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ORIGINAL ARTICLE

Chemical speciation and bio-availability of selected trace metals in the mudflat core sediments of the tropical estuaries, India

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Abstract Mudflat core sediments collected from the middle region of Mandovi and Sharavathi estuaries, India, were analysed for grain size, organic carbon and bulk metals. Further, speciation of Fe, Mn, Ni, Co and Cr was carried out to understand mobilization, bio-availability and their toxicity, and risk to biota was assessed using sediment quality values (SQV) and risk assessment code (RAC). The analysis showed deposition of relatively high finer sediments and organic carbon in the Mandovi estuary, which facilitated adsorption of Fe, Mn, Co and Cr in the bulk sediments. Speciation analysis revealed mobilization of Mn and Co in Fe–Mn oxide and/or organic phases in the studied estuaries. The high concentration of Mn and Co in one or more bio-available phases towards the surface suggested their bio-availability in both the estuaries. SQV revealed concern from Mn, while the RAC indicated medium degree of risk from Mn and Co to the biota in the studied estuaries.

Keywords Estuarine environment · Mud flats · Trace metals · Speciation · Mobilization · Bio-availability

Introduction

Estuarine mudflat sediments are known as a sink for metals (Feng et al. 2004) that are introduced as a result of natural processes as well as from pollutants released by human induced activities (Jordao et al. 2002). The rapidly

expanding human settlements, tourism activity, deforestation, intense fishing, and agricultural, mining, industrial and aqua-cultural activities have increased metal input to estuaries (Wolanski 2007) in the recent years, leading to the degradation of mudflat environment. The study of metals in the estuarine mudflat sediments has therefore become one of the important areas of environmental research (Chakraborty et al. 2012). The total metal content in sediments provides information about the spatial extent (Martin et al. 2012); however, it may not be able to provide a mechanism and abundance of the metal loadings and their mobility, bio-availability and toxicity with changing environmental conditions (Clozel et al. 2006). It is in fact the mineralogical and chemical forms of the metals, namely exchangeable ions, metal carbonates, oxides, sulphides, organometallic compounds, ions in the crystal lattices of minerals in which they occur (Baeyens et al. 2003) that determine the potential bio-availability and toxicity. Each chemical form of a particular metal has considerable impact on the ecosystem (Tessier et al. 1979). The chemical state of elements is strongly influenced by sediment grain size, organic matter content, salinity, pH and Eh which undergo frequent change due to the natural dynamics of estuaries (Choueri et al. 2009). Anthropogenic input further alters the prevailing environmental conditions with respect to pH, redox potential, organic matter (Kumar and Ramanathan 2015). Further, physical, chemical and biological processes, groundwater discharge, continuous mixing of waters and diffusion of trace metals from sediments into the water column are likely to take place (Silva Filho et al. 2010; Sanders et al. 2012) which in turn make metals bio-available to the biota. Trace metals released from the sediment into the environment may have adverse impacts on living organisms (Delgado et al. 2011). The study of speciation of trace metals from the mudflat

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sediments is therefore essential as it may continue to release trace metals into estuarine waters even after the cessation of inputs from effluent sources.

Using the sequential extraction procedure, it is possible to identify a number of fractions: exchangeable, carbonates, Fe/Mn oxides, organic/sulphide and residual (Tessier et al. 1984). The non-residual, including exchangeable, carbonate, reducible and oxidizable, is considered to be mobile and environmentally reactive fraction with respect to geological and chemical processes (Hseu 2006) as the metals associated with this fraction have an anthropogenic origin (Sundaray et al. 2011). In contrast, the residual fraction is usually considered to be immobile or environmentally unreactive (Chakraborty et al. 2015). Speciation of metals therefore not only helps in identifying the degree of association of metals in different sediment fractions, but also distinguishes the origin (lithogenic or anthropogenic) of trace metals in the environment (Kumar and Ramanathan 2015). Most of the existing studies on trace metals within the mudflat sediments of the Mandovi and Sharavathi estuaries (Alagarsamy 2006; Siraswar and Nayak 2011; Nasnodkar and Nayak 2015; Fernandes and Nayak 2015) give an account of total metal concentration, and there is a need to study the vertical sediment profile of speciation of trace metals to understand the mobilization and possible bio-availability of metals. The present study on the speciation and mobility of selected trace metals (Fe, Mn, Ni, Co and Cr) in the core sediments thus provides information on the bio-availability and the risk they pose to the Mandovi and Sharavathi estuarine ecosystems.

Study area

The Mandovi and Sharavathi Rivers originate in the Western Ghats and drain into the Arabian Sea along central west coast of India. The Mandovi and Sharavathi Rivers receive an annual average rainfall of about 2932 and 3521 mm, respectively (Avinash et al. 2008). The Mandovi River has a total length of 84 km and a catchment area of 1150 km^2 (Pathak et al. 1988), while the Sharavathi River is approximately 130 km long with a catchment area of 3600 km^2 (Ramachandra et al. 2004). The tidal range in the Mandovi is 2.3 and 1.5 m during spring and neap tides, respectively (Rao et al. 2011), whereas in the Sharavathi the high tide is 1.41 m which decreases to 0.66 m during neap tide (Kumar et al. 2011). The rock types in the Mandovi River catchment area belong to Western Dharwar Craton (WDC) of mesoarchaean age. The WDC is characterized by high-Mg basalts and komatites with meta-volcanic and meta-sedimentary rocks (Naqvi 2005), whereas in the Sharavathi River metamorphic rocks and the peninsular gneisses are present. The catchment area of

these estuaries has been subjected to open cast mining activities for the last two decades (Shynu et al. 2011; EMPRI 2012). The loading of ore onto barges, transport through river channel, and reloading at the port or midstream onto giant ships for export were done in an open system, and one would expect abundant spilled-over ore material into the Mandovi estuary contributing to anthropogenic input. Most of the mines in the Sharavathi estuary are not in working condition. In addition, industries- and agriculture-related activities, along with sewage waste, are also contributing to anthropogenic input in these estuaries.

