr and Co to determine their distribution in five geochemical phases (Exchangeable, carbonate, Fe–Mn oxide (reducible) organic bound (oxidisable) and residual). The total metal content, sand, silt, clay and organic carbon were also determined of the surface sediments. The total metal contents were found to be greater than the background concentrations of average shale values as well as to that of earlier studies indicating enrichment probably due to the anthropogenic origin of metals. The results obtained from sequential procedure showed that among the studied elements, Mn and Co are potentially available in the bioavailable fractions (exchangeable, carbonate and Fe–Mn oxide bound fractions) indicating their importance in toxicity whereas rest of the metals viz. Fe, Cu, Zn and to some extent Cr are largely available in residual phase although they are available in other fractions. The main

source of metals to the estuary is mining and its associated activities in the study area. Chemical speciation by sequential extraction procedure has helped in assessing the mobility, bioavailability, diagenesis and toxicity of metals and hence giving a better insight into the ultimate fate of pollutants, which are introduced into the estuarine environment. To understand the risk of the metals to the sediment dwelling organisms the data were compared with the Sediment Quality Values (SQV) using SQUIRT. Also, correlation and Factor analysis were carried out to understand the associations of metals in the different fractions with sand, silt, clay, organic carbon and with other metals.

Keywords Estuary · Metals · Sediment · Speciation · Bioavailability · Pollution

Introduction

Metals are natural constituents and some of them are even essential for many living organisms but become toxic at higher concentrations. Metals get transported to the estuaries either in the form of suspended matters or dissolved ions, which are subsequently removed from water and are adsorbed on to and finally incorporated into the sediments. The estuarine sediments therefore are major reservoirs for the metals and their concen-

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trations are controlled by a variety of physical and chemical factors (Binning and Baird 2001). The sediments due to this reason are widely used as indicators of environmental contamination by trace metals in estuaries (Helz et al. 1975). Further, contamination due to heavy metals leads to severe environmental problems has been proved (Savvides et al. 1995; Ma and Rao 1997; Banerjee 2003; Jiries 2003; Frignani and Belluci 2004; Demirbas et al. 2005). As a sink and source, sediments constitute reservoir of the bioavailable trace metals and play important role in geochemical cycle (Yuan et al. 2004). The mobility and bioavailability of metals in sediments strongly depend on the mineralogical and chemical forms in which they occur (Baeyens et al. 2003). Therefore it is necessary to study different forms in addition to the total metal content to understand bioavailability of metals. Many factors such as sediment particle-size distribution, organic matter content also salinity, pH, and redox potential affect the chemical speciation of metals (Soon et al. 1999; Dollar et al. 2001). The behaviour of metals and their species in estuarine environment is complicated because of its highly dynamic character, subjected to changing environmental conditions governed by alternating low and high tide. In the present study an attempt is made to understand behaviour of metals and their species in Zuari estuary.

Rivers Zuari and Mandovi are the most important navigable rivers of Goa. They originate in the Western Ghats and flow through the state of Goa to join the Arabian Sea. Goa is known for its iron and manganese ore industry in addition to international tourist destination. The Mandovi–Zuari estuarine system along with Cumbharjua canal is extensively used for the transport of iron and manganese ores from hinterland to harbour. The present study focuses on the Zuari estuary. River Zuari is tide dominated coastal plain estuary and it receives water and sediment discharge from a catchment area of 550 km². The average annual freshwater run off approximated to be 9 km³, with negligible summer run off of about 0.03 km³ per year. Ten large mines are located in this basin generating 1,000–4,000 tons of rejects/day/mine. On the southern bank of Zuari estuary, near the mouth, Marmugoa harbour is situated which facilitates export of more than 10 million tons of iron

ore annually. Also barge building and repairing activities, coastal construction, dumping wastes do take place.

Considering environmental significance of Zuari estuary, in the present study, five-step sequential extraction protocol proposed by Tessier et al. (1979) was adopted to evaluate the possible chemical association of metals in the sediments, bioavailability, diagenesis and possible potential environmental impact.

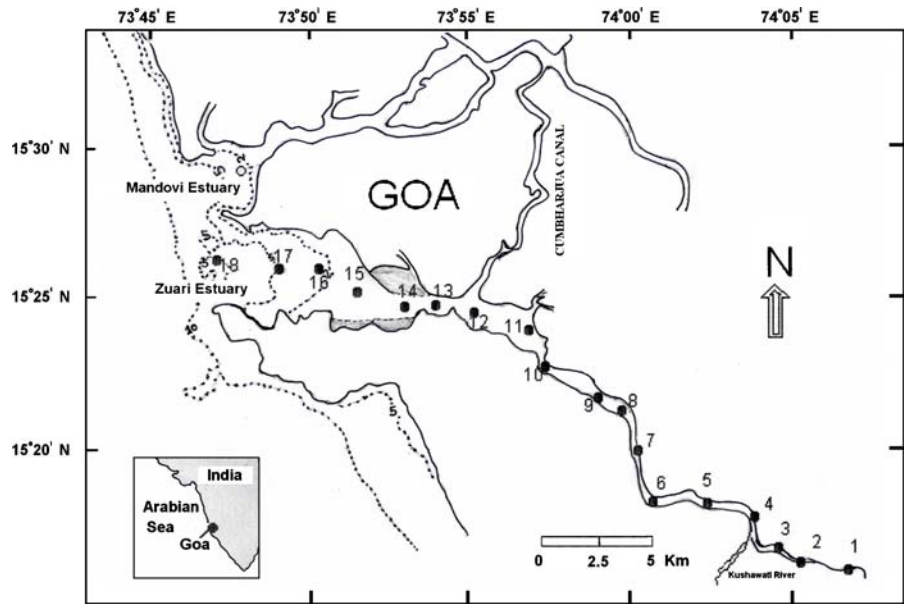
Material and methods

A total of 54 surface sediment samples were collected representing monsoon, post-monsoon and pre-monsoon covering the estuarine limits of Zuari River (Fig. 1). The sediment samples were collected by using a Van Veen grab sampler on board hired fishing trawler. Sub-sampling of the sediments was done by taking upper ~ 5 cm of the sample from the grab with the help of plastic spatula. Care was taken to avoid any contamination. Sediment samples were then frozen at ~ 4°C prior to analysis. Station locations were obtained by the Global positioning system (GPS).

Sediment samples were then oven dried at 60°C for further analysis. Pipette analysis was carried out to compute sand, silt and clay fractions. Part of the sediment sample was finely ground in an agate mortar and, homogenized and was used for the geochemical analysis. Organic carbon was determined by using Walkey–Black method (1947), adopted and modified by Jackson (1958). Total metal digestion was done by decomposing the sediment with HF, HClO₄ and HNO₃. Twenty-seven samples out of 54 were taken up for speciation studies. Various parameters of these 27 samples are only presented in this paper. Modified sequential extraction procedure proposed by Tessier et al. (1979) was adopted which involves following brief procedure:

1. Exchangeable phase: 1 g of dried and finely ground sediment sample was extracted with 8 ml of 1 M MgCl₂, pH 7 at room temperature in a 50 ml plastic centrifuging tubes with frequent agitation for 1 h. The solution was then

Fig. 1 Map showing locations of surface sediment samples from Zuari estuary



centrifuged at 8,000 rpm for 10 min and the supernatant was collected for the metals analysis. The residue was washed with deionised water.

2. Carbonate phase: the residue from the step 1 was extracted with 8 ml of 1 M NaOAc adjusted to pH 5.0 with acetic acid. Periodically agitated for 5 h at room temperature on orbital shaker. Centrifuged at 8,000 rpm for 10 min. Supernatant was collected and the residue was washed with the deionised water.
3. Fe–Mn oxide phase: the residue from step 2 was extracted with 20 ml of 0.04 M NH₂OH·HCl in 25% (v/v) HOAc at 96° ± 3°C with occasional agitation for 6 h. The solution was then centrifuged at 8,000 rpm for 10 min and the supernatant was collected for the metals analysis. The residue was washed with deionised water.
4. Organic matter/sulfide bound phase: the residue from the step 3 was digested first for 2 h with 5 ml of 30% H₂O₂ and 3 ml of 0.02 M HNO₃ adjusted to pH 2 with HNO₃ at 85° ± 2°C, 2 h and then again with 3 ml of 30% H₂O₂ (pH 2 with HNO₃) for 3 h at 85° ± 2°C with intermittent agitation. After cooling, 5 ml of 3.2 M NH₄OAc in 20% (v/v) HNO₃ was added and agitated continuously for 30 min.

After agitation, solution was centrifuged, decanted and was stored.

5. Residual phase: the residue from the step 4 was washed with the deionised water and was transferred to Teflon beakers and was digested totally with the concentrated mixture of HF, HNO₃ and HClO₄.

