



Assessment of metal enrichment and contamination in surface sediment of Mandovi estuary, Goa, West coast of India

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Abstract

Metal concentration in the sediments was determined to assess the metal enrichment and level of contamination in the Mandovi estuary. The metal distribution in the Mandovi estuary revealed preferential input through open-cast iron-ore mining, industrial, fishing, and agricultural activities. The heavy riverine runoff associated with high rainfall influenced the distribution of Mn, Zn, and Pb during monsoon season. In addition, sediment grain size and associated organic matter governed metal distribution in surface sediments. The role of grain size and organic matter along with Fe-Mn oxides in the distribution of metals was construed through correlation and factor analysis. Geo-accumulation index, contamination factor, and potential contamination index indicated contamination of surficial sediments of the Mandovi estuary with Cr and Pb.

Keywords Mandovi estuary · Sediments · Metals · Seasonal variation · Pollution indices · Pollution

Introduction

Metal contamination in the natural ecosystems has always been a subject of much discussion and has gained much more interest from environmental researchers over the past few years (Hu et al. 2013; Wang et al. 2014; Xu et al. 2014; Venkatramanan et al. 2015; Wang et al. 2015). Estuaries are hubs of rivers and seas that react compassionately to natural processes and anthropogenic activities (Li et al. 2007). Trace metals in the estuarine environment have been broadly accepted to be either lithogenic or anthropogenic origin (Chakraborty and Babu 2015). Estuaries are frequently polluted with trace metals released by industrial, agricultural, mining activities in addition to the inland waste (Hu et al. 2013). Upon, entering an estuarine environment, metal undergo modifications by the action of physico-chemical processes. A portion of the metal ion remains in the water column, while most of it settle down and become part of cohesive sediments through processes, viz., hydrolysis, adsorption, and co-precipitation (Gaur et al. 2005). Therefore, estuarine

sediments are known as the effective sink for metals (Ip et al. 2004). The input of trace metals in the estuary would be projected through their content in the sediments, and in recent years, it is of concern due to their enhanced additions. Thus, the chemistry of estuarine sediments reflects the degree of natural and anthropogenic influences (Soares et al. 1999).

Post-industrialization has resulted in the elevated levels of metal in estuaries. Although metals get adsorbed onto sediments, they possess tendency to desorb from the estuarine sediment and thus released in overlying water column in response to change in pH, Eh, salinity, and organic matter (Nasnodkar and Nayak 2015). Moreover, the variations in these physico-chemical properties are frequent in the estuaries due to their dynamic nature. Estuaries are the most productive ecosystems providing suitable habitat for numerous marine flora and fauna. Therefore, it is necessary to characterize metal nature and assess its contamination in sediments which can get transferred to biota and humans with time (Ruilian et al. 2008). The metal contamination and associated ecological risk have been successfully evaluated in the past using the environmental assessment indices by Muller (1969), Hakanson (1980), Salomons and Forstner (1984), Harikumar and Nasir (2010), Kalender and Uçar (2013), Goher et al. (2014), Atibu et al. (2016), and Malvandi (2017). Besides, analytical and statistical methods have been designed in response to environmental issues and as useful pollution tools for monitoring estuarine ecosystem.

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The understanding of metal accumulation and contamination in the Mandovi estuarine sediments is essential as the estuary has been a recipient of metal waste through open-cast mining activities (Alagarsamy 2006; Attri and Kerkar 2011; Kessarkar et al. 2015). In the current study, grain size and organic carbon (OC) were characterized, and the concentration and distribution of trace metals in surficial sediments were examined (Fig. 1). The metal pollution status in the Mandovi estuary was assessed using several pollution indices. The main purpose of the study was to determine trace metal distribution, sources, enrichment, and status of metal pollution in surficial sediments of the Mandovi estuary.

Material and methods

Mandovi River is one of the Goa’s major rivers which originates at Bhimgad (Western Ghats) of the Belagavi District in Karnataka. It is ~ 70 km long with basin area of 1530 km² and flows into the Arabian Sea. Based on geographical features, the Mandovi estuary can be divided into two regions, namely the Aguada Bay (~ 4 km wider) and the channel (~ 40 km long) (Shetye et al. 2007). The region is influenced by the Southwest monsoon.

The average monthly rainfall in the Mandovi estuary during June to September reported was 35–145 cm and during

October to May 0.33–4.15 cm (Ibrampurkar 2012). Most of the precipitation (~ 90 %) occurs during the monsoon (June–September) period in comparison to premonsoon (February–May) and postmonsoon (October–January) periods. Therefore, the Mandovi estuary experiences extreme seasonal variability with almost freshwater dominance during June–September months and nearly marine dominance during the postmonsoon and premonsoon seasons (Qasim and Gupta 1981). As a result, the fishing trawlers are moored in the lower estuarine region, and the fishing activity is at halt in the monsoon season.

Physiochemical parameters salinity (‰), temperature (°C), pH and DO ($mg\ l^{-1}$), and TSM ($mg\ l^{-1}$) in surface waters of the Mandovi estuary were 0.74–5.79 (1.61 ± 1.54), 27.83–28.20 (28.01 ± 0.10), 6.86–7.31 (7.05 ± 0.16), 4.56–6.16 (5.46 ± 0.44), and 11.30–38.30 (23.48 ± 9.37) during monsoon; from 8.48 to 31.99 (17.83 ± 8.85), 28.38 to 29.50 (29.06 ± 0.40), 7.79 to 8.08 (7.95 ± 0.08), 3.77 to 4.46 (4.16 ± 0.20), and 7.55 to 19.30 (16.07 ± 3.72) during postmonsoon; and from 22.56 to 34.90 (28.36 ± 4.00), 30.50 to 32.83 (31.85 ± 0.75), 7.86 to 7.97 (7.92 ± 0.04), 3.58 to 4.24 (3.93 ± 0.17), and 12.70 to 30.75 (22.68 ± 5.91) during premonsoon, respectively. For bottom waters, the range and average values were 0.61–7.27 (2.54 ± 2.94), 27.53–27.90 (27.70 ± 0.11), 6.81–7.36 (7.09 ± 0.19), 4.55–6.00 (5.35 ± 0.46), and 14.60–94.60 (39.76 ± 27.62) during monsoon; from 9.63 to 33.59 ($19.47 \pm$