Materials and methods

Two mudflat sediment cores were collected one each from Mandovi (MD) and Sharavathi (SH) estuaries using hand-operated PVC corer during the field survey conducted in May 2013 (Fig. 1). The length of the cores MD and SH was 82 and 60 cm, respectively, which were sectioned at 2-cm intervals. The core sections (41 and 30 sub-samples of cores MD and SH, respectively) were packed in a pre-cleaned polythene bags, stored in an ice box, transferred to the laboratory and stored at 4 °C. Later, the sub-samples were oven dried at 60 °C. Each sub-sample (2-cm section) was physically mixed, and part of that sample was taken for grain size (sand/silt/clay) analysis which was carried out by pipette method (Folk 1974). Another part of the dried sample was powdered and homogenized. Small portion of the powdered and homogenized sample was used for the estimation of organic carbon following modified Walkley–Black method (Gaudette et al. 1974). From the remaining part of the homogenized samples, small portion was used for the metal analysis, in which after complete digestion of known weight of sediment sub-samples with 7:3:1 HF/HNO$_3$/HClO$_4$ acid mixture, sample solutions were analysed for bulk metal chemistry (Fe, Mn, Ni, Co and Cr) using atomic absorption spectrophotometer (Varian AA240FS). The average of grain size, organic carbon and bulk metals were computed using 41 and 30 sub-samples of cores MD and SH, respectively. The modified sequential extraction procedure (Dessai and Nayak 2009) proposed by Tessier et al. (1979) was used for selected sub-samples of cores MD and SH in order to understand the association of metals with different sediment fractions and to understand their risk to sediment associated biota. The accuracy of the analytical method was tested by digesting standard reference material 2702 obtained from National Institute of Standards and Technology (NIST) and was aspirated into the AAS. The average recoveries ± standard deviations found for each metal were 89 ± 12, 91 ± 15, 86 ± 16, 74 ± 12 and 79 ± 14 for Fe, Mn, Ni, Co and Cr, respectively.
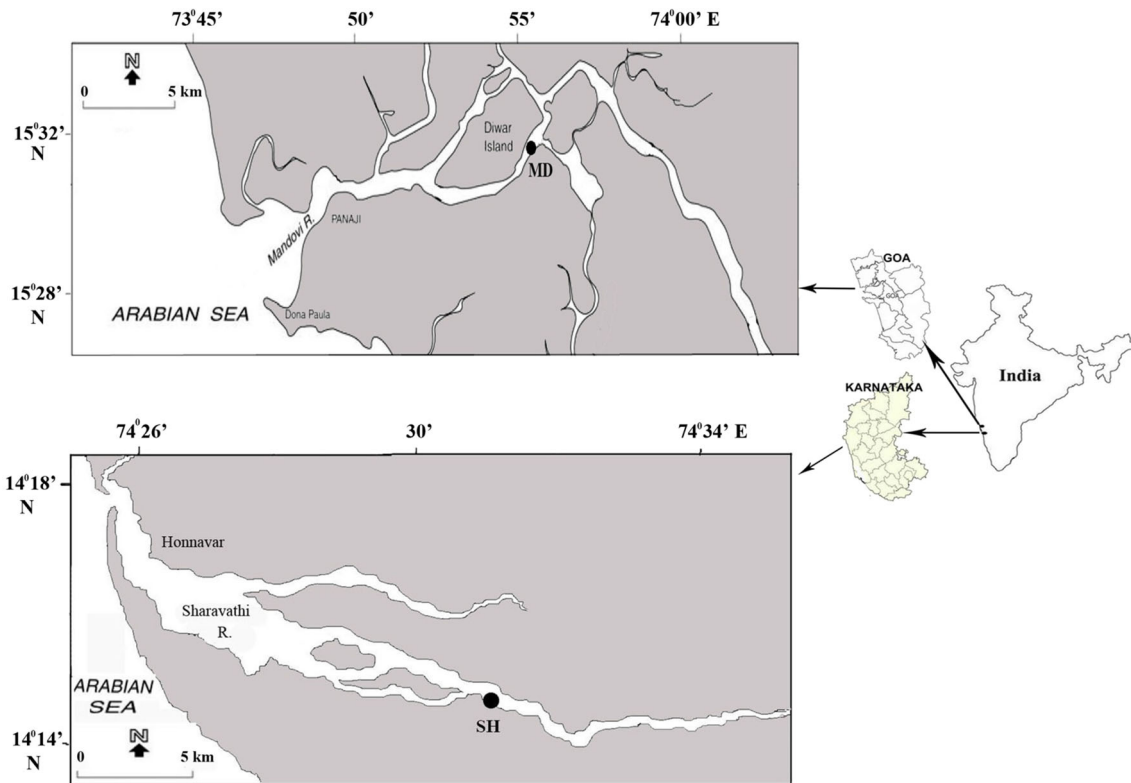
Fig. 1 Map showing sampling locations

In order to achieve information on the toxicity of metals to the biota and to understand the impact of metals on the environment, the data set of the metals in bulk sediments and bio-available fractions (sum of the first four fractions) was compared with the sediment quality value (SQV) using the screening quick reference table (SQUIRT). The SQUIRT was developed by National Oceanic and Atmospheric Administration (NOAA), and the guideline values were categorized by Buchman (1999) into five classes. The sediment guidelines and terms used in the SQUIRT are presented in Table 1.