The concentration of the different metals viz. Fe, Mn, Cr, Cu, Zn and Co were analysed on atomic absorption spectrophotometer (AAS; GBC 932 AA model) equipped with the deuterium background corrections. Blank corrections were applied wherever it is necessary. The accuracy of the analytical method was analysed by the standard reference material MAG-1 (Marine mud from the United Geological Survey) and GR-1 (Green River sediment). The recoveries of all the total metals were good which lie between 89% and 95% except for Cr, for which it was 80%. Also the recovery of each metal from sequential extraction procedure was good which was computed by using the formula: (sum of the metal concentration in the five fractions / total metal concentration obtained after total acid digestion) × 100. The average recoveries and ±SD found for each metal were 91 ± 15, 82 ± 21, 85 ± 14, 79 ± 15, 78 ± 24, 83 ± 22% for Fe, Mn, Cu, Zn, Cr, and Co respectively.

Statistical correlation analyses between metals, sand, silt, clay and OC in five different fractions of surface sediments for three different seasons were performed. Also Varimax R-mode factor analysis by principal component analysis (PCA) was attempted to understand source and association by using the software STATISTICA (StatSoft 1999).

Results and discussion

Grain size and organic carbon

Seasonal variations in sediment components and organic carbon are detailed here below. During monsoon, sand content for the studied samples varies from 3.01–94.79% where as silt and clay content varies from 1.66–51.36% and 2.40–57.44% respectively. Sand content shows decreasing trend from station 4 up to the station 14 and further downstream shows increasing trend. Whereas silt and clay show increasing trend up to station 16 and 14 respectively and then decreases towards the mouth. Organic carbon in the same season varies from 0.03–2.35% which follows the similar trend as that of silt and clay.

In case of post-monsoon, sand, silt, clay and OC varies from 30.09–95.43%, 0.51–17.88%, 1.15–60.67% and 0.09–1.92% respectively. Sand content shows decreasing trend from station 3 up to the station 14 and further increases towards the mouth region. Silt shows increasing trend up to the station 12 with lower value at station 4 and further downstream it shows decreasing trend. In general clay and OC shows decreasing trend from station 3 up to the station 8 and further downstream they show increasing trend till the station 14 and then show decreasing trend towards the mouth.

During pre-monsoon, sand content varies from 13.36–79.70%, silt from 5.93–30.61% clay from 14.37–61.63% and OC from 0.44–2.63%. Sand shows increasing trend from station 2 up to the station 8 and further downstream shows decreasing trend up to the station 14 and then again it increases towards the mouth. Silt content decreases from station 2 to 8 and further shows increasing trend up to 16 and then decrease at station 18. Clay shows decreasing trend up to station 8

further it showed increasing trend up to station 14 and then decrease towards the mouth region. OC shows decreasing trend from station 2 up to the station 8 with slightly higher value noted at station 3. Further downstream it showed increasing trend up to the station 14 and then decrease towards the mouth.

In general sand is dominating in the upper estuarine region i.e. up to the station 8 whereas silt, clay and OC are mostly enriched in the lower part of the estuary.

Total metal content

The range of total metal content analysed for the sediment samples is as follows. Iron (Fe): Monsoon (3.78–13.21%), Post-monsoon (2.53–13.38%) and Pre-monsoon (4.18–13.66%). Manganese (Mn): Monsoon (613–5,075 µg/g), Post-monsoon (575–4,663 µg/g) and Pre-monsoon (800–4,963 µg/g). Copper (Cu): Monsoon (22–166 µg/g), Post-monsoon (13–54 µg/g) and Pre-monsoon (29–73 µg/g). Zinc (Zn): Monsoon (32–159 µg/g), Post-monsoon (56–159 µg/g) and Pre-monsoon (41–106 µg/g). Chromium (Cr): Monsoon (23–242 µg/g), Post-monsoon (82–280 µg/g) and Pre-monsoon (194–502 µg/g). Cobalt (Co): Monsoon (27–75 µg/g), Post-monsoon (28–48 µg/g) and Pre-monsoon (32–67 µg/g).

Fe in general shows decreasing trend from head of the estuary up to station 8 and further maintains relatively higher values between stations 10 and 14, which then shows decreasing trend towards the mouth region in all the three seasons. Mn decreases from head up to station 6 and then shows increasing trend up to station 14 with minor variations in between which further downstream shows decreasing trend towards the mouth region during monsoon and pre-monsoon season while in case of post-monsoon season it decreases from station 3 to 6. Increase in Mn concentration is observed at station 8 which further downstream shows constant trend up to station 16 with slightly higher value at station 12. Lower values are observed at the mouth region. Cu shows decreasing trend from head up to station 6 in case of monsoon and pre-monsoon season and up to station 8 in case of post-monsoon which further

downstream shows increasing trend up to station 14 and then decreases towards the mouth region. Zn in general decreases from head up to station 6 and then shows increasing trend up to station 14 in case of monsoon and pre-monsoon season and at station 12 during post-monsoon which further downstream shows decreasing trend towards the mouth region. Cr during monsoon decreases from station 4 to 6, from here increasing trend is observed up to station 10 which further downstream decreases up to station 14. Higher value is recorded at station 16 and lower at station 18. While during post-monsoon and pre-monsoon, Cr shows decreasing trend from head up to station 8 which further shows increasing trend up to station 14 and then decreases towards the mouth region. Co during monsoon season shows increasing trend from head up to station 12 with minor fluctuations in between which further shows decreasing trend towards the mouth region. During post-monsoon season it decreases from station 3 to 4 which then increases up to station 6. From here decreasing trend is seen up to station 12 which further downstream shows slight increase towards the mouth region. In case of pre-monsoon season Co increases from head up to station 14 with minor variations in between and then decreases at station 18.

Variations in total metal content are largely systematic along the estuary with seasons. Most of the studied metals in three seasons show higher concentration between stations 10 and 14. Further, when their distribution is compared with sediment size and organic carbon distribution, it is clear that the higher metal concentration is associated with finer sediment size (silt + clay) and organic carbon. The total metal concentrations when compared with that of average shale values (Turekian and Wedepohl 1961) showed

that the concentration of the metals are above the background level, in the Zuari estuary with a few exceptions at some stations. Singh (2000) studied the distribution of Fe, Mn, Cu, Zn, Cr and Co in the surface sediments of Zuari estuary. The average concentrations of metals in the present study and reported by Singh (2000) are presented in the Table 1. Most of the metals showed higher concentration in the present study indicating anthropogenic input to some extent. Study carried out by Singh (2000) also showed higher concentrations in the upper as well as in the lower half of the Zuari estuary similar to the present study. Also Mesquita and Kaisary (2007) reported higher concentrations of Fe and Mn in mid-estuarine region in addition to upper estuarine region during 2002.

Higher concentrations of metals in the upstream region could be related to the release of material from mining activities. In the lower estuary, higher concentrations of the metal content associated with finer sediments (silt + clay) and organic carbon indicate largely the processes involved in their deposition. Factors such as salinity, geomorphological setup, tide and associated current and land runoff must have played role in the distribution of metals in the estuary.

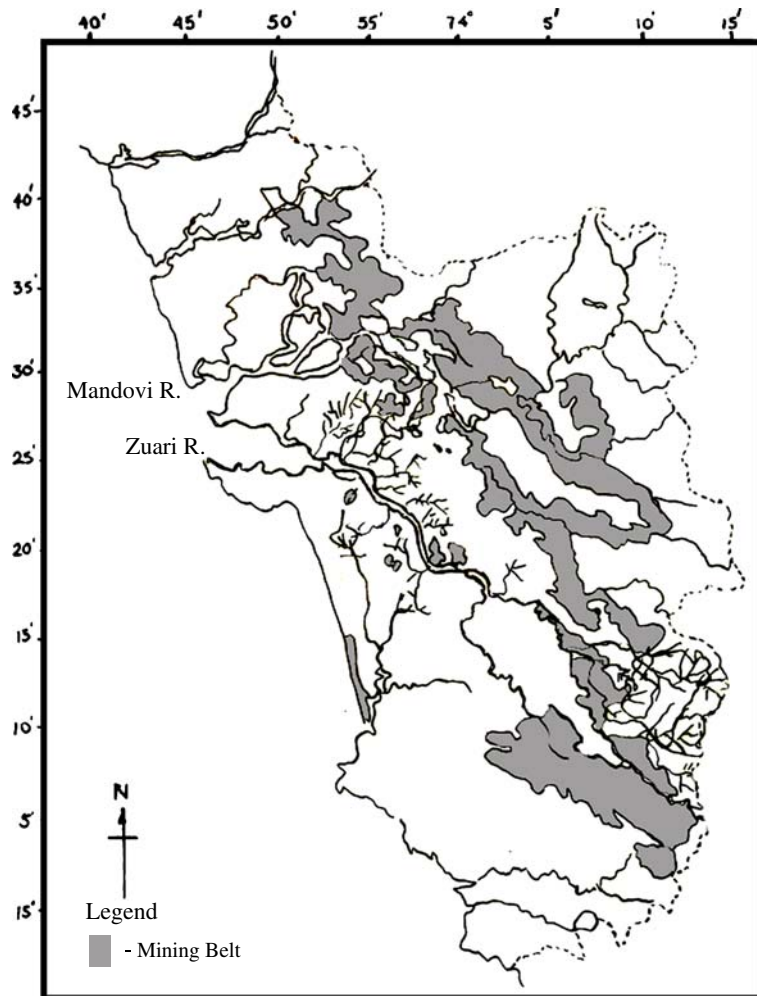
It is important to mention here the anthropogenic activities which are being carried out in the catchment area of Zuari River. As mentioned in the introduction, under the study are, the catchment area of Mandovi and Zuari rivers are important as they cover 69% of geographical area of the state. The mining activity along the central portion of the state involves open caste mining largely for iron in the northern portion and iron and manganese in the southern sector. It is pertinent therefore to mention here that in the catchment area of Zuari River, mining of Fe and Mn is