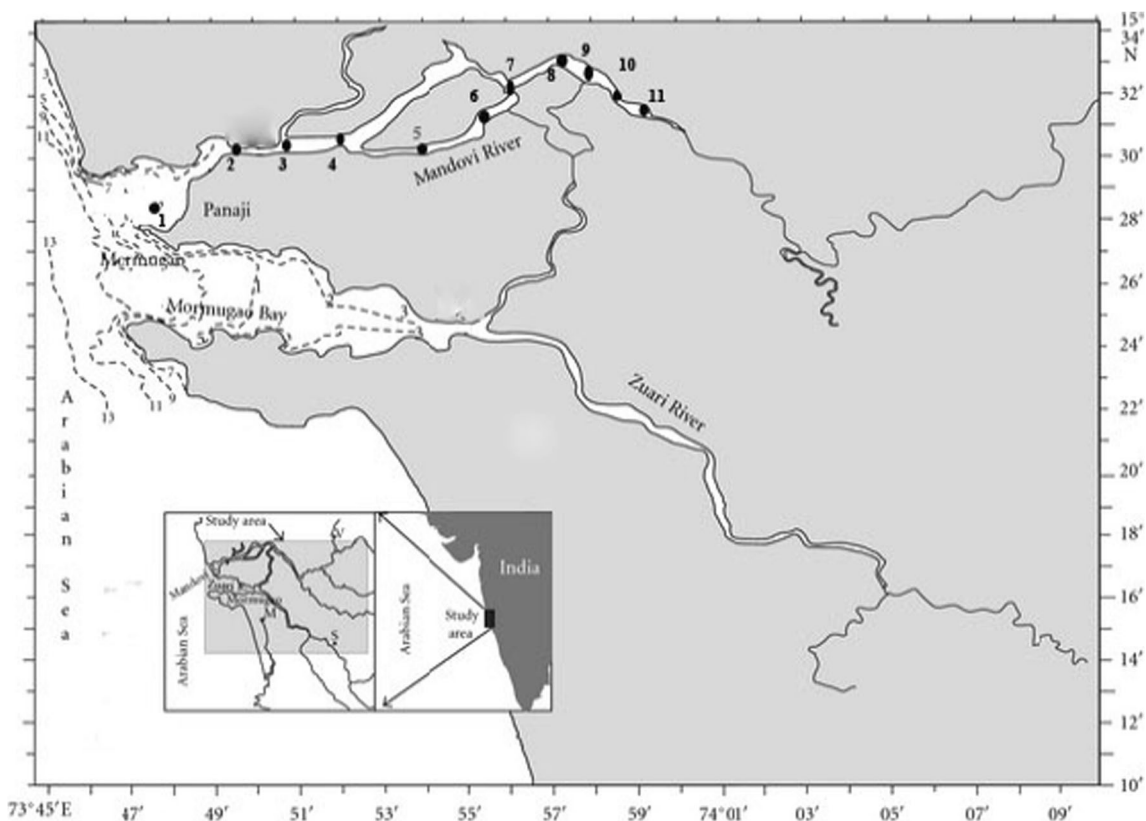


Fig. 1 Map showing sample location for surface sediments in the Mandovi Estuary

9.18), 28.13 to 29.13 (28.71 ± 0.36), 7.86 to 8.15 (7.98 ± 0.10), 3.71 to 4.23 (3.99 ± 0.16), and 12.65 to 28.35 (19.84 ± 5.54) in postmonsoon; and from 21.38 to 34.38 (28.27 ± 4.22), 30.00 to 32.60 (31.63 ± 0.82), 7.83 to 8.07 (7.94 ± 0.06), 3.61 to 4.29 (3.89 ± 0.20), and 13.20 to 38.35 (23.26 ± 7.26) in premonsoon season, respectively. Spatial variation of salinity, pH, and TSM showed remarkable increase towards seaward stations than in riverside stations. On the other hand, DO in surface and bottom waters exhibited a distinct trend, i.e. decreasing trend in its concentration from the riverine side (head) to marine side (mouth) of the estuary in all three seasons. Temperature however remains almost constant throughout the study period (see supplementary material).

Goa is known for mining of Fe-Mn ores, and nearly two-thirds of the overall mining activities are located within the riverine basin of the Mandovi estuary. The Mandovi estuary is broadly utilized to carry Fe-Mn ores to adjacent Marmagao port. Mandovi River has 37 loading points, and nearly 19.1 mt. of ore has been exported via Mandovi estuary in the past (Siraswar and Nayak 2013; Kessarkar et al. 2015). Thus, the Mandovi estuary plays an imperative part in Goa's economy by providing a cheap and effective means of ore transport (Nayak 2002). Though mining boosted the economic growth of Goa, it did lead to additions of metals to the Mandovi estuary. Additionally, the Mandovi estuary also receives metal waste from urban, industrial, and agricultural activities.

Sediment sampling and analytical procedure

Eleven surface sediment samples from eleven stations were collected during monsoon, postmonsoon, and premonsoon seasons with the help of a Van Veen grab for a period August 2012 to July 2013. Sampling stations were chosen depending on salinity gradient covering distance up to 45km from mouth/lower estuary (stations 1 to 5) to head/upper estuary (stations 6 to 11). Collected eleven surface sediment samples were packed into labeled Ziploc polythene bags and then stored at -4°C . A portion of the oven-dried surface sediment sample was used to determine grain size using the pipette method (Folk 1968). Remaining portion of sediment sample was disaggregated in an agate mortar and used for estimation of OC and total trace metals. Percentage of OC was estimated using Walkley-Black wet oxidation procedure adopted and revised by Jackson (1958). For metal analysis, powdered sediment sample weighing 0.3g was digested using an acid mixture of 10ml of HF:HNO₃:HClO₄ (7:3:1) on a hot plate near to dryness (Loring and Rantala 1992). Further, sample was treated with 5ml of same acid mixture. Finally, concentrated HCl (2ml) was added to the residue and dried completely. After ensuring complete drying, 10ml of 1:1 HNO₃ was added to the final residue, and the clear digested solution was filtered and transferred in 100ml volumetric flask.

The determination of total metal concentration (Fe, Mn, Zn, Cr, Cu, and Pb) in digested samples was performed with

the atomic absorption spectrophotometer (Model: GBC 932 A). A standard stock solution was prepared using Merck standard metal solutions for each metal. Instrument sensitivity was frequently monitored with respect to standard solutions. Blank samples (without sediment) were analyzed together with digested sediment samples. The precision and accuracy of metals analyzed were checked against reference standard Cody shale (Sco-1) in triplicate which showed 94.88, 95.19, 91.64, 92.04, 94.51, and 88.64 % recovery for Fe, Mn, Zn, Cr, Cu, and Pb, respectively.

Data analysis

Sediments are archives of metal history and point to the level of metal contamination. In present study, different pollution indices and criteria are used to assess the level of contamination in investigated sediments with pollutant (metal) by comparing the measured concentration with preindustrial geochemical reference material. Several researchers considered the average shale or crustal value as a benchmark reference (Loska and Wiechula 2003; Singh et al. 2005; Olivares-Rieumont et al. 2005). In present analysis of surface sediments, average shale value proposed by Turekian and Wedepohl (1961) has been used as the geochemical background value.

Geo-accumulation index (Igeo)

To evaluate the degree of metal pollution in sediment, geo-accumulation index (Igeo) has been calculated by means of method proposed by Muller (1979). The geo-accumulation index is computed by using the following formula:

$$I_{\text{geo}} = \log_2(C_n/1.5 \cdot B_n) \quad (1)$$

where C_n is measured concentration of analyzed metal and B_n is metal concentration in average shale (Turekian and Wedepohl 1961).

Factor 1.5 is the background concentration factor due to lithogenic variability (Loska et al. 2004). Muller (1979) has classified index of geo-accumulation into seven classes from $I_{\text{geo}}=0$ (unpolluted) to $I_{\text{geo}} > 5$ (extremely polluted).

Contamination factor

The contamination factor is the ratio of measured concentrations of individual metal in sediment to the background geochemical concentrations in average shale value (Turekian and Wedepohl 1961) and is given by the formula:

$$CF = \frac{\text{Measured concentration (collected sediment samples)}}{\text{Background concentration (average shale value)}} \quad (2)$$

where average shale value given by Turekian and Wedepohl (1961) is used as the background value of metal. According to Hakanson (1980), the CF values are rated in four classes from low (CF=<1) to very high contamination (CF=>6).

Pollution load index (PLI)

The metal pollution level in the Mandovi estuary was assessed through the pollution load index computed using the method proposed by Tomlinson et al. (1980).

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n) 1/n \tag{3}$$

According to Tomlinson et al. (1980), pollution index value >1 is considered to be polluted sediment, where PLI<1 signifies no pollution in sediment.

Contamination degree (Cd)

To understand the synergetic action of metals in sediments, the contamination degree was measured using the following formula:

$$Cd = \sum_{i=1}^n Fi \tag{4}$$

where CF_i is contamination factor of individual metal “i.”