The Risk Assessment Code (RAC) was also attempted to assess the potential mobility and environmental risk of trace metals in the sediments to the associated biota (Kumar et al. 2012). The percentage of trace metals bound to exchangeable and carbonate fractions was used to assess the availability from the sediments using the following criteria proposed by Perin et al. (1985): percentage of the total concentration < 1: no risk, will be considered safe for the environment, 1–10: low risk, 11–30: medium risk, 31–50: high risk, > 50: very high risk, and can easily enter the food chain.

Results and discussion

Sediment texture and organic carbon

The range and the average concentration of grain size and organic carbon are presented in Table 2. The grain size of

Table 1 Sediment guidelines and terms used in the 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 concentration 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

Table 2 Range and the average concentration of (a) grain size and organic carbon in cores MD and SH, (b) metals in cores MD and SH

Core MD	Min	Max	Avg	Core SH	Min	Max	Avg
(a)							
Sand (%)	4.60	71.78	25.78	Sand (%)	10.09	78.21	44.96
Silt (%)	22.82	59.70	46.38	Silt (%)	10.31	66.75	34.65
Clay (%)	0.16	43.64	27.84	Clay (%)	1.40	42.00	20.38
Org. C (%)	0.62	3.00	2.12	Org. C (%)	0.15	3.04	1.93
(b)							
Fe (%)	11.87	19.91	15.42	Fe (%)	2.10	7.23	4.94
Mn (ppm)	1379	5175	3069	Mn (ppm)	250	1907	1056
Ni (ppm)	39	111	77	Ni (ppm)	43	141	102
Co (ppm)	20	38	31	Co (ppm)	12	54	27
Cr (ppm)	166	337	259	Cr (ppm)	74	183	123

the Mandovi mudflat sediments followed the order of silt > clay > sand, whereas in the Sharavathi mudflat sediments, grain size followed the order of sand > silt > clay. The sediment texture analysis differentiated the grain size among the studied estuaries. The rate and intensity of weathering of the rocks present in the catchment area vary with respect to properties of minerals and their resistance (Mukherjee 2013). The rock types present in the catchment area, therefore, might contribute to the variation in grain size between Mandovi and Sharavathi estuaries. Moreover, channel morphology, abrasion, corrosion and deposition of the sediment also influence the textural pattern in a given region (Kumar and Ramanathan 2015). The organic carbon concentration was higher in the Mandovi estuary than the Sharavathi estuary and was incorporated onto the finer fractions of sediment by adsorption phenomena (Keil et al. 1994).
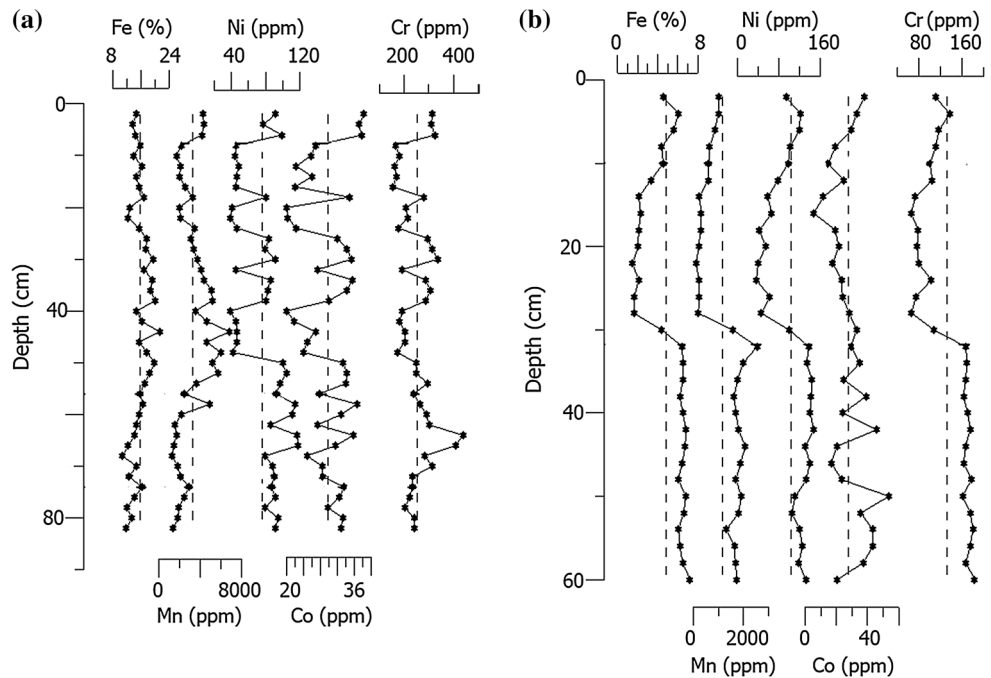
Bulk metals (Fe, Mn, Ni, Co and Cr)