Table 1 Average metal concentrations in the sediments of Zuari estuary in the three different seasons

	Fe (%)		Mn (%)		Cu		Zn		Cr		Co	
	a	b	a	b	a	b	a	b	a	b	a	b
Monsoon	8.36	7.64	0.31	0.33	96.88	40.03	90.18	93.33	113.47	204.26	52.60	25.76
Postmonsoon	7.61	7.66	0.29	0.34	34.34	29.50	101.95	83.60	178.89	127.13	39.14	23.13
Pre-monsoon	8.72	4.27	0.31	0.30	44.78	36.41	70.39	87.25	267.43	148.67	53.46	17.49
Avg.	8.23	6.52	0.30	0.32	58.67	35.31	87.51	88.06	186.60	160.02	48.40	22.13

a Present study, b Singh (2000), except for Fe and Mn all other values are in µg/g

Fig. 2 Mining belt within Goa and drainage pattern of Zuari estuary



actively being carried out. The region being largely controlled by southwest monsoon, it is expected that the large quantity of material flow from open cast mining to the estuary through tributaries. The map (Fig. 2) of mining belt superimposed on the drainage pattern supports this.

Metal speciation

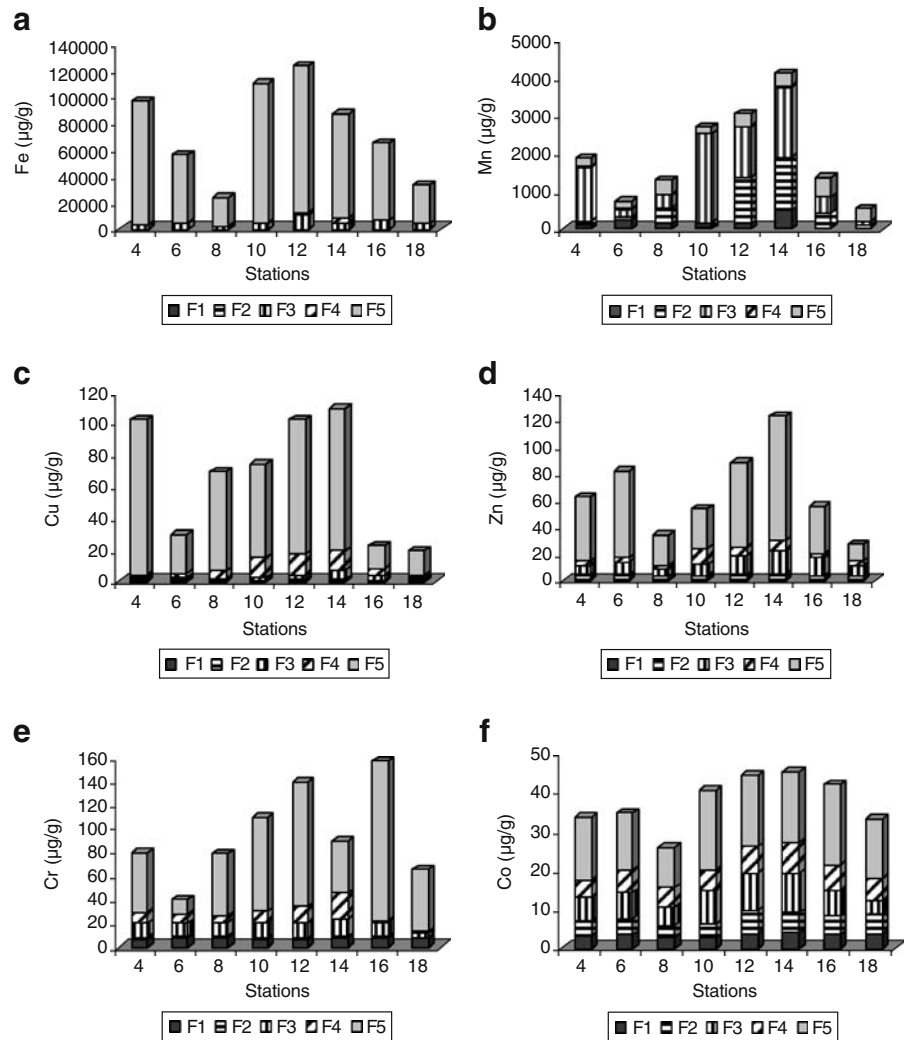
The distribution of different fractions of six metals viz. Fe, Mn, Cu, Zn, Cr and Co is diagrammatically represented (Figs. 3, 4 and 5).

Iron (Fe)

Major quantity of Fe is found to be associated with residual fraction and least with the exchangeable

fraction in all the three seasons (Figs. 3, 4 and 5a). The residual Fe ranges from 21,888–110,500 $\mu\text{g/g}$ (Avg. 68,442), 15,900–120,225 $\mu\text{g/g}$ (Avg. 68,368) and 27,775–98,513 $\mu\text{g/g}$ (Avg. 67,478) during monsoon, post-monsoon and pre-monsoon season respectively. Large amount of Fe is available in the residual fraction, probably because this is an element basically of natural origin and it is one of the most common elements in the earth's crust. The present results are in good agreement with the data reported by Usero et al. (1998) and Yuan et al. (2004). They found more than 89% of the total Fe in the residual fraction. Next to residual fraction, Fe is mainly bound to Fe–Mn oxides fraction, which ranges from 1,821–10,704 $\mu\text{g/g}$ (Avg. 4,936), 2,733–11,501 $\mu\text{g/g}$ (Avg. 5,927) and 3,860–9,660 $\mu\text{g/g}$ (Avg. 6,003) during three

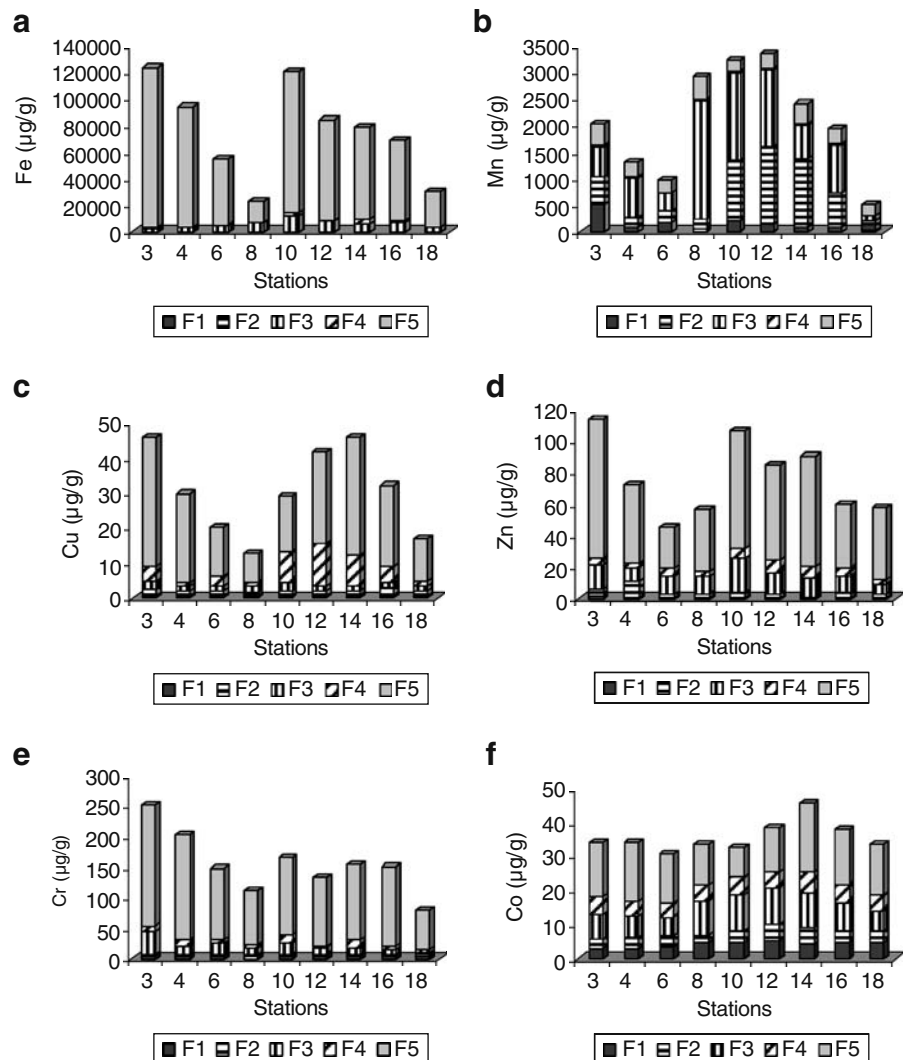
Fig. 3 Extractable contents of metals in surface sediments using Tessier sequential extraction protocol for monsoon season, **a** Fe, **b** Mn, **c** Cu, **d** Zn, **e** Cr, **f** Co where, *F1* exchangeable fraction, *F2* carbonate bound, *F3* Fe–Mn oxide, *F4* organic/sulfide bound, *F5* residual