Likewise contamination factor, Hakanson (1980) classified contamination degree into four groups from low Cd (Cd<6) to very high Cd (Cd>24).

Modified degree of contamination

The modified degree of contamination was calculated using the equation proposed by Abraham and Parker (2008) modified from Hakanson (1980):

$$mCd = 1/n \sum_{i=1}^n CF_i \tag{5}$$

where n is number of analyzed elements and CF is contamination factor.

The following six grades have been proposed from mCd < 1.5 = low contamination to mCd ≤ 32 = ultra-high contamination.

Potential contamination index (Cp)

The Cp was calculated as:

$$Cp = \text{Metal (sample max)}/\text{Metal (background)} \tag{6}$$

where Metal (sample max) is maximum value of an individual analyzed metal and Metal (background) is geochemical background value of an individual metal.

Dauvalter and Rognerud (2001) interpreted Cp values into three grades from Cp<1 = low contamination to Cp>3 which is severe contamination.

Potential ecological risk

The risk index (RI) and potential ecological risk factor are calculated by using the following formula:

$$\text{Risk Index (RI)} = \sum E_r^i \tag{7}$$

$$E_r^i = T_r^i Cf \tag{8}$$

where RI is sum of potential risk factors of individual metals, E_rⁱ is ecological risk index for individual metal, T_rⁱ is toxic response for given element (Mn, Zn = 1, Cr = 2, Cu, Pb = 5) (Hakanson 1980), and CF is contamination factor of an individual metal.

Hakanson (1980) proposed five grades of E_rⁱ from E_rⁱ <40 = low to E_rⁱ > 320 = very high ecological risk and four grades of RI from RI<95 = low potential ecological risk to RI > 380 = very high ecological risk.

Statistical analysis

Multivariate statistical analyses, such as Pearson correlation and factor analysis, were performed using Statistica 7. Pearson correlation coefficient was used to examine the relationship between metal pairs in sediment, while R-mode factor analysis with Varimax-normalized rotation by means of the principal components extraction method was used to identify the sources wherein the Kaiser criterion method (Kaiser 1960) is followed, which will retain only those factors having eigenvalue >1.

Results and discussion

Sediment grain size (sand-silt-clay) and organic carbon

The coarser sediments (sand %) in monsoon, postmonsoon, and premonsoon varied from 64.82 to 90.56 (77.03 ± 7.45), 27.03 to 81.48 (67.66 ± 15.13), and 21.64 to 9.03 (66.22 ± 20.73), respectively. Relatively higher percentage of sand was reported towards upper estuarine region (Fig. 2a). Silt (%) varied from 5.09 to 17.51 (12.11 ± 4.05), 12.17 to 34.77 (19.01 ± 6.55), and 4.94 to 50.46 (20.57 ± 14.18) during monsoon, postmonsoon, and premonsoon, respectively. Higher content of silt was observed at lower estuarine region for monsoon, postmonsoon, and premonsoon periods (Fig. 2a). Clay (%) varied from 2.99 to 17.82 (10.95 ± 3.96), 5.42 to 38.20 (13.39 ± 9.29), and 6.13 to 27.90 (13.32 ± 6.96) during monsoon, postmonsoon, and premonsoon,

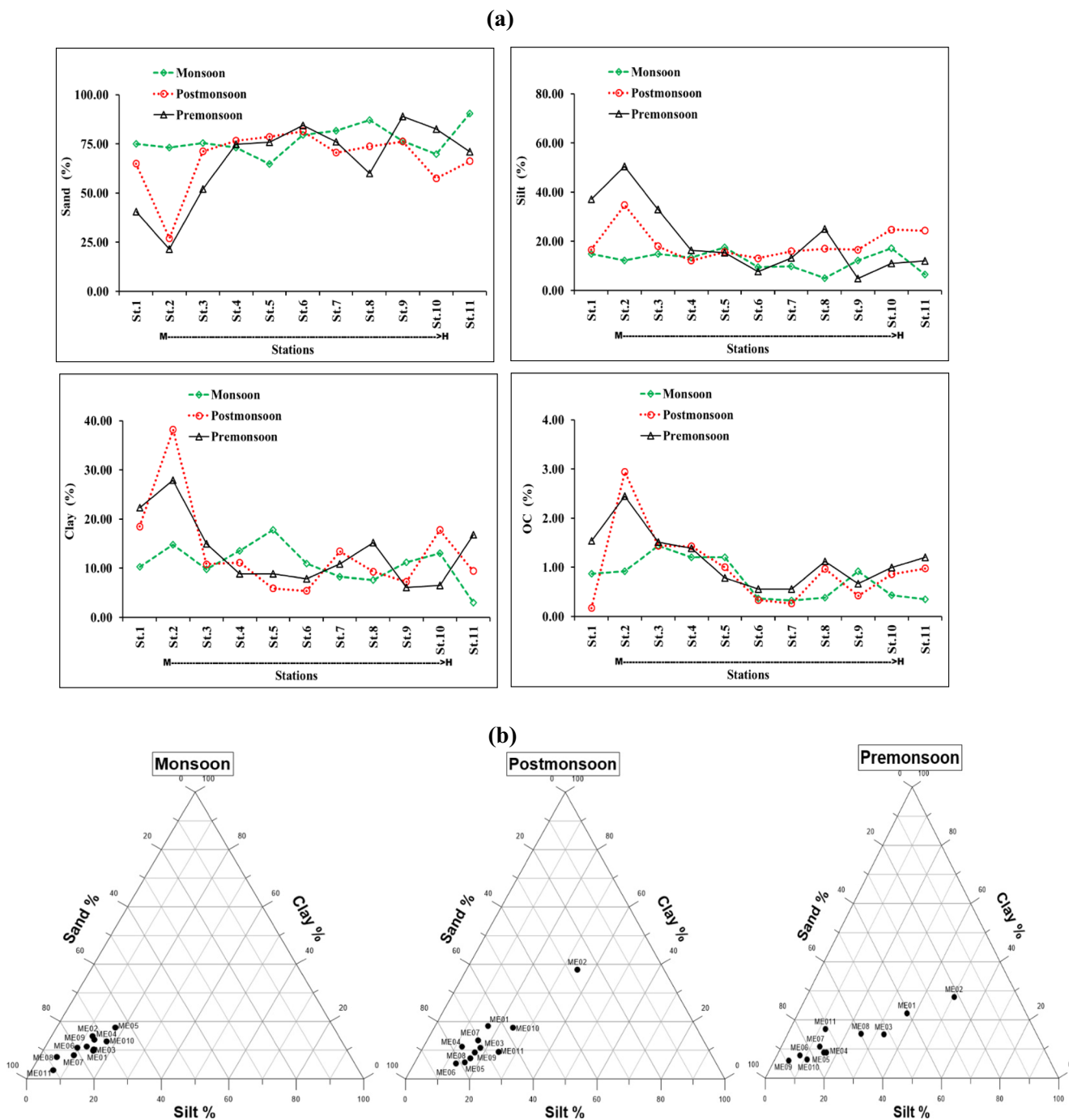


Fig. 2 **a** Variation of grain size and organic carbon in surface sediments and **b** ternary diagram of grain size distribution of surface sediments in the Mandovi estuary

respectively. Relatively higher clay was reported towards lower estuarine region with some minor peaks towards upper estuarine region during the study period (Fig. 2a). Further, the ternary diagram of grain-size distribution indicated that sediment samples of monsoon season are characterized by high proportion of sand followed by silt. On the other hand, during premonsoon and postmonsoon seasons, sediment falls under silty sand and clayey silt, respectively (Fig. 2b).