The range and the average concentration of Fe, Mn, Ni, Co and Cr in the bulk sediments are presented in Table 2. The concentration of Fe, Mn, Co and Cr was higher in the mudflat sediments of the Mandovi estuary, while Ni in the Sharavathi estuary. The higher concentration of most of the metals in the Mandovi estuary than in the Sharavathi estuary is attributed to the release from open cast ferromanganese ores and associated with higher finer sediments and organic carbon content, facilitating adsorption of metals (Mikulic et al. 2008) Fine-grained sediments are an important sink for a wide range of contaminants, particularly trace metals (Spencer et al. 2003). The crustal average values reported by Taylor (1964) for Fe, Mn, Ni, Co and Cr are 5.63%, 950, 75, 25 and 100 ppm, respectively. In case of Mandovi estuary, Fe, Mn, Ni, Co and Cr were higher than the crustal average values by 9.79%, 2119, 2, 6 and 159 ppm, respectively. The average value of Fe was less by 0.69% than the crustal average value in the Sharavathi

estuary, while the average value of Mn, Ni, Co and Cr was higher than the crustal average value by 106, 27, 2 and 23 ppm, respectively. The comparison of the trace element concentrations with crustal average values revealed that the sediments of the Mandovi and Sharavathi estuaries are contaminated due to open cast mining activities in the catchment area and are the major source of metal pollution in these estuaries. The values reported in this study will, however, act as a standard for future studies on metal concentration in these estuaries as well as other estuaries along west coast of India.

Further, to understand the distribution and abundance of metals with time, depth profiles of the studied metals were plotted for both Mandovi and Sharavati estuaries. In core MD (Fig. 2a), Fe and Mn exhibited overall increase from bottom to 44 cm. Further, concentration of Fe decreased towards the surface, while Mn decreased up to 8 cm and then increased towards the surface. Ni and Co showed overall decrease with fluctuations from bottom to 8 cm and then increased towards the surface. Cr concentration increased from bottom to 64 cm, followed by an overall decrease up to 8 cm. Similar to Mn, Ni and Co, the concentration of Cr was higher in the top 8 cm of the core. An increase in Mn, Ni, Co and Cr towards the surface of the core suggested their enrichment in the oxic environment. However, Mandovi estuary being a reservoir of mining wastes, addition of metals in the recent years from mining-related activities cannot be ruled out. In case of core SH (Fig. 2b), Fe, Mn, Ni and Cr did not show much variation from bottom to 32 cm and further, exhibiting a sharp decrease up to 28 cm followed by nearly constant concentration up to 14 cm depth. Thereafter, the metals exhibited an overall increasing trend towards the surface of the core. Co showed an overall decrease from bottom to 14 cm, followed by an increase towards the surface. A similar point-to-point distribution of Fe and Mn observed from bottom to 14-cm depth indicated strong association of the geochemical matrix between the two elements

Fig. 2 Variation of Fe, Mn, Ni, Co and Cr with vertical lines of average values in cores MD (**a**) and SH (**b**)

(Jonathan et al. 2010). Further, a prominent increase in concentration of Fe from 14 cm towards the surface must be the result of higher supply from catchment area during recent years or remobilization of Fe towards surface which must have regulated the distribution of Ni and Cr.

Speciation of Fe, Mn, Ni, Co and Cr

The range and the average concentration of Fe, Mn, Ni, Co and Cr in different fractions in cores MD and SH are given in Table 3. After the sequential extraction procedure, the higher concentrations of metals in both cores MD and SH remained in the residual fraction. In core MD, concentrations of Fe, Ni, Co and Cr were above 65% and Mn around 40%. In core SH, concentrations of Fe, Ni and Cr were above 70%, while those of Mn and Co were 60.62 and 55.93%, respectively. In core MD, next to the residual fraction, Mn and Co were associated with the Fe–Mn oxide fraction, while Cr with the organic bound fraction. Metals viz. Fe, Ni, Co and Cr were available in least concentration in the carbonate fraction. Mn was least in the organic bound fraction. The concentration of Fe was the lowest in

Table 3 Range and the average concentration of Fe, Mn, Ni, Co and Cr in different fractions of cores MD and SH

	Exchangeable		Carbonate		Fe–Mn		Organic/sulphide		Residual	
	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average
MD										
Fe (%)	0.005–0.0074	0.0013	0.0001–0.0024	0.0006	1.45–4.10	2.25	1.37–4.51	2.35	92.35–96.59	95.4
Mn (%)	1.38–34.18	11.29	2.06–16.99	11.18	5.60–50.05	30.74	2.29–12.31	6.72	22.06–61.71	40.08
Ni (%)	2.46–28.41	5.77	2.65–4.62	3.75	5.03–11.74	7.94	4.75–8.94	7.33	57.23–80.95	75.21
Co (%)	3.94–14.60	6.38	3.87–5.86	5.08	5.20–18.94	14.56	2.62–11.17	8.86	56.68–72.87	65.13
Cr (%)	0.52–2.92	1.67	0.18–1.33	0.73	5.31–9.41	6.66	4.32–11.69	8.72	78.79–86.31	82.22
SH										
Fe (%)	0.0002–0.0070	0.0014	0.001–0.006	0.004	6.77–10.90	8.58	0.07–0.86	0.43	88.93–93.12	90.98
Mn (%)	2.27–20.99	16.25	1.80–6.84	3.58	8.48–25.91	16.66	0.71–11.28	2.88	46.57–84.76	60.62
Ni (%)	1.50–7.13	3.7	2.82–9.83	4.67	5.32–9.96	7.04	4.48–6.34	5.28	68.64–84.51	79.31
Co (%)	4.19–14.24	8.1	5.52–15.13	8.28	13.30–24.84	19.27	1.19–36.52	8.42	38.01–62.89	55.93
Cr (%)	1.07–3.89	2.07	0.39–6.65	2.89	4.21–9.84	7.33	7.21–13.89	10.86	67.93–86.59	76.86

the bio-available fractions. In core SH, next to the residual fraction, Fe, Mn, Ni and Co were associated with the Fe–Mn oxide phase and Cr with the organic phase. Mn was available in considerable concentration in the exchangeable fraction. Fe, Ni, Co and Cr showed least concentration in the exchangeable phase, while Mn in the organic phase.