seasons. Fe concentration in exchangeable fraction ranges from 1–10 $\mu\text{g/g}$ (Avg. 3), 1–4 $\mu\text{g/g}$ (Avg. 3) and 2–18 $\mu\text{g/g}$ (Avg. 8) during respective seasons. Organic bound Fe ($\mu\text{g/g}$) found to be comparatively higher during post-monsoon season (Avg. 1,077) followed by pre-monsoon (Avg. 1,047) and monsoon season (Avg. 984). Whereas, Fe in carbonate fraction was observed to be higher during post-monsoon season (Avg. 53 $\mu\text{g/g}$) followed by monsoon (Avg. 41 $\mu\text{g/g}$) and then pre-monsoon (Avg. 28 $\mu\text{g/g}$). In general, the distribution of exchangeable, carbonate bound and organic/sulfide bound Fe is less in the whole estuarine region in all the three seasons. Organic/sulfide bound Fe is comparatively higher in the

lower half of the estuary and at two stations in the upper estuary during pre-monsoon season. Residual Fe is observed to be higher in the extreme end of the upper estuary, further it decreases up to around station 8 and then again it shows increase in the lower estuary, which then decreases towards the mouth of the estuary in all the three seasons. Correlation between metals, sand, silt, clay and OC in five different fractions of surface sediments for three different seasons is presented in the tables (Tables 2, 3, 4). While describing the relations, “Significant” word is used for the values, which are statistically significant ($p < 0.05$) and are made bold in the tables and “Good” word is used for $p \leq 0.1$. During monsoon, cor-

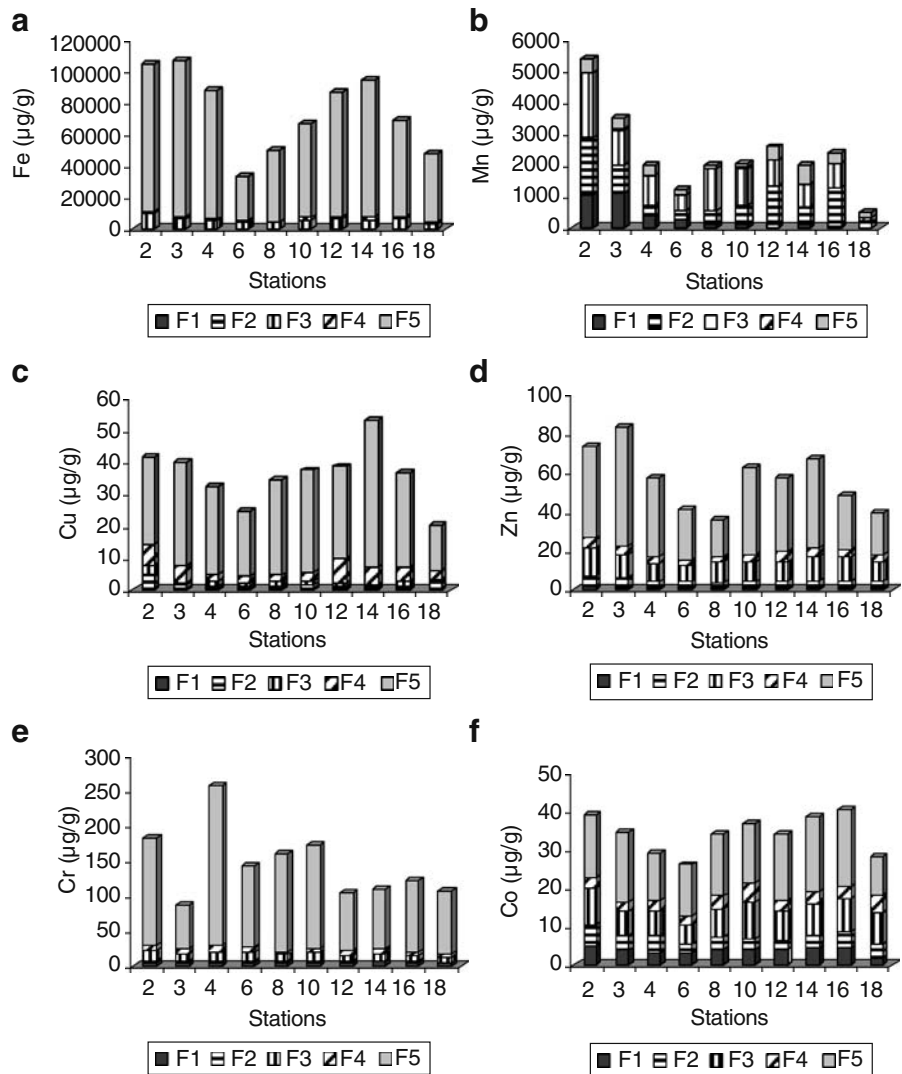
Fig. 4 Extractable contents of metals in surface sediments using Tessier sequential extraction protocol for post-monsoon season, **a** Fe, **b** Mn, **c** Cu, **d** Zn, **e** Cr, **f** Co where, *F1* exchangeable fraction, *F2* carbonate bound, *F3* Fe–Mn oxide, *F4* organic/sulfide bound, *F5* residual



relation obtained between different metals, sand, silt and clay in five fractions indicate good relationship of Fe with Mn, Cu, Co and significant relationship with clay and OC in exchangeable fraction (Table 2). Fe does not show any significant relationship with metals as well as with sand, silt and clay in carbonate bound fraction. It shows good relationship with Zn and Co in the Fe–Mn oxide fraction and, in organic/sulfide bound it shows significant relationship with Mn, Cr, Co, clay and organic carbon and also shows good relationship with Cu. Further it shows good relationship with Cu and Co in the residual fraction. In case of post-monsoon season, Fe does not show significant relationship with most of the

metals in the exchangeable as well as carbonate bound fractions but shows good relationship with Cr in exchangeable fraction and with Mn in carbonate fraction (Table 3). It shows significant relationship with Mn, Zn, Co and also good relationship with silt in Fe–Mn oxide bound. Fe exhibits significant relationship with Mn, Cu, Zn, Cr, Co, Clay and OC in organic/sulfide bound fraction. In residual fraction, it shows significant relationship with Cu, Zn and Cr. During pre-monsoon, Fe shows good relationship with Mn and Zn in the exchangeable fraction and significant relationship with Cu, Zn and Co and good relationship with Mn and Cr in carbonate fraction. In Fe–Mn oxide it exhibits significant relationship

Fig. 5 Extractable contents of metals in surface sediments using Tessier sequential extraction protocol for pre-monsoon season, **a** Fe, **b** Mn, **c** Cu, **d** Zn, **e** Cr, **f** Co where, F1 exchangeable fraction, F2 carbonate bound, F3 Fe–Mn oxide, F4 organic/sulfide bound, F5 residual



with Mn and Zn and also good relationship with Cu, Cr, Co and silt. It shows significant relationship with Mn, Cu, Zn, clay, OC and also with silt in organic bound/sulfide bound. With sand it shows significant negative relationship. While in the residual fraction it shows significant relationship with Mn and Zn and good relationship with Cu, Co, Clay and OC (Table 4). Strong relationship between iron and other elements can be due to the high adsorption capacity of its oxide as has been reported earlier by Algan et al. (2004) and Niencheski et al. (2002). The distribution of Fe in residual fraction during all the three seasons largely agrees with the total Fe metal content distribution in the surface sediments representing

higher concentration in the lower estuary between stations 10 to 14 and also in the upstream end of upper estuary. Further, its significant relationship obtained with finer sediments, organic matter and metals viz. Mn, Cr, Co, Cu and Zn during all the seasons in organic/sulfide fraction indicates their strong association in the sediments.