Seasonally, higher sand was reported during the monsoon season compared to premonsoon and postmonsoon seasons. It was ascribed to the predominance of terrestrial over marine sediments (Upkong 1997; Siraswar and Nayak 2013). Sediment samples from the upper estuarine region reflect the input from the main river channel and thus retained more sand during monsoon season. In the lower estuary, silt and clay percentage were generally higher during non-monsoon season

indicating the role of tidal currents in distribution and settling of finer fractions of sediments. The energy associated with waves and tides is relatively higher during the monsoon than the non-monsoon period. Thus, low energy facilitated settling of fine sediment particles during non-monsoon period. The OC (%) varied from 0.33 to 1.44 (0.77 ± 0.41) in monsoon, 0.17 to 2.95 (0.98 ± 0.79) in postmonsoon, and 0.56 to 2.45 (1.16 ± 0.56) in premonsoon seasons. Average OC concentration was higher during premonsoon compared to postmonsoon and monsoon seasons. Organic carbon was higher at the lower estuary similar to finer sediments and was present in low concentration at the upper estuary. This suggested its association with silt and clay size particles as compared to sand. One of the important characteristics of the organic carbon in sediments is that its concentration often increases with decrease in the sediment particle size. It is further well endorsed by significant positive association of OC with finer sediment (silt and clay) and significant negative association with sand (Table 1). In general, the spatial distribution of sediment components in the Mandovi estuary revealed organic carbon with its high specific storage capacity as a key determinant that governed the distribution of trace metal.

Distribution of trace metals in surface sediments

Iron

Fe (%) concentrations ranged from 1.19 to 2.36 (1.72 ± 0.36) in monsoon, 1.13 to 2.47 (1.77 ± 0.44) in postmonsoon, and 0.82 to 2.27 (1.89 ± 0.45) premonsoon seasons. Fe was relatively higher during premonsoon than rest of the seasons. The relative high concentration of Fe during premonsoon season was attributed to adsorption onto sediments due to low volume of water which is associated with high rate of evaporation (Obasohan 2008), high OC, and fine-grained sediments. Likewise, higher concentration of Fe during premonsoon season was also reported by Alagarsamy (2006) in the Mandovi estuary. Fe (spatial distribution) showed positive peaks at stations towards the lower estuarine region and was attributed to the sediment grain size, OC (Gopal et al. 2017), and re-suspension of sediments at higher salinity (Fig. 3).

Manganese

Concentration of Mn ($\mu\text{g g}^{-1}$) ranged from 34.00 to 213.23 (90.87 ± 59.85), 38.41 to 103.66 (61.12 ± 21.75), and 34.83 to 113.03 (68.18 ± 25.02) for monsoon, postmonsoon, and premonsoon periods, respectively. Mn showed relatively higher average concentration during monsoon as compared to other seasons. Heavy rainfall in the Mandovi River during monsoon season carries mining waste from the catchment area into the estuarine region. This might have resulted in the

enrichment of Mn during the monsoon season. Mn exhibited higher concentration in the lower estuarine region during post and premonsoon seasons (Fig. 3). Several processes such as the effect of salinity and ionic strength, sorption phenomena between particles and sediments, and flocculation and coagulation processes increase Mn concentration in the lower estuary. On the other hand, during monsoon season, higher value of Mn was reported at station towards the upper estuarine region. In general, the behavior of Mn is different from rest of the metals in estuaries. For instance, at low (10 ppt) salinity Mn is available in dissolved form (Kerdijk and Salomons 1981) while Mn flocculates and eventually precipitates under high salinity conditions (Balachandran et al. 2006). Relatively high concentration of Mn between stations 1 to 5 during pre- and postmonsoon seasons might be due to the precipitation of Mn in high saline conditions in the lower estuarine region. Many ore deposit points are located along the upper reaches of the Mandovi estuary. Flushing of ores from these points during monsoon caused an increase in Mn concentration in some stations. The stations 9 and 10 are located in the vicinity of ore deposits hence recorded higher concentrations, whereas station 11 is located away from the ore deposit point hence it recorded lower concentrations. A similar observation was also made by Dessai and Nayak (2009) and Gaonkar and Matta (2020) in the Zuari estuary. Moreover, an increase in Mn at the upper estuarine region during the monsoon season contradictory to rest of the seasons was attributed to its input to the estuary through riverine runoff containing mining waste.

Zinc

Zn ($\mu\text{g g}^{-1}$) concentration for monsoon, postmonsoon, and premonsoon seasons ranges from 98.32 to 172.57 (145.14 ± 21.50), 53.91 to 136.81 (83.71 ± 24.41), and 57.33 to 115.41 (75.73 ± 17.44), respectively. It was relatively more for monsoon period than post- and premonsoon periods. High Zn concentration during the monsoon season might be due to heavy freshwater runoff deriving high load of suspended/fine sediments and organic matter that facilitated the binding of Zn in sediments, in addition to its anthropogenic input. Spatial distribution of Zn registered an increase in concentration during post- and premonsoon periods at the lower estuary (Fig. 3). The accumulation of Zn in sediments was regulated by sediment texture, organic matter, and its anthropogenic source.

Chromium

Cr ($\mu\text{g g}^{-1}$) concentration varied from 197.40 to 341.54 (289.26 ± 41.73) in monsoon, 171.48 to 500.78 (360.18 ± 111.46) in postmonsoon, and 204.48 to 438.37 (334.94 ± 75.82) in premonsoon seasons. The mean concentration of Cr exhibited relatively higher concentration during postmonsoon than premonsoon and monsoon seasons.

Table 1 Correlation between metals, sand, silt, clay, and OC in different fractions of the surface sediments for three different seasons in Mandovi estuary

	Sand	Silt	Clay	OC	Fe	Mn	Zn	Cr	Cu	Pb
Monsoon										
Sand	1.00									
Silt	-0.94	1.00								
Clay	-0.93	0.75	1.00							
OC	-0.63	0.63	0.56	1.00						
Fe	-0.14	-0.12	0.39	-0.12	1.00					
Mn	-0.36	0.38	0.27	0.04	-0.15	1.00				
Zn	-0.34	0.18	0.46	0.23	0.66	0.24	1.00			
Cr	0.39	-0.49	-0.23	-0.22	0.63	-0.46	0.43	1.00		
Cu	-0.04	-0.14	0.22	0.16	0.39	-0.10	0.59	0.35	1.00	
Pb	-0.61	0.63	0.50	0.22	-0.14	0.77	0.25	-0.65	-0.10	1.00
Postmonsoon										
Sand	1.00									
Silt	-0.97	1.00								
Clay	-0.97	0.89	1.00							
OC	-0.41	0.31	0.50	1.00						
Fe	0.21	-0.34	-0.06	0.43	1.00					
Mn	-0.45	0.39	0.50	0.79	0.24	1.00				
Zn	-0.36	0.21	0.49	0.74	0.69	0.52	1.00			
Cr	0.58	-0.58	-0.55	-0.25	0.41	-0.28	-0.03	1.00		
Cu	-0.27	0.14	0.40	0.86	0.75	0.57	0.84	-0.11	1.00	
Pb	-0.67	0.60	0.70	0.79	0.05	0.89	0.44	-0.35	0.50	1.00
Premonsoon										
Sand	1.00									
Silt	-0.98	1.00								
Clay	-0.98	0.92	1.00							
OC	-0.74	0.76	0.70	1.00						
Fe	0.49	-0.43	-0.53	0.01	1.00					
Mn	0.09	0.02	-0.18	0.31	0.59	1.00				
Zn	-0.38	0.41	0.34	0.74	0.48	0.70	1.00			
Cr	0.26	-0.10	-0.39	-0.34	0.23	0.17	-0.21	1.00		
Cu	0.07	-0.01	-0.13	0.46	0.84	0.80	0.84	-0.01	1.00	
Pb	0.88	-0.85	-0.87	-0.50	0.78	0.31	-0.08	0.21	0.43	1.00