Fe did not show much variation with depth in the core MD (Fig. 3a). Mn associated with the exchangeable fraction showed an overall decrease from bottom to surface with very high values at 60, 18 and 10 cm depths. In carbonate and Fe–Mn oxide fractions, Mn concentration increased from the bottom to 30 cm depth followed by an overall decrease up to 10 cm depth. Further, Mn exhibited an increasing trend towards the surface in these fractions. Mn bound to the organic fraction showed an overall

increase towards the surface. Ni bound to the exchangeable phase showed an increase at 60 and 4 cm depths. Co in the exchangeable phase exhibited a slight increase at 60, 18 and 10 cm, similar to Mn. In the Fe–Mn oxide phase, Co showed higher concentration in the middle portion of the core between 50 and 14 cm, and also at 8 cm and surface. The concentration of Co decreased from the bottom to 60 cm in the organic phase and then showed slightly increasing values up to 18 cm. Further, concentration of Co slightly decreased up to 4 cm followed by an increase towards the surface. Cr in the organic phase exhibited higher values towards the surface.

The distribution of Fe showed a slight increase in the residual phase from the bottom to the surface (Fig. 3b). Mn was with a high concentration in the exchangeable fraction,
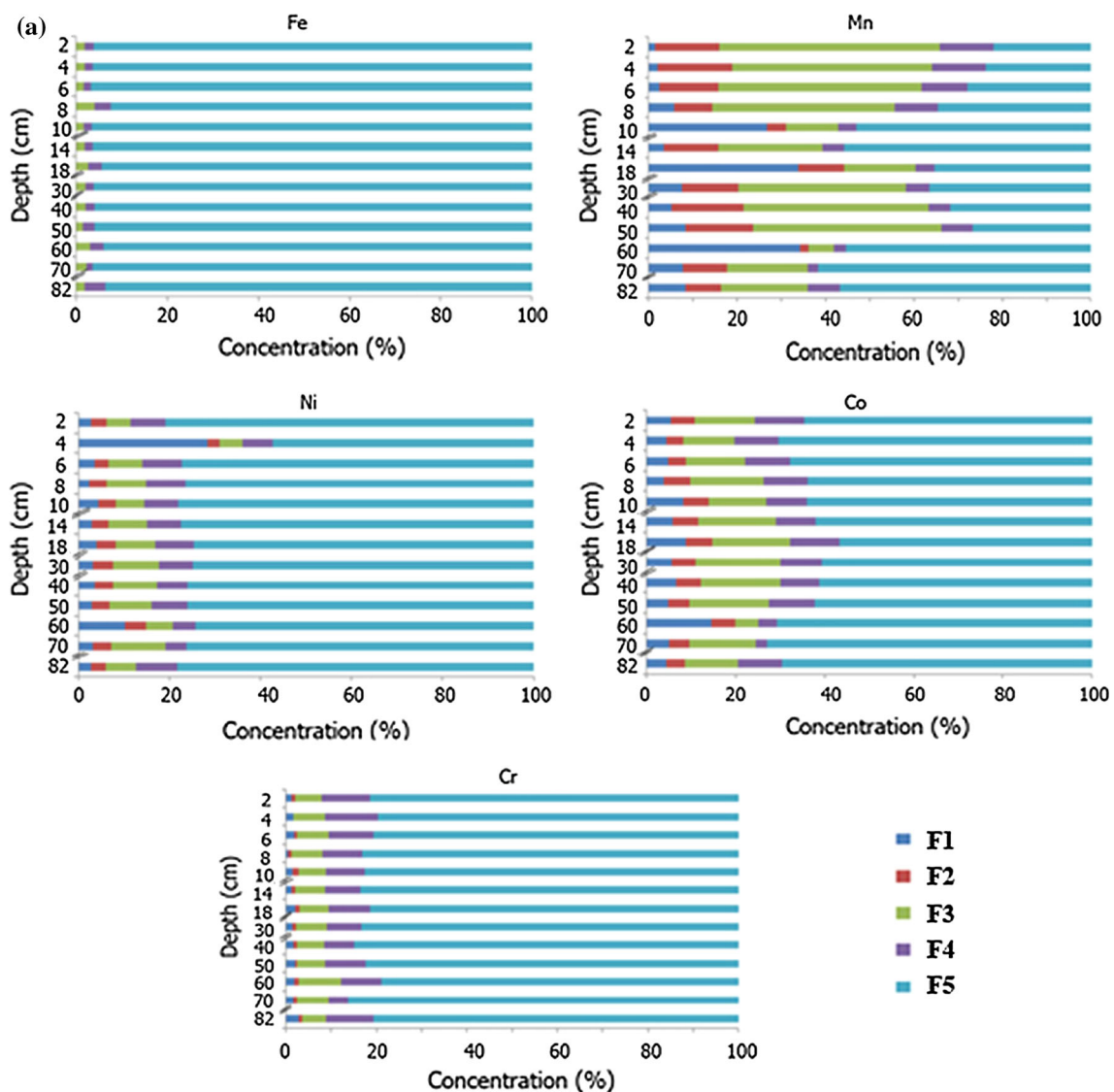