Manganese (Mn)

Significant amount of Mn is available in the bioavailable phases (exchangeable, carbonate bound and Fe–Mn oxide) in all the three seasons. The level of Mn is found to be higher in Fe–Mn oxide bound in case of all the three seasons

Table 2 Correlation between metals, sand, silt, clay and OC in different fractions of the surface sediments for monsoon season

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Exchangeable										
Fe	1.000									
Mn	0.655	1.000								
Cu	0.675	0.831	1.000							
Zn	0.122	0.362	0.056	1.000						
Cr	0.037	0.547	0.359	-0.240	1.000					
Co	0.567	0.439	0.326	0.147	0.342	1.000				
Sand	-0.681	-0.696	-0.408	-0.189	-0.476	-0.557	1.000			
Silt	0.340	0.286	0.008	0.040	0.382	0.530	-0.853	1.000		
Clay	0.820	0.898	0.679	0.279	0.435	0.463	-0.866	0.477	1.000	
OC	0.829	0.858	0.656	0.286	0.334	0.356	-0.827	0.420	0.989	1.000
Carbonate										
Fe	1.000									
Mn	-0.130	1.000								
Cu	0.279	0.559	1.000							
Zn	-0.163	0.910	0.495	1.000						
Cr	-0.220	-0.516	-0.178	-0.761	1.000					
Co	0.310	0.621	0.743	0.740	-0.659	1.000				
Sand	0.364	-0.782	-0.182	-0.893	0.668	-0.611	1.000			
Silt	-0.242	0.493	0.068	0.607	-0.453	0.580	-0.853	1.000		
Clay	-0.381	0.844	0.241	0.921	-0.689	0.473	-0.866	0.477	1.000	
OC	-0.367	0.841	0.237	0.886	-0.638	0.436	-0.827	0.420	0.989	1.000
Fe-Mn oxide										
Fe	1.000									
Mn	0.153	1.000								
Cu	0.219	0.436	1.000							
Zn	0.681	0.326	0.840	1.000						
Cr	0.200	0.652	0.509	0.502	1.000					
Co	0.525	0.748	0.629	0.745	0.816	1.000				
Sand	-0.390	-0.317	-0.969	-0.926	-0.496	-0.646	1.000			
Silt	0.427	0.041	0.796	0.789	0.305	0.339	-0.853	1.000		
Clay	0.248	0.493	0.869	0.802	0.543	0.762	-0.866	0.477	1.000	
OC	0.270	0.609	0.841	0.780	0.606	0.832	-0.827	0.420	0.989	1.000
Organic bound										
Fe	1.000									
Mn	0.967	1.000								
Cu	0.660	0.744	1.000							
Zn	0.439	0.508	0.851	1.000						
Cr	0.909	0.946	0.697	0.562	1.000					
Co	0.807	0.730	0.531	0.263	0.558	1.000				
Sand	-0.833	-0.783	-0.494	-0.315	-0.645	-0.941	1.000			
Silt	0.436	0.400	0.198	0.032	0.199	0.808	-0.853	1.000		
Clay	0.984	0.935	0.641	0.498	0.894	0.809	-0.866	0.477	1.000	
OC	0.973	0.955	0.725	0.602	0.933	0.759	-0.827	0.420	0.989	1.000

which ranges from 89–2,333 µg/g (Avg. 996), 96–2,223 µg/g (Avg. 953) and 119–2,064 µg/g (Avg. 959) during monsoon, post-monsoon and pre-monsoon respectively. The next important phase

is the carbonate bound where Mn ranges from 84–1,410 µg/g (Avg. 485) during monsoon, 167–1,434 µg/g (Avg. 639) during post-monsoon and 183–1,799 µg/g (Avg. 749) during pre-monsoon

Table 2 (continued)

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Residual										
Fe	1.000									
Mn	-0.409	1.000								
Cu	0.615	-0.312	1.000							
Zn	0.446	-0.176	0.497	1.000						
Cr	0.310	0.622	-0.112	-0.230	1.000					
Co	0.688	0.056	0.012	0.262	0.621	1.000				
Sand	-0.257	-0.357	-0.192	-0.723	-0.237	-0.551	1.000			
Silt	0.106	0.661	-0.149	0.399	0.552	0.636	-0.853	1.000		
Clay	0.330	-0.031	0.465	0.834	-0.129	0.318	-0.866	0.477	1.000	
OC	0.442	-0.107	0.546	0.821	-0.095	0.364	-0.827	0.420	0.989	1.000

Bold figures are statistically significant at $p < 0.05$

Table 3 Correlation between metals, sand, silt, clay and OC in different fractions of the surface sediments for post-monsoon season

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Exchangeable										
Fe	1.000									
Mn	-0.363	1.000								
Cu	0.018	0.156	1.000							
Zn	-0.316	0.899	-0.216	1.000						
Cr	0.477	0.268	-0.240	0.418	1.000					
Co	0.357	-0.527	0.230	-0.685	-0.459	1.000				
Sand	-0.044	0.135	-0.809	0.480	0.380	-0.560	1.000			
Silt	-0.016	0.353	0.323	0.071	0.055	0.356	-0.536	1.000		
Clay	0.053	-0.248	0.817	-0.557	-0.441	0.529	-0.973	0.326	1.000	
OC	-0.169	0.250	0.805	-0.095	-0.179	0.217	-0.900	0.642	0.832	1.000
Carbonate										
Fe	1.000									
Mn	0.511	1.000								
Cu	-0.198	-0.232	1.000							
Zn	-0.315	-0.438	0.041	1.000						
Cr	0.437	-0.068	0.085	-0.254	1.000					
Co	0.371	0.781	-0.277	-0.221	0.230	1.000				
Sand	-0.353	-0.856	0.016	0.576	-0.195	-0.826	1.000			
Silt	0.401	0.821	-0.404	-0.429	-0.156	0.549	-0.536	1.000		
Clay	0.285	0.733	0.092	-0.527	-0.261	0.774	-0.973	0.326	1.000	
OC	0.361	0.864	-0.019	-0.415	-0.019	0.741	-0.900	0.642	0.832	1.000
Fe–Mn oxide										
Fe	1.000									
Mn	0.690	1.000								
Cu	0.329	0.399	1.000							
Zn	0.703	0.439	0.789	1.000						
Cr	-0.202	-0.088	0.732	0.534	1.000					
Co	0.770	0.762	0.409	0.585	-0.092	1.000				
Sand	-0.362	0.047	0.125	-0.191	0.285	-0.577	1.000			
Silt	0.575	0.435	0.368	0.677	0.248	0.744	-0.536	1.000		
Clay	0.248	-0.172	-0.241	0.029	-0.387	0.442	-0.973	0.326	1.000	
OC	0.248	-0.069	0.135	0.383	0.128	0.556	-0.900	0.642	0.832	1.000

Table 3 (continued)

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Organic bound										
Fe	1.000									
Mn	0.847	1.000								
Cu	0.682	0.544	1.000							
Zn	0.717	0.555	0.948	1.000						
Cr	0.713	0.672	0.276	0.199	1.000					
Co	0.846	0.820	0.532	0.568	0.502	1.000				
Sand	-0.691	-0.578	-0.809	-0.846	-0.153	-0.806	1.000			
Silt	0.395	0.358	0.875	0.817	0.103	0.191	-0.536	1.000		
Clay	0.665	0.550	0.666	0.724	0.143	0.850	-0.973	0.326	1.000	
OC	0.684	0.624	0.824	0.809	0.369	0.764	-0.900	0.642	0.832	1.000
Residual										
Fe	1.000									
Mn	-0.078	1.000								
Cu	0.713	0.282	1.000							
Zn	0.775	0.249	0.688	1.000						
Cr	0.834	0.236	0.739	0.534	1.000					
Co	0.022	0.234	0.615	0.037	0.293	1.000				
Sand	-0.105	-0.019	-0.475	-0.311	0.156	-0.325	1.000			
Silt	0.372	0.097	0.291	0.471	0.053	-0.370	-0.536	1.000		
Clay	0.015	-0.006	0.452	0.219	-0.189	0.465	-0.973	0.326	1.000	
OC	0.434	0.191	0.751	0.557	0.242	0.379	-0.900	0.642	0.832	1.000

Bold figures are statistically significant at $p < 0.05$

Table 4 Correlation between metals, sand, silt, clay and OC in different fractions of the surface sediments for pre-monsoon season

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Exchangeable										
Fe	1.000									
Mn	0.514	1.000								
Cu	-0.389	-0.576	1.000							
Zn	0.543	0.828	-0.240	1.000						
Cr	-0.030	-0.185	0.521	-0.021	1.000					
Co	0.363	0.274	0.417	0.622	0.522	1.000				
Sand	0.129	-0.051	-0.146	-0.191	-0.589	-0.448	1.000			
Silt	0.066	0.141	-0.128	0.397	0.273	0.324	-0.793	1.000		
Clay	-0.233	-0.022	0.299	0.006	0.669	0.428	-0.910	0.469	1.000	
OC	0.128	-0.003	0.169	0.162	0.496	0.529	-0.801	0.534	0.789	1.000
Carbonate										
Fe	1.000									
Mn	0.626	1.000								
Cu	0.954	0.509	1.000							
Zn	0.797	0.621	0.753	1.000						
Cr	0.616	0.701	0.512	0.831	1.000					
Co	0.780	0.487	0.724	0.676	0.473	1.000				
Sand	-0.220	-0.434	-0.174	-0.342	-0.207	-0.211	1.000			
Silt	0.442	0.664	0.489	0.558	0.373	0.425	-0.793	1.000		
Clay	0.017	0.176	-0.081	0.115	0.046	0.016	-0.910	0.469	1.000	
OC	-0.208	0.274	-0.291	0.144	0.228	0.013	-0.801	0.534	0.789	1.000

Table 4 (continued)