Values in bold are significant as it reflects the correlation between different variables. Correlation is significant at the 0.05 level (n = 11)

Several scientists reported that Cr probably present as adsorbed species on sediments (Salmon et al. 1987). The adsorption of Cr also depends on the chemical form of Cr in seawater. Cr (III) prefers to adsorb on oxides and hydroxides of Fe, whereas Cr (VI) prefers to adsorb on oxides and hydroxides of Mn. Relative high concentrations of Cr during postmonsoon may probably due to high suspended matter and preferential adsorption of Cr (III) on to oxides and hydroxides of iron. Spatial distribution of Cr exhibited higher concentration at stations towards the upstream region of the Mandovi estuary except for the premonsoon season wherein higher concentration was reported at the lower estuarine region (Fig. 3). In an estuary, Cr is known to decrease rapidly

during mixing of freshwater with saline waters. The loss of Cr is due to conversion of Cr (III) to particulate Cr. Adsorption of Cr on to surfaces of suspended matter is enhanced by the increase concentration of suspended matter and the tendency of Cr (III) and Cr (VI) to adsorb at lower salinity (Mayer and Schick 1981). Relative high concentration of Cr at stations towards the upstream region is attributed to preferential adsorption of Cr (VI) on suspended matter at lower salinities.

Copper

The concentration of Cu ($\mu\text{g.g}^{-1}$) in the Mandovi estuary varied from 21.65 to 52.20 (33.74 ± 12.03) in monsoon,

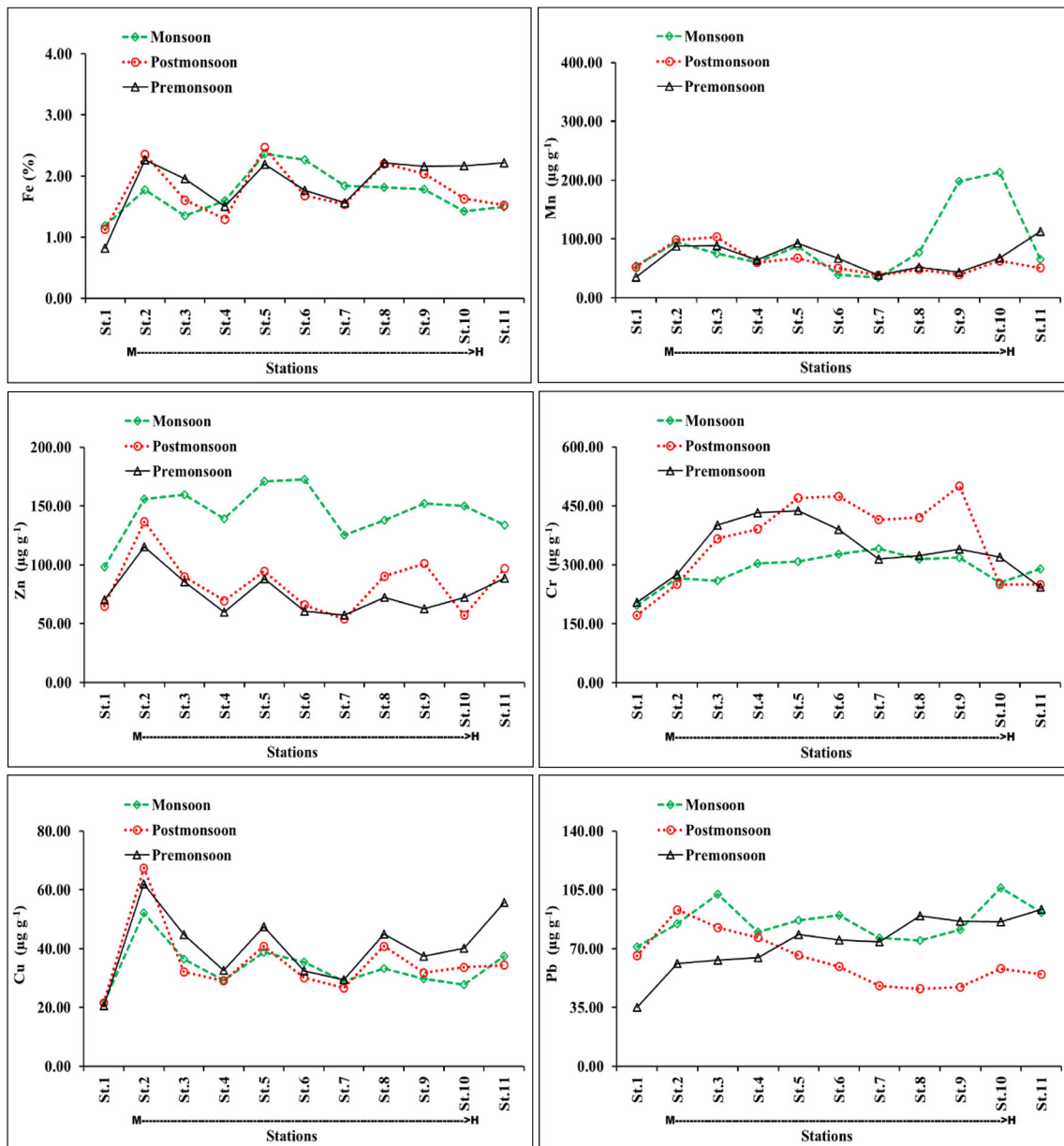


Fig. 3 Spatio-temporal variation of trace metals (Fe, Mn, Zn, Cr, Cu, and Pb) in surface sediments of the Mandovi estuary