Fig. 3 a Speciation of metals in core MD where F1 exchangeable, F2 carbonate bound, F3 Fe–Mn oxide, F4 organic/sulphide bound, F5 residual fractions. **b** Speciation of metals in core SH where F1 exchangeable, F2 carbonate bound, F3 Fe–Mn oxide, F4 organic/sulphide bound, F5 residual fractions
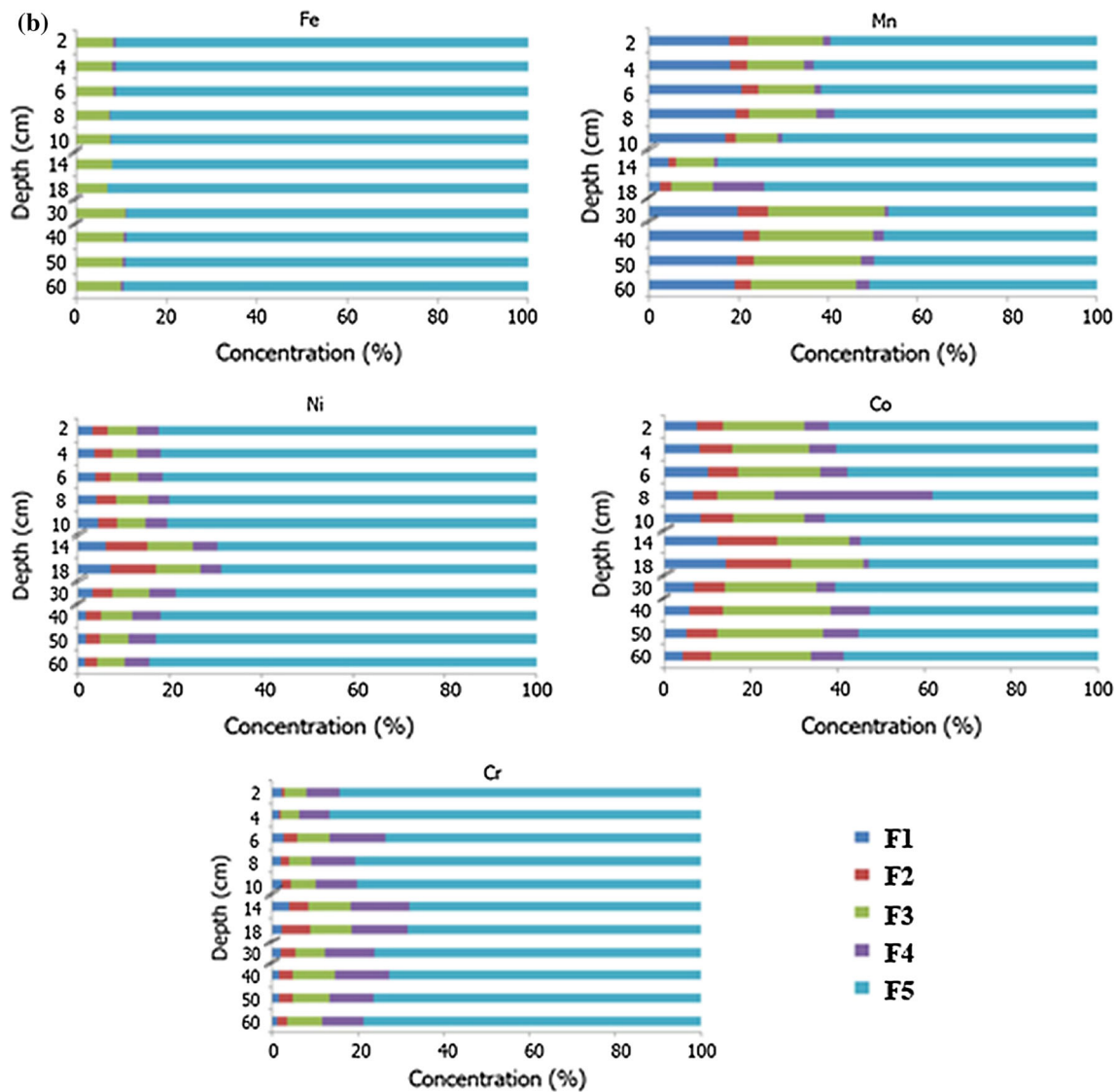
Fig. 3 continued

except between 18 and 14 cm where it showed less concentration. Mn in carbonate and organic bound fractions was less and almost constant with depth, except higher value at 30 and 18 cm, respectively. Mn in the Fe–Mn oxide phase showed a slight increase from the bottom to 30 cm which was followed by a sharp decrease at 18 cm. Further, Mn maintained low concentration up to 10 cm and showed slightly higher values from 8 cm to surface. Ni exhibited an increase in the bio-available fractions from the bottom to 18 cm. Ni was highest and constant between 18 and 14 cm, and then gradually decreased towards the surface. Co in the exchangeable fraction increased from the bottom to 18 cm and then showed overall decrease towards the surface. The concentration of Co in both exchangeable and carbonate fractions was much higher between 18 and 14 cm. In the Fe–Mn oxide fraction, Co decreased from the

bottom to 8 cm followed by an increase towards the surface. Cr showed an overall increase from the bottom to 14 cm in exchangeable, carbonate and organic phases and then exhibited an overall decrease towards the surface. The organic and Fe–Mn oxide phases showed slightly higher values between 18 and 14 cm.