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe–Mn oxide										
Fe	1.000									
Mn	0.769	1.000								
Cu	0.565	0.481	1.000							
Zn	0.836	0.671	0.535	1.000						
Cr	0.484	0.580	0.223	0.124	1.000					
Co	0.501	0.427	0.422	0.631	−0.049	1.000				
Sand	−0.485	−0.095	−0.174	−0.714	0.168	−0.467	1.000			
Silt	0.553	0.089	0.489	0.719	−0.366	0.559	−0.793	1.000		
Clay	0.326	0.076	−0.081	0.545	0.005	0.297	−0.910	0.469	1.000	
OC	0.271	−0.056	−0.291	0.542	−0.244	0.189	−0.801	0.534	0.789	1.000
Organic bound										
Fe	1.000									
Mn	0.686	1.000								
Cu	0.759	0.781	1.000							
Zn	0.721	0.688	0.929	1.000						
Cr	0.188	0.389	0.245	0.292	1.000					
Co	−0.007	−0.425	−0.329	−0.150	−0.564	1.000				
Sand	−0.850	−0.436	−0.652	−0.708	−0.406	0.066	1.000			
Silt	0.629	0.368	0.714	0.747	0.323	−0.039	−0.793	1.000		
Clay	0.805	0.382	0.459	0.518	0.368	−0.069	−0.910	0.469	1.000	
OC	0.767	0.306	0.499	0.509	0.260	−0.170	−0.801	0.534	0.789	1.000
Residual										
Fe	1.000									
Mn	0.759	1.000								
Cu	0.574	0.601	1.000							
Zn	0.843	0.522	0.530	1.000						
Cr	−0.010	−0.216	−0.114	−0.069	1.000					
Co	0.475	0.525	0.776	0.380	−0.413	1.000				
Sand	−0.519	−0.887	−0.582	−0.314	0.294	−0.521	1.000			
Silt	0.422	0.677	0.120	0.122	−0.366	0.373	−0.793	1.000		
Clay	0.465	0.825	0.762	0.372	−0.177	0.502	−0.910	0.469	1.000	
OC	0.482	0.740	0.775	0.388	−0.427	0.784	−0.801	0.534	0.789	1.000

Bold figures are statistically significant at $p < 0.05$

season. The higher level of Mn in this fraction is most likely due to the similarity in ionic radii to that of calcium which allows them to substitute for Ca in carbonate phase (Pedersen and Price 1982; Zhang et al. 1988). Significant amount of Mn is also available in the exchangeable fraction especially during pre-monsoon season, which ranges from 25–1,122 µg/g (Avg. 343). Tessier et al. (1979) and Jingchun et al. (2006) have reported elsewhere, high concentration of exchangeable Mn in sediments. Heavy metal concentration in the exchangeable fraction is known to play important role in the evaluation of environment and act as a pollution indicator (Forstner and Wittmann

1979) for its environmental mobility and bioavailability. Also, Hseu (2006) stated that metals associated with the two fractions i.e. exchangeable and carbonate bound are more labile and readily leachable or bioavailable. Comparatively less concentration of Mn (Avg. 17 µg/g) is available in the organic/sulfide bound fraction, which ranges from 3–49 µg/g, 4–33 µg/g and 6–31 µg/g during monsoon, post-monsoon and pre-monsoon respectively, can be due to weak affinity of Mn for organics (Bendell-Young and Harvey 1992). The average concentration of Mn in the residual phase is 316 µg/g during monsoon, 308 µg/g during post-monsoon and 295 µg/g during pre-monsoon

season. The higher concentration of Mn in the non-residual phase can be directly related to the input from anthropogenic activities like mining carried out in the catchment area of Zuari estuary. During monsoon higher concentration of Mn is observed in the lower half of the estuary with decreasing trend towards the mouth in case of all the fractions. While during other seasons, in general higher concentrations were observed in the upstream end and also in the lower half of the estuary with decreasing trend towards the mouth. Mn exhibits significant relationship with Cu, clay and OC in the exchangeable fraction and also it shows good relationship with Cr during monsoon season (Table 2). In carbonate fraction it shows significant relationship with Zn, clay and OC and also shows good relationship with Cu, Co and silt in the same fraction. It shows significant relationship with Co, and good relationship with Cr, OC and clay in Fe–Mn oxide bound and shows significant relationship with Cu, Cr, Co, clay and OC and also shows good relationship with Zn in organic bound fraction. It exhibits good relationship with Cr and silt in residual fraction in the same season. In case of post-monsoon, Mn shows significant relationship with Zn in the exchangeable fraction and with Co, silt, clay and OC in the carbonate bound phase (Table 3). Sand shows significant negative relation with Mn in this fraction. In Fe–Mn oxide phase, Mn shows significant relation with Co and in organic/sulfide bound with Cr and Co and also shows good relationship with Cu, Zn, clay and OC. In residual fraction it does not show any significant relationship with metals and also with sand, silt and clay. During pre-monsoon, it shows significant relationship with Zn in exchangeable fraction and with Cr and silt in carbonate fraction. Also it shows good relationship with Cu, Zn and Co in the carbonate fraction. It shows significant relationship with Zn and good relationship with Cu and Cr in Fe–Mn oxide phase. In organic/sulfide bound fraction it exhibits significant relationship with Cu and Zn. In case of residual fraction it exhibits significant relationship with silt, clay and OC and also good relationship with Cu, Zn and Co indicating their association (Table 4).

Distribution and association of Mn in different seasons indicates that it is predominantly available in bioavailable fractions.

Copper (Cu)

Substantial amount of Cu is present in the residual fraction, which ranges from 14–98 $\mu\text{g/g}$ (Avg. 56) during monsoon, 8–37 $\mu\text{g/g}$ (Avg. 22) during post-monsoon and from 14–45 $\mu\text{g/g}$ (Avg. 28) during pre-monsoon season. The higher concentration of Cu in the residual fraction is due to natural sources such as weathering of rocks and decomposition of biota detritus (Badri and Aston 1983). Next to residual fraction, Cu is associated with organic/sulfide bound fraction, which varies from 1–14 $\mu\text{g/g}$ (Avg. 7), 1–12 $\mu\text{g/g}$ (Avg. 5) and 2–7 $\mu\text{g/g}$ (Avg. 4) during monsoon, post-monsoon and pre-monsoon season. Cu forms highly stable complexes with the organics matter/sulfide (Li et al. 2001). Cu bound to other three fractions is comparatively low which can be seen from the figures (Figs. 2, 3 and 4c). The average concentration of Cu in the exchangeable and carbonate bound fraction is around 1 $\mu\text{g/g}$ during all the three seasons while in case of Fe–Mn bound Cu varies from 1–6 ($\mu\text{g/g}$), 1–3 ($\mu\text{g/g}$) and 0–3 ($\mu\text{g/g}$) in the respective seasons. Organic/sulfide and also exchangeable bound Cu is observed to be higher in the lower half of the estuary. Distribution of Cu in the residual fraction is similar to that of Fe in same fraction. Cu does not show any significant relationship with metals in exchangeable fraction during monsoon season (Table 2) but shows good relationship with Fe, clay and OC. Correlation analysis indicated significant relation of Cu in carbonate fraction with Co and also good relationship with Zn in the same season. In case of Fe–Mn oxide fraction, it shows significant relationship with Zn, silt, clay and OC and also good relationship with Cr and Co. It shows significant negative relationship with sand in the same fraction. In organic/sulfide bound, Cu exhibits significant relationship Mn, Zn and OC and also good relationship with Fe, Cr, Co and clay, while in case of residual fraction it shows good relationship with Fe, Zn, OC and also to some extent with clay in the same season. In case of post-monsoon, also Cu does not show significant relationship with metals in the exchangeable fraction as well as in carbonate fraction however, it exhibits significant relationship with Zn and Cr in Fe–Mn oxides fraction and with Fe, Zn, silt, clay and OC in organic/

sulfide bound (Table 3). In the residual fraction it shows significant relationship with Fe, Zn, Cr and OC. It exhibits good relationship with Co in organic bound and in residual fraction. During pre-monsoon, Cu shows good relationship with Cr in the exchangeable fraction. It exhibits significant relationship with Fe, Zn and Co and also good relationship with Cr and Mn in carbonate fraction. Cu shows good relationship with Fe, Mn, Zn and silt in the Fe–Mn bound whereas in organic/sulfide bound it exhibits significant relationship with Fe, Mn, Zn and silt and good relationship with clay and OC. In the residual fraction Cu shows significant relationship with Co, clay and OC and also it shows good relationship with Fe, Mn and Zn (Table 4).

The distribution of Cu and significant relationship obtained indicated that similar to Fe, Cu is also associated with finer sediments, organic matter and metals in residual and organic/sulfide bound fractions.