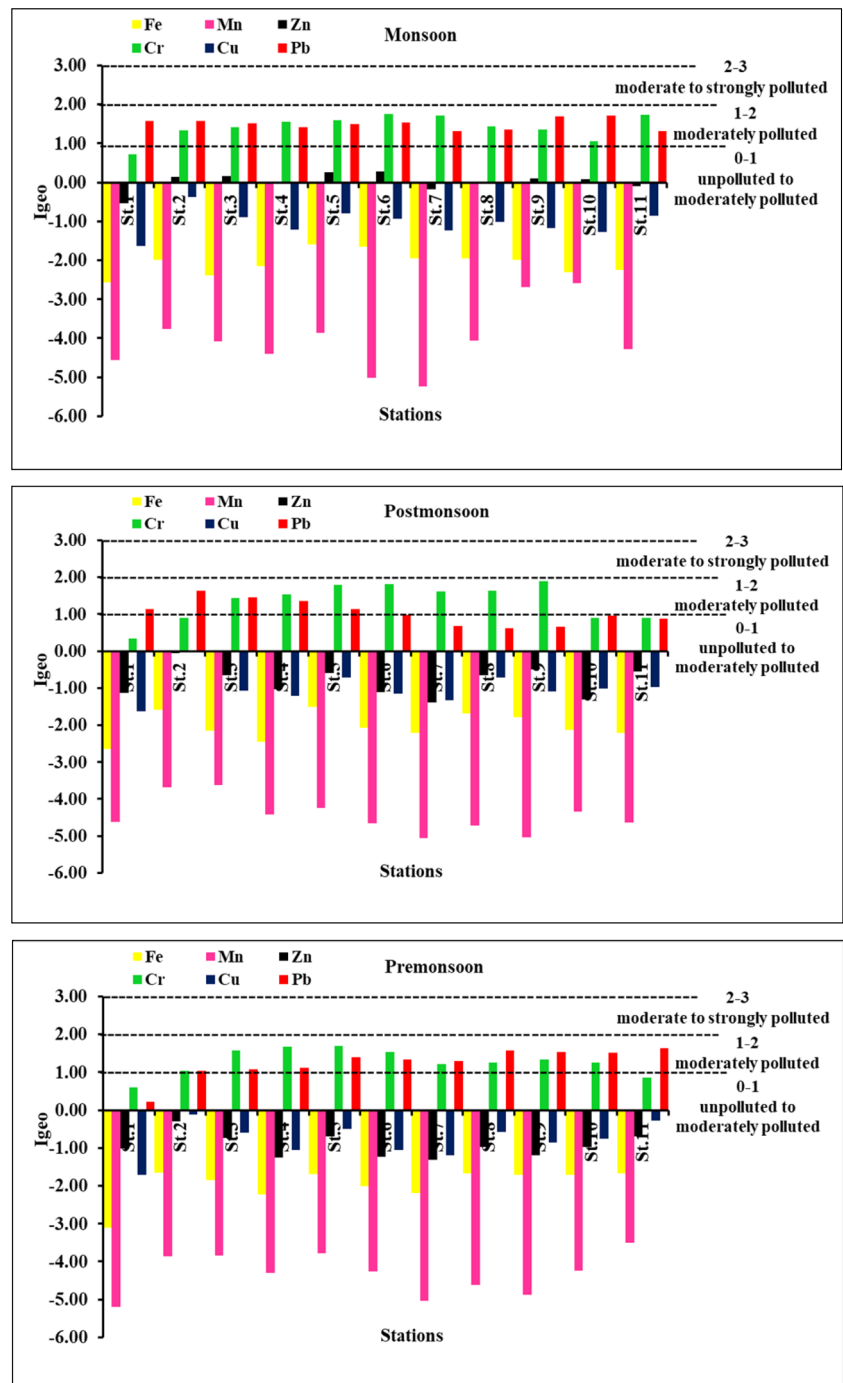
21.65 to 67.43 (35.33 ± 12.03) in postmonsoon, and 20.65 to 62.10 (40.72 ± 12.01) in premonsoon seasons. Cu concentration was higher during premonsoon season than rest of the seasons which was attributed to high saline conditions that might have caused the precipitation of dissolved Cu (Ananthan et al. 2005, 2006). Cu exhibited highest concentration towards the lower estuarine region during all three seasons (Fig. 3). Such a spatial distribution of Cu in the Mandovi estuary can be explained by the role of sediment grain size and OC in its distribution. Moreover, Cu has an ability to form organic complexes and accelerate out as an insoluble form and, consequently, deposited in estuarine sediments (Silambarasan et al. 2012).

Lead

The concentration of Pb ($\mu\text{g g}^{-1}$) in surface sediments ranged from 74.33 to 98.57 (85.97 ± 8.30) in monsoon, 46.25 to 93.16 (63.46 ± 15.33) in postmonsoon, and 35.00 to 93.41 (73.40 ± 16.81) in premonsoon seasons. Seasonally, maximum Pb was reported in monsoon season which might be due to freshwater runoff that carried natural product. Spatial distribution of Pb in the Mandovi estuary showed high concentration towards the upper estuarine region during monsoon and premonsoon seasons, while it was relatively high at the lower estuarine region during the postmonsoon season (Fig. 3).

It is evident from spatial and seasonal variations of metals that the Mandovi estuary was severely affected by activities such

Fig. 4 Plots showing Igeo values for each metal in the surface sediments of the Mandovi estuary

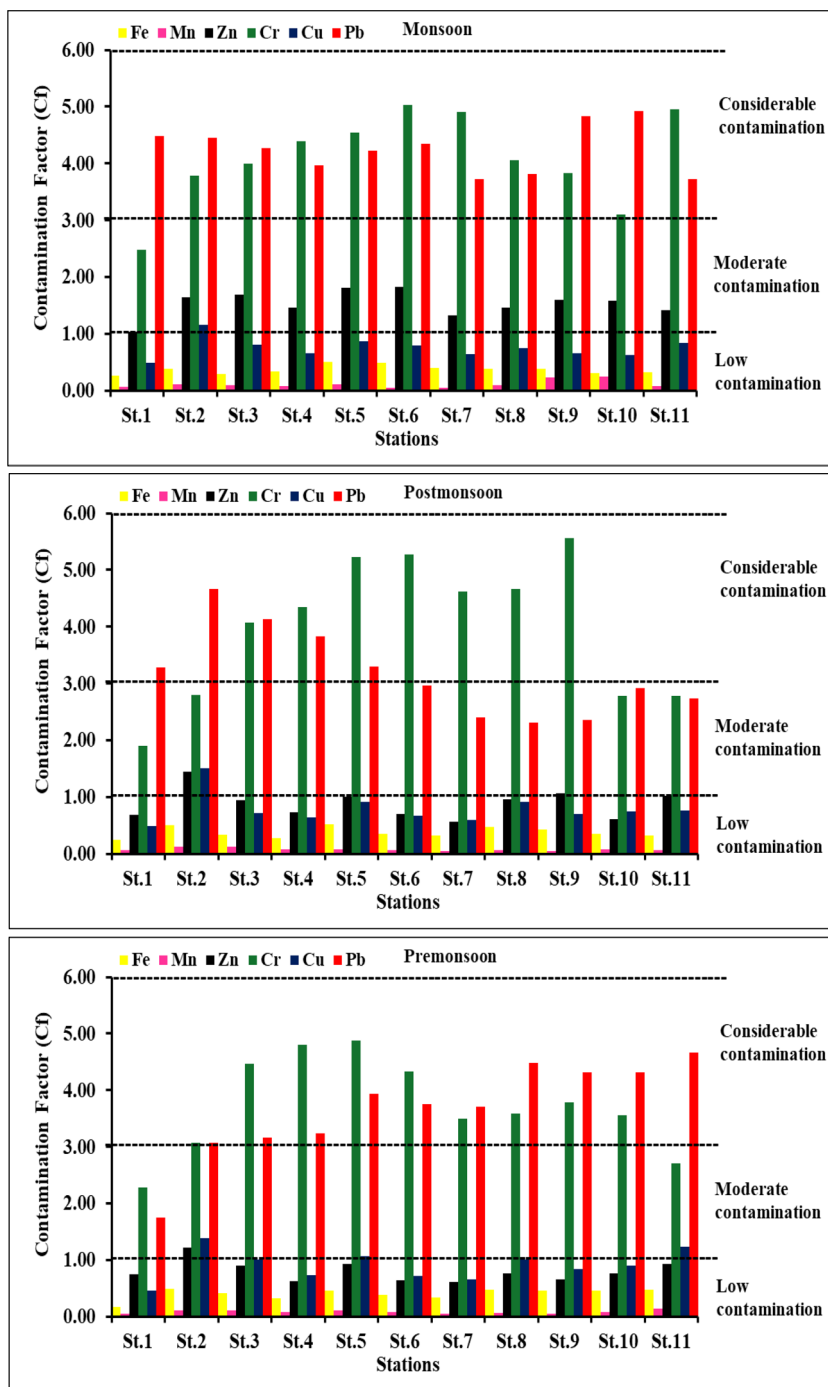


as ore mining in the catchment area, transportation of Fe-Mn ores by barges, shipbuilding and maintenance of fishing trawlers, land reclamation, and boat cruises for tourists through which a considerable amount of metal was added to the estuary over a period of time. Besides, the ore deposited at various barge loading points all along the banks of the estuary get flushed into the main estuarine channel during monsoon. Within the estuarine region, a proportion of the total metal content gets incorporated onto sediments in the estuary. Such a process is also responsible for the enhanced metal level in the Mandovi estuary

(Alagarsamy 2006; Dessai and Nayak 2009; Shynu et al. 2012). Further, spatial distribution of metals along the estuarine region as well as seasonal differences highlighted the significant role of fine sediment particles and organic matter in their distribution in the Mandovi estuary. Positive correlation of majority of analyzed metals with silt, clay, and OC (Table 1) especially during postmonsoon and premonsoon seasons construed the key role of sediment grain size and OC in metal distribution.