The speciation study of sediment cores collected from the two tropical estuaries showed the highest concentration of all the metals in the residual phase indicating their natural occurrence and derived from the parent rock (Ratuzny et al. 2009). However, some metals (Mn, Ni, Co and Cr) with very high concentration in the bio-available phases (exchangeable, carbonate bound, Fe–Mn oxides/hydroxides and organic matter/sulphide fractions) indicated their anthropogenic origin. Metals associated with these four fractions are readily available for uptakes and bio-

accumulation in aquatic biota (Gambrell 1994; Ladigbolu 2014). In the present study, the higher concentration of metals viz. Mn, Ni, Co and Cr in the bio-available phases (Table 3) in cores MD (59.93, 24.79, 34.88 and 17.78%, respectively) and SH (39.37, 20.69, 44.07 and 23.15%, respectively) indicated their anthropogenic source, such as mining-, chemical industry-, agriculture-related activities and sewage runoff in the estuarine environment. The catchment area of the Mandovi and Sharavathi estuaries was extensively exploited for mining of iron-ore, mining and associated smelting, and metal processing activities, and it must have led to the cycling of metals in the estuarine environment. Iron-ore mining and its tailing wastewaters usually show high levels of dissolved metal ions and particulate suspended matter that can change the water as well as sediment chemistry and even influence the bio-availability of metals (Holopainen et al. 2003).

In core MD, the dominance of Fe in the residual fraction indicated its existence as crystalline Fe peroxides like goethite, limonite, magnetite, haematite (Massolo et al. 2012). Mn was present in significant concentration (30.74%) in the Fe–Mn oxide phase. Moreover, an increase in distribution of Mn in the Fe–Mn oxide phase towards the surface indicated its diagenetic mobilization and re-precipitation in the near surface sediments. Under constantly varying Eh conditions within the aquatic environment, metals do not remain permanently sequestered (Depledge and Fossi 1994). This results in the mobilization of sediment-bound metals (Fytianos and Lourantou 2004) and later metals precipitate in oxic conditions. Mn also exhibited mobilization in the organic phase, and its increase near the surface in carbonate and organic phases suggested that it is environmentally significant for mobility, availability for uptake by aquatic biota and possible toxicity. It is important to relate metal bio-availability with metal bio-accumulation in benthic biota to understand the role of biota in extracting and retaining the metals and also in bio-remediation. Such studies can enhance our understanding on the metal remobilization better. The concentration of Co was more than 10% in the Fe–Mn oxide fraction, i.e. second most dominant fraction, suggesting adsorption of Co onto the Fe–Mn colloids which act as important scavengers of Co in sediments, thus indicating the role of Fe–Mn colloids in regulating the mobility of Co in the estuarine environment (Kaasalainen and Yli-Halla 2003). It is important to note that the distribution of Mn and Co in the exchangeable fraction was higher at 60-, 18- and 10-cm depths which suggested the role of Mn in the distribution of Co. The higher concentration of Co between 50 and 14 cm in the Fe–Mn oxide and organic bound phases, followed by an overall decrease up to 4 cm, suggested its mobilization. Co thus mobilized from the sediments must have adsorbed onto re-precipitated Fe–Mn oxides under more oxic

conditions as well as onto the organic matter which is construed from the higher Co concentration in these fractions observed at the surface. The vertical profile of Cr also indicated its adsorption onto organic matter in the recent years. Apart from the hydrous oxides of Fe and Mn, organic matter is also an important binding phase for metals in sediments (Chakraborty et al. 2011). Further, adjacent mangrove environment is known as pool of organic matter as it retains large amount of organic matter brought from terrestrial sources. Though the mangrove sediments have a high capacity to retain heavy metals, they can also act as source of metals and facilitate migration of metals from mangroves to mudflats and vice versa depending on the conditions regulated by the tide.

In core SH, the higher concentration of Fe in the residual fraction, similar to the core MD, suggested that it was largely present in the immobile state and non-availability under prevailing natural conditions. It is unlikely for metals associated with the residual fraction to be released into solution through dissolution as they remain fixed in sediments within the matrix of silicates and other detrital minerals (Wang et al. 2012). However, rest of the metals were present in considerable concentration in the bio-available phases. Metals viz. Mn (16.66%) and Co (19.27%) were associated with Fe–Mn oxide fraction as the second most dominant fraction and also showed an increase towards the surface in this phase. In addition, Mn was also considerably higher towards the surface in the exchangeable fraction. The distribution of Mn and Co in the Fe–Mn oxide phase suggested their diagenetic mobilization. The higher concentration of Mn and Co in the bio-available phases towards the surface indicated their availability to the sediment associated biota. Co is rapidly removed from solution by co-precipitation and sorption in most oxidizing, near-neutral or alkaline stream water as the dissolved Fe and Mn precipitate out as secondary oxides, hydrous Mn oxides having a particularly strong sorption affinity for Co (Longhinos 2011). The concentration of Ni, Co and Cr was higher in the bio-available phases, namely exchangeable and/or carbonate and/or Fe–Mn oxide and/or organic from 18 to 14 cm depth interval which must be due to the higher anthropogenic addition of these metals in the past.