Zinc (Zn)

Like Fe and Cu, significant amount of Zn is also available in the residual fraction, which varies from 13–93 $\mu\text{g/g}$ (Avg. 46) during monsoon, 26–89 $\mu\text{g/g}$ (Avg. 55) during post-monsoon and 18–61 $\mu\text{g/g}$ (Avg. 37) pre-monsoon seasons and least quantity in the exchangeable fraction (Avg. 1 $\mu\text{g/g}$) which varies from 0–1 $\mu\text{g/g}$ during monsoon and 0–2 $\mu\text{g/g}$ in both during post-monsoon and pre-monsoon. The low concentration of Zn is probably due the fact that metals in this form can easily be absorbed and utilized by organisms in the aquatic environment (Campbell 1995). Similar results have been reported by Pizarro et al. (2003). Among the non-residual fractions the Fe–Mn oxide phase was much more important than the other fractions in which the concentration of Zn ranges from 5–17 $\mu\text{g/g}$ (Avg. 10), 6–22 $\mu\text{g/g}$ (Avg. 12) and 9–15 $\mu\text{g/g}$ (Avg. 11) during monsoon, post-monsoon and pre-monsoon respectively. The association of Zn with the Fe and Mn oxides of soils and sediments has been widely recognized by Kuo et al. (1983) and Gonzalez et al. (1994) showing that the Zn adsorption onto these oxides has high stability constants. The availability of Zn in different fractions in Zuari

sediments is in the following ascending order exchangeable < carbonate < organic/sulfide bound < Fe–Mn oxide < residual in case of all the three seasons. In organic bound fraction, Zn content varies from 3–12 $\mu\text{g/g}$ (Avg. 5), 2–8 $\mu\text{g/g}$ (Avg. 5) and 2–5 $\mu\text{g/g}$ (Avg. 4) during monsoon, post-monsoon and pre-monsoon respectively where as in carbonate bound it varies from 3–4 $\mu\text{g/g}$ (Avg. 3), 1–11 $\mu\text{g/g}$ (Avg. 4) and 3–5 $\mu\text{g/g}$ (Avg. 4) during respective seasons. Results obtain indicate that Zn has higher potentials for mobilization from the sediments than Cu because of its higher concentration in the Fe–Mn oxide fraction in all the three seasons. Zn is observed to be comparatively less in the exchangeable fraction than in the rest of the fractions. Exchangeable Zn is observed to be higher in the upstream end of the estuary in all the three seasons. During monsoon, carbonate (Stn. 12 and 14), Fe–Mn oxide bound (Stn. 12, 14 and 16), organic bound (Stn. 10, 12 and 14) and residual Zn (Stn. 12 and 14) is observed to be higher in the lower half of the estuary with decreasing trend towards the mouth with minor variations. In case of other two seasons the distribution of Zn in the first three fractions are almost similar with some variations with relatively higher concentrations in the upstream and at station 10 in case of post-monsoon in Fe–Mn oxide fraction. Organic/sulfide bound Zn is observed to be comparatively higher in the lower half of the estuary in all the three seasons and residual follows largely trend of Fe and Cu in all the seasons.

Chromium (Cr)

In general, residual fraction is the main carrier for Cr in all the three seasons in which Cr content varies from 12–134 $\mu\text{g/g}$ (Avg. 66), 63–198 $\mu\text{g/g}$ (Avg. 125) and 63–228 $\mu\text{g/g}$ (Avg. 121) respectively during monsoon, post-monsoon and pre-monsoon, followed by Fe–Mn oxide bound which varies from 4–15 $\mu\text{g/g}$ (Avg. 12) during monsoon, 4–37 $\mu\text{g/g}$ (Avg. 15) during post-monsoon and 6–14 $\mu\text{g/g}$ (Avg. 11) during pre-monsoon. The association of Cr in Fe–Mn hydroxide phase may be result of the insoluble Cr^{+3} hydroxide (Eary and Rai 1988; Morel 1983), which eventually is incorporated into Fe–Mn matrix during precipitation and as Fe containing Mn phase of the

particle provide more surface sites for Cr to be adsorbed (Sager 1992). The next important phases are organic/sulfide bound and exchangeable. The Cr ($\mu\text{g/g}$) content varies from 1–22 (Avg. 9), 2–14 (Avg. 7) and 3–10 (Avg. 6) in organic bound and from 6–9 (Avg. 7), 5.8–6.4 (Avg. 6) and 5–6 (Avg. 6) in exchangeable fraction during monsoon, post-monsoon and pre-monsoon respectively. Comparatively less percentage of Cr ($\mu\text{g/g}$) is available in the carbonate fraction viz. monsoon (avg.1), post-monsoon (avg. 3) and pre-monsoon (avg. 2) the same is presented in figures (Figs. 2, 3 and 4e). In general, the distribution of Cr in the different five fractions follows the following order, carbonate < exchangeable < organic/sulfide bound < Fe–Mn oxide < residual. Cr content in the different fractions, in general showed higher content in the upper estuarine region and also between stations 10 to 16 then further downward it shows decreasing trend towards the mouth with few exceptions.

Cobalt (Co)

Significant amount of Co is available in the bioavailable phases even though individually, residual fraction accounts more amount of Co. During monsoon Co concentration ranges from 3–4 $\mu\text{g/g}$ (Avg. 3), 3–6 $\mu\text{g/g}$ (Avg. 4), 3–10 $\mu\text{g/g}$ (Avg. 7), 5–8 $\mu\text{g/g}$ (Avg. 6), 10–20 $\mu\text{g/g}$ (Avg. 17) in exchangeable, carbonate, Fe–Mn oxide, organic bound and residual phase respectively. While, in case of post-monsoon, it ranges from 3–5 $\mu\text{g/g}$ (Avg. 4), 2–5 $\mu\text{g/g}$ (Avg. 3), 6–11 $\mu\text{g/g}$ (Avg. 8), 4–6 $\mu\text{g/g}$ (Avg. 5) and 9–20 $\mu\text{g/g}$ (Avg. 15) in the respective fractions. During pre-monsoon,

Co ($\mu\text{g/g}$) ranges from 2–5 (Avg. 4), 2–6 (Avg. 4), 5–10 (Avg. 8), 2–5 (Avg. 3) and 10–20 (Avg. 16) in the same fractions. Next to residual fraction, important phase is the Fe–Mn oxide phase (similar observations were made by Calmano and Forstner 1983; Jones and Turki 1997). During monsoon and post-monsoon, exchangeable and carbonate bound Co shows increase towards the downstream region. Comparatively higher amounts of carbonate bound, Fe–Mn oxide and to some extent the residual bound Co is observed in the lower half of the estuary in all the three seasons.

The residual fraction is the main carrier of most of the studied metals most importantly for Fe and Cu, which comprises detrital silicate, resistant sulfides and refractory organics (Tessier et al. 1979). Metals in this phase mostly remain stable and do not react during sedimentation and diagenesis, and therefore have less potential bioavailability. This phase could be considered as inert phase corresponding to the part of metal that cannot be mobilized and as the geochemical background values for the elements in the sediments (Tessier et al. 1979). While Mn and also Co was found to be relatively higher in the bioavailable fractions.

In order to understand the risk of the studied metals to the sediment dwelling organisms, the data set of both the total metals in sediment and metals in the bioavailable fractions (sum of first four fractions) Table 5 were compared with sediment quality values (SQV) using SQUIRT (screening quick reference table) Table 6. SQUIRT was developed by NOAA for screening purposes. Based on SQUIRT, the guideline values are categorized into five classes which are presented in the Table 7 (Buchman 1999). The implication of SQV is to achieve the

Table 5 Average concentrations of total metals and bioavailable fractions in the three different seasons

	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon
	Total metals			Sum of bioavailable fractions		
Fe (%)	8.36	7.61	8.72	5,964.41	7,059.42	7,086.62
Mn	3,069.17	2,936.72	3,099.31	1,640.14	1,769.45	2,067.64
Cu	96.88	34.34	44.78	10.20	8.86	7.20
Zn	90.18	101.95	70.39	19.64	21.58	19.59
Cr	113.47	178.89	267.43	28.98	30.46	24.06
Co	52.60	39.14	53.46	20.63	20.91	18.23

Except for Fe in total metals, all values are in $\mu\text{g/g}$

Table 6 Screening quick reference table for metals in marine sediments (Buchman 1999)

Elements	Threshold effect level (TEL)	Effects range low (ERL)	Probable effects level (PEL)	Effects range median (ERM)	Apparent effects threshold (AET)
Fe	–	–	–	–	22% (Neanthes)
Mn	–	–	–	–	260 (Neanthes)
Cu	18.7	34	108	270	390 (Microtox and Oyster Larvey)
Zn	124	150	271	410	410 (Infaunal community)
Cr	52.3	81	160	370	62 (Neanthes)
Co	–	–	–	–	10 (Neanthes)

Except for Fe, all values are in µg/g

information on toxicity of metals to the biota and thus to understand the impact on environment. The total Cu fall under effects range low (ERL) to probable effect level (PEL) but the sum of the bioavailable fractions fall below threshold effect level (TEL) indicating no harm to the aquatic life. The values of total Zn itself are below TEL suggesting no risk to biota while total Cr values are nearer to PEL. However sum of the bioavailable fractions fall below TEL level indicating no potential bioavailability of this element. The percentage of Fe is also very low compared to apparent effect threshold (AET) indicating no harm and also it was observed to be maximum in the residual fractions in all the three seasons. There are no reported values for Mn and Co for first three classes but the values of both these metals exceeds the AET suggesting these two elements are potentially bioavailable and thus indicating their toxicity to environment.