The metal distribution showed seasonal variability in the Mandovi estuary. In monsoon season, Mn, Zn, and Pb showed

Fig. 5 Contamination factor of surface sediments from the Mandovi estuary



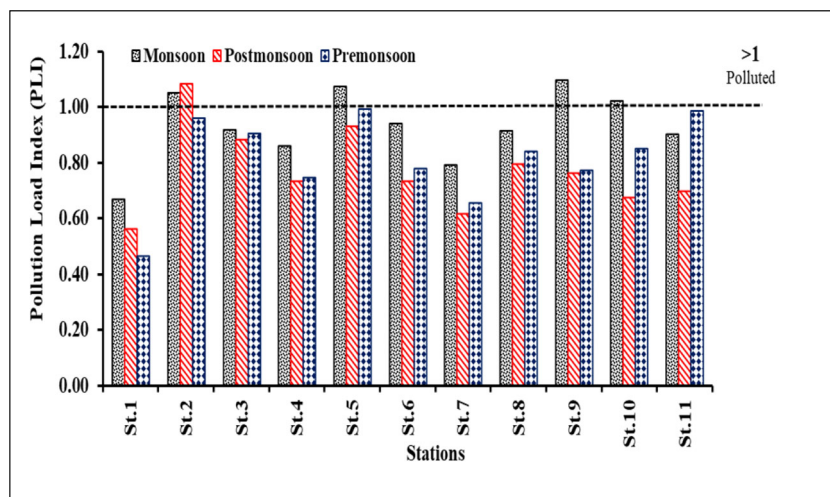
high average concentration than other seasons attributed to heavy freshwater runoff contributing to a significant amount of suspended/fine sediments and organic matter load in the estuary and, thus, facilitated their binding on sediments. On the other hand, a rise in concentration of Fe, Cr, and Cu during non-monsoonal period indicated the mobilization of metals from the over-flooding of metal-rich wastewater into the estuary during monsoon and by reworking of the sediments, and the geochemical processes might have facilitated the metal dispersion and mobilization in estuarine sediments after large-scale

sediment-water movement during the monsoon period. Moreover, industrial activities, agricultural waste, and municipal sewage disposal waste might have also increased the concentration of metals during the non-monsoon period.

Correlation coefficient

Metal pairs showed significant positive correlation in monsoon Fe-Zn ($r = 0.66$), Fe-Cr ($r = 0.63$), and Mn-Pb ($r = 0.77$); postmonsoon Fe-Zn ($r = 0.69$), Fe-Cu ($r = 0.75$), Mn-

Fig. 6 Pollution load index (PLI) of surface sediments from the Mandovi estuary



Pb ($r = 0.89$), and Zn-Cu ($r = 0.84$); and premonsoon Fe-Cu ($r = 0.84$), Fe-Pb ($r = 0.78$), Mn-Zn ($r = 0.70$), Mn-Cu ($r = 0.80$), and Zn-Cu ($r = 0.84$) seasons at the significance level $p < 0.05$ (Table 1). Positive association between trace metals indicated that they had similar sources and similar geochemical behavior during the transport in the estuary (Bastami et al. 2015). Also, trace metals (Zn, Cr, Cu, and Pb) exhibited significant correlation with Fe and Mn indicating scavenging nature of Fe-Mn oxyhydroxides in the estuary that regulated the distribution of metals in sediments (Jayaprakash et al. 2008; Nasnodkar and Nayak 2015). Often, finer sediments with their larger surface area facilitate metal adsorption; however, metals do tend to get associated with coarser sediments (sand) fraction particularly when derived from anthropogenic sources. Similar observations were reported in the present study during premonsoon season where sand exhibited a significant positive association with Fe and Pb. Sand particles remain in place for a longer period (Tessier et al. 1982) and occasionally develop coatings of oxides that might have helped the retention of Pb on Fe oxide coatings present on sand particles (Badr et al. 2009). The greater surface area of finer grained sediments, chelating nature of OC, and the scavenging nature of Fe-Mn oxides seem to have facilitated the adsorption of trace metals in sediments.

Pollution indices

Geo-accumulation index (Igeo)

According to Muller scale (Muller 1979), the average Igeo values of Cr (1.42 ± 0.31 , 1.34 ± 0.50 , 1.27 ± 0.11) and Pb (1.50 ± 0.14 , 1.04 ± 0.34 , 1.25 ± 0.4) in monsoon, postmonsoon, and premonsoon seasons respectively suggest that the estuarine sediments of the Mandovi estuary range from unpolluted to moderately polluted (Fig. 4). It was attributed to their anthropogenic input through sewage sludge, antifouling paints from fishing

boats, boat exhaust, and barges used for transportation of Fe-Mn ores.

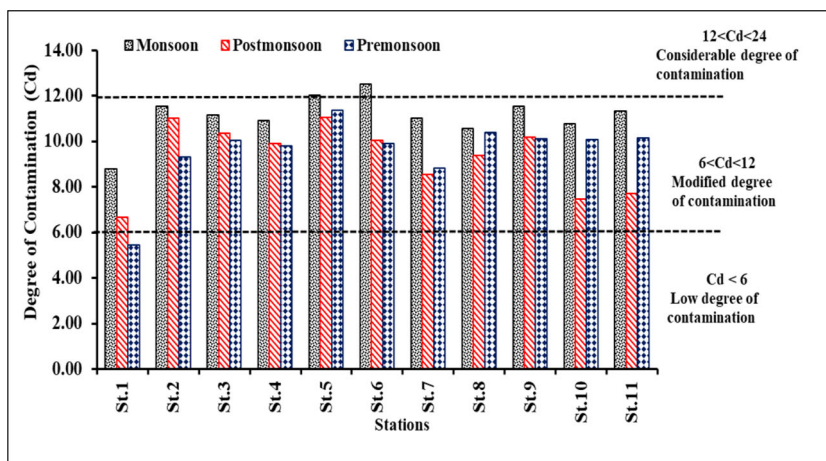
Contamination factor

In the Mandovi estuary, Fe and Mn showed low contamination throughout the estuarine region during all three seasons (Fig. 5). Cu, however, showed a moderate contamination at station 2. CF for zinc showed moderate contamination during monsoon season while a low contamination during postmonsoon and premonsoon seasons. On the other hand, Cr displayed considerable contamination for all three seasons along the estuarine region, except at station 1 in monsoon; stations 1, 2, 10, and 11 in postmonsoon; and stations 1 and 11 during the premonsoon seasons where a moderate contamination was reported. Likewise, Pb showed a considerable contamination during monsoon and premonsoon seasons with the exception at station 1. In postmonsoon season, moderate contamination of Pb in surface sediments was reported from stations 6 to 11 towards the upper estuarine region, whereas stations 1 to 5 towards the lower estuarine region were considerably contamination with Pb. The calculated CF value for individual trace metals was found in the respective decreasing order of abundance: Pb (4.25) > Cr (4.10) > Zn (1.53) > Cu (0.75) > Fe (0.36) > Mn (0.11) during monsoon; Cr (4.00) > Pb (3.17) > Zn (0.88) > Cu (0.79) > Fe (0.37) > Mn (0.07) during postmonsoon; and Cr (3.72) > Pb (3.67) > Cu (0.90) > Zn (0.80) > Fe (0.40) > Mn (0.08) during premonsoon season. In Mandovi estuary, CF inferred considerable contamination of Cr and Pb which was attributed to their anthropogenic sources. Their presence in high concentration in sediments can have adverse effects on the Mandovi estuarine ecosystem.