Among the metals studied for the purpose of speciation, Mn in core MD was available in more than 10% in exchangeable and carbonate fractions individually, while in the core SH, Mn was present in more than 10% in the exchangeable fraction. In exchangeable and carbonate fractions, metals are weakly sorbed and are retained on the sediment surface by weak electrostatic interaction and as a result can be released by ion exchange processes and precipitated or co-precipitated with the carbonates present in the sediments (Filgueiras et al. 2004). Mn in these fractions

poses a significant environmental risk for sediment associated biota, as it may easily leach in neutral or slightly acidic waters (Alvarez-Valero et al. 2009). Thus, it is prone to assimilation by organisms and could, therefore, may impose potential ecological risks.

Sediment quality value

When concentration of metals in the bulk sediments and the sum of their bio-available fractions (Table 4) were compared with the screening quick reference table (Table 5), it was observed that the percentage of total Fe and the sum of bio-available Fe was lower than the apparent effect threshold (AET) in both the estuaries indicating no harm from Fe to the sediment associated biota. Total Mn as well as the sum of bio-available Mn in Mandovi and Sharavathi estuaries exceeded AET, suggesting its probable toxicity to the sediment associated organisms. Although total Ni in both the estuaries exceeded the threshold effect level (TEL), the sum of bio-available Ni was lower than the TEL, suggesting not much concern to the associated biota from Ni. Total Co exceeded the AET in both Mandovi and Sharavathi estuaries, while the sum of bio-available Co was lower than the AET, revealing concern to the aquatic life. Total Cr ranged from probable effect level (PEL) to effect range median (ERM) in the Mandovi estuary, whereas in the Sharavathi estuary, it ranged from effect range low (ERL) to PEL. In both the estuaries, total Cr was more than the ERM; however, the sum of bio-available Cr was lower than the TEL, indicating not much concern to the associated organisms. The speciation of elements therefore indicated concern from Mn and Co to the sediment-associated organisms in Mandovi and Sharavathi estuaries.

Risk assessment code

The sum of the percentage of metals in exchangeable (fraction 1) and carbonate fractions (fraction 2) at studied cores (Table 4) were compared with the risk assessment code criteria. In cores MD and SH, Mn and Co fell within the degree of medium risk. The risk associated with Fe, Ni and Cr was minimal for both the sediment core profiles, as RAC fell under the low-risk category. Though Mn and Co are required as essential nutrients for sediment associated biota, their excess concentration in the sediments of both Mandovi and Sharavathi estuaries, leading to medium risk to the associated biota, may have harmful effects on health of estuary, sediment associated biota and may be human population who consumes biota associated with the sediments.

Conclusion

The mudflat core sediments collected from Mandovi and Sharavathi estuaries showed higher concentration of trace metals viz., Fe, Mn, Co and Cr in the bulk sediments of the Mandovi estuary compared to the Sharavathi estuary, which was attributed to the role of finer particles, organic matter and clay minerals. Speciation of trace metals suggested that all the metals are dominant in the residual fraction in both the cores. In core MD, Fe, Ni, Co and Cr were > 65%, while Mn was 40.08% in the residual fraction. In core SH, Fe, Ni and Cr were > 70%, while Mn and Co were 60.62 and 55.93%, respectively, in the residual phase. In core MD, Mn (30.74%) and Co (14.56%) were significantly high in the Fe–Mn oxide fraction and exhibited mobilization in Fe–Mn oxide and organic bound fractions. An increase in Mn towards the surface in Fe–Mn

Table 4 Average concentrations of total metals and bio-available fractions in cores MD and SH

	Total metals concentration	Sum of bio-available fractions	F1 + F2 (%)
MD			
Fe (%)	15.42	0.76	0.001
Mn (ppm)	3069	1596	22.46
Ni (ppm)	77	15	9.52
Co (ppm)	31	7	11.45
Cr (ppm)	259	19	2.40
SH			
Fe (%)	4.94	0.80	0.004
Mn (ppm)	1056	365	19.83
Ni (ppm)	102	10	8.37
Co (ppm)	27	9	16.38
Cr (ppm)	123	22	4.94

F1 = exchangeable fraction and F2 = carbonate fraction, together make labile fraction. Only labile fraction is presented in percentage to classify under risk assessment code

Table 5 Screening quick reference table for metals in marine sediments (Buchman 1999)

Elements	Threshold effect level (TEL)	Effect range low (ERL)	Probable effect level (PEL)	Effect range median (ERM)	Apparent effect threshold (AET)
Fe%	–	–	–	–	22 (Neanthes)
Mn	–	–	–	–	260 (Neanthes)
Ni	15.9	20.9	42.8	51.6	110 (Echinoderm larvae)
Co	–	–	–	–	10 (Neanthes)
Cr	52.3	81	160	370	62 (Neanthes)

Except for Fe, all values are in µg/g

oxide, carbonate and organic fractions suggested its bio-availability to the sediment associated biota. In core SH, Mn (16.66%) and Co (19.27%) were present in considerable concentration in the Fe–Mn oxide phase. In this core, Mn and Co indicated their diagenetic mobilization in the Fe–Mn oxide phase. Further, an increase in Mn bound to Fe–Mn oxide and exchangeable fractions, and Co associated with the Fe–Mn oxide fraction towards the surface suggested their bio-availability to the sediment associated biota. Moreover, Mn in the core MD was available in more than 10% in exchangeable and carbonate fractions individually, while in the core SH, Mn was present in more than 10% in the exchangeable fraction. As metals in these fractions are extremely leachable with change in pH and ionic composition, Mn is readily bio-available in the Mandovi and Sharavathi estuarine environments. SQV suggested concern from Mn, whereas RAC indicated medium degree of risk from Mn and Co to the sediment-associated organisms in both the estuaries.

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