Fe–Mn oxide phase (reducible phase) consists of hydrous oxides of Fe (III) and Mn (IV) (Tessier et al. 1979; Kersten and Forstner 1989) and is the major metal host in the estuarine sediments (Calmano and Forstner 1983). This fraction along with exchangeable and carbonate fractions is an

important bioavailable metal source (Luoma and Davis 1983). Diagenesis is a common process, which occurs in the estuarine environment. The higher concentration of Fe and Mn along with Cr, Zn, Co and Cu is observed in the surface sediments of Zuari estuary in the Fe–Mn oxide bound is largely controlled by the process of diagenesis. During early diagenesis, microbial mediated redox reactions quickly result in the reduction of insoluble Fe (III) and Mn (IV) oxides and release of Fe (II) and Mn (II) species to pore water (Canfield 1989). Dissolution results in release of metals associated with the oxide phases to the pore water and also to some extent possibly to the overlying water (Petersen et al. 1995) and hence to the surface sediments. Higher concentration of Mn is observed in this phase is because of upward diagenetic mobilization from reducibly bound metals of near surface sediments. Further, metals originally bound to oxide phases may initially transferred into monosulfides, but eventually be fixed as pyrites as sulphidization progresses and the efficiency with which this transfer occurs differs significantly between metals (Huerta-Diaz and Morse 1992). When the sulphidization of iron minerals is complete, pyrite will be the

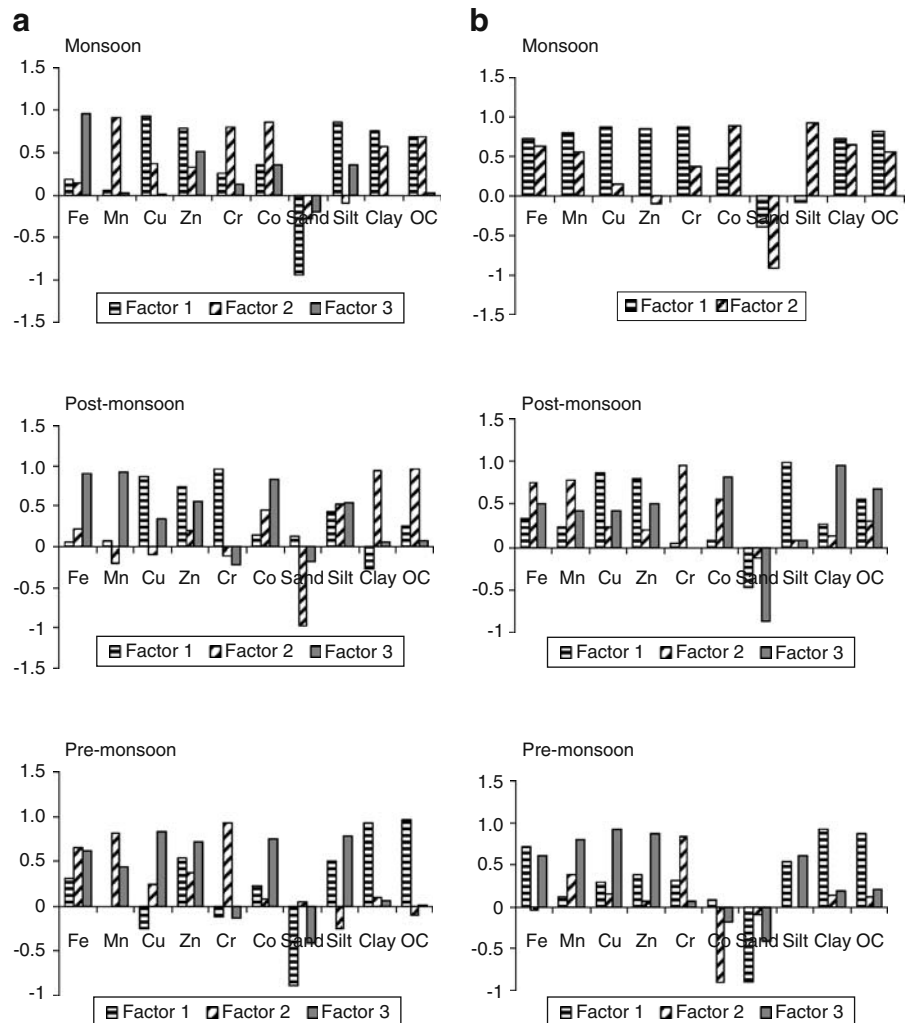
Table 7 Sediment guidelines and terms used in SQUIRT

Sediment guidelines	
Threshold effect level (TEL)	Maximum concentration at which no toxic effects are observed
Effects range low (ERL)	10th percentile values in effects or toxicity may begin to be observed in sensitive species
Probable effects level (PEL)	Lower limit of concentrations at which toxic effects are observed
Effects range median (ERM)	50th percentile value in effects
Apparent effects threshold (AET)	Concentration above which adverse biological impacts are observed

dominant host for metals. As long as the conditions within the sediment remain reducing, these pyrite bound metals will be unavailable for further reaction or uptake by biota. Cr and Zn, which are in significant amount in the present study, are comparatively less in organic/sulfide phase indicating that they likely to remain in more labile phase throughout early diagenesis, or to be lost from sediment (Huerta-Diaz and Morse 1992). Similar observations were reported earlier in the Tees estuary (Jones and Turki 1997). The oxidisable fraction is mainly dominated by Cu following residual fraction indicating its association with organic/sulfide fraction. The affinity of Cu to organic substances is well known. Under oxidizing condition significant amount of Cu reaching

to the surface sediment can be transferred into the overlying water column and some must be reaching to the upper sediment layer (Petersen et al. 1995). A small amount of Zn can also be remobilized for the same reason (Petersen et al. 1995). Further mobilization of Cr, Zn, Co, Cu may occur due to microbial oxidation of organic substrate. However most of the Cu and some of Cr and Zn is mainly fixed as pyrite (Huerta-Diaz and Morse 1992) and remain immobilized as long as the sediments remain reducing. But processes such as mixing of sediment with oxygenated layer, materials dredged from the river channel may enhance oxidative degradation of organic matter, which would have lead to mobilization of Cr, Zn, Co and to lesser extent Cu in the present study.

Fig. 6 R-mode factor analysis for Fe–Mn oxide (a) and organic/sulfide bound (b) fractions of surface sediments of Zuari estuary in the different seasons



Factor analysis

Varimax R-mode factor analysis for eigen value above 1 by using principal components extraction method was attempted for organic/sulfide bound and Fe–Mn oxide fraction to identify common sedimentological and geochemical characteristic of the original data as these two fractions are important carriers of metals. Factor analysis extracted two/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, which are presented in the Fig. 6. Factor analysis indicated that in case of Fe–Mn oxide fraction, most of the metals are associated with the finer sediments, organic matter, Fe and Mn indicating their role in the distribution of metals in the estuarine system. Also in case of organic/sulfide fraction, most of the metals are associated with the finer sediments and relatively strong associations are seen in case of monsoon season. This is also supported by the correlation analysis.

Conclusions

Sequential extraction procedure proposed by Tessier et al. (1979) used in the present study has helped in providing information about chemical association of metals in the sediments including their mobility, bioavailability, diagenesis and toxicity. Residual phase is the main carrier for Fe, Cu Zn and also to some extent for Cr indicating locked nature of these metals. The significant amount of metals in the residual fraction also point to weathering effect. The next important phase for these elements is the Fe–Mn oxide except for Cu for which it is organic bound phase. Mn and also Co were observed to be relatively higher in the bioavailable phases. Mn is relatively higher in the Fe–Mn oxide and carbonate bound fraction while Co is dominating in the residual but is also observed to be higher in the bioavailable phases.

It is evident from the present study that, the surface sediments of Zuari estuary are largely polluted by Mn, which is then followed by Co and least with Cu, Zn, Cr and Fe in all the three seasons studied. The data of metals compared

with the SQV from SQUIRT indicated low risk of Cu, Zn, Cr and Fe to the benthic dwelling organisms while Mn and Co are potentially available to the aquatic life. The main source of these metals in the Zuari estuary is mining and its associated activities such as transportation of ore to the platforms, ore loading and barge building. Other anthropogenic activities such as sewage outfall, agricultural practices, coastal construction and indiscriminate waste dumping are also sources of pollution. Relatively higher concentrations of metals are observed in the upper as well in the lower half of the estuary. Concentration of metals in the lower estuarine region indicates presence of favourable condition with reference to the presence of higher finer sediments and organic matter in this region. Elemental distribution and concentration are further guided by the processes within the estuary.

Factor analysis has helped in identifying associations of different elements in the Fe–Mn oxide phase and organic bound. The strong association of metals in these phases indicates that both organic bound and Fe–Mn oxide phases are the main carriers of the studied metals.

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