Pollution load index (PLI)

The PLI values are presented in Fig. 6. Notably PLI values at stations 2, 5, 9, and 10 during monsoon and at stations 2

Fig. 7 Variation of degree of contamination for surface sediments of the Mandovi estuary



during postmonsoon seasons were > 1. The sampling stations with PLI values > 1 suggested metal pollution in sediments. Further, more number of stations exhibited PLI value >1 during monsoon which was attributed to intensive river runoff carried metal input to the Mandovi estuary.

Contamination degree (Cd)

The results of contamination degree are presented in Fig. 7. Cd indicated moderate degree of contamination in sediments during all three seasons, with the exception of low degree of contamination at St.1 during premonsoon season and considerable degree of contamination at St.5 and 6 during monsoon season.

Modified degree of contamination

The modified degree of contamination was calculated using the equation proposed by Abraham and Parker (2008) modified from Hakanson (1980). The mCd varied from 1.46 to

2.08 (avg.1.85) in monsoon, 1.11 to 1.84 (avg. 1.55) in postmonsoon, and 0.91 to 1.89 (avg. 1.60) in premonsoon seasons (Fig. 8). In general, mCd values in the study area suggest low level of contamination (mCd<2) at all the sampling stations in all the three seasons except at station 6 in monsoon season where mCd values were >2 thus indicating moderate level of contamination.

Potential contamination index (Cp)

The potential contamination index (Cp) was measured for Fe, Mn, Zn, Cr, Cu, and Pb for monsoon, postmonsoon, and premonsoon seasons. Results of Cp values are given in Fig. 9. The Cp values for Fe and Mn, in all three seasons, showed low contamination while a moderate degree of contamination by Zn and Cu. Metals, viz., Pb and Cr, showed severe contamination in surface sediments based on the Cp values during all three seasons. The Cp showed the following decreasing order Cr> Pb > Zn> Cu > Fe > Mn during monsoon and

Fig. 8 Variation of modified degree of contamination mCd in surface sediment of the Mandovi estuary

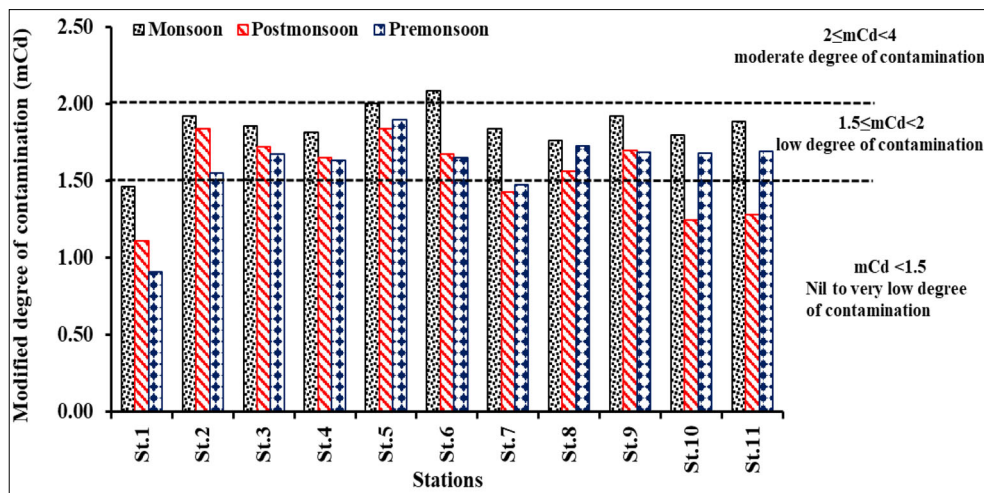
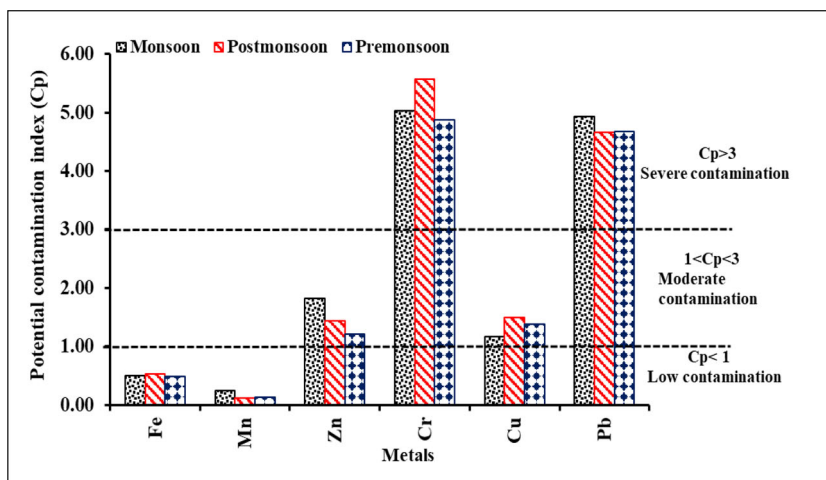


Fig. 9 Variation of potential contamination index (Cp) of trace metals in surface sediment of the Mandovi estuary



Cr > Pb > Cu > Zn > Fe > Mn during postmonsoon and premonsoon seasons.

Potential ecological risk

The values of potential ecological risk factor (E_r^i) and the ecological risk index (RI) are given in Table 2. The average E_r^i of Mn, Zn, Cr, Cu, and Pb was less than 40 during all three seasons and, thus, suggested low ecological risk in the Mandovi estuary. The order of single potential ecological risk coefficient (E_r^i) decline in the following sequence: Pb > Cr > Cu > Zn > Mn. Risk index ranged from 30.82 to 37.57 in monsoon season, 23.40 to 37.92 in postmonsoon season, and 16.37 to 36.01 in premonsoon season, thereby indicating low risk level at all the sampling stations where the RI values were below 40.

It is evident from the above data that there is no significant environmental risk occurring in the Mandovi estuary. However, environmental risk assessment in different seasons revealed relative higher risk during monsoon season as compared to other seasons. The higher environmental risk during monsoon can be directly related to the material input from the catchment area as well as heavy freshwater runoff. Many station points during non-monsoon periods were found to be under lower risk indicating lower ecological risk.

Factor analysis

The factor analysis matrix accounted by using ten sediment variables for monsoon, postmonsoon, and premonsoon seasons (Table 3). Factor analysis revealed three factors during monsoon season, two factors in

Table 2 Evaluation on potential risk of trace metals pollution in sediments from the Mandovi estuary

Sampling stations	Ecological risk for single metal E_r^i RI						Ecological risk for single metal E_r^i RI						Ecological risk for single metal E_r^i RI					
	Monsoon						Postmonsoon						Premonsoon					
	Mn	Zn	Cr	Cu	Pb	RI	Mn	Zn	Cr	Cu	Pb	RI	Mn	Zn	Cr	Cu	Pb	RI
St.1	0.06	1.03	4.94	2.41	22.37	30.82	0.06	0.68	3.81	2.41	16.44	23.40	0.04	0.74	4.54	2.29	8.75	16.37
St.2	0.11	1.64	7.57	5.80	22.23	37.35	0.12	1.44	5.58	7.49	23.29	37.92	0.10	1.21	6.13	6.90	15.33	29.68
S.t3	0.09	1.68	8.00	4.05	21.37	35.20	0.12	0.95	8.15	3.57	20.64	33.44	0.10	0.90	8.93	4.99	15.79	30.71
S.t4	0.07	1.46	8.79	3.25	19.85	33.43	0.07	0.73	8.69	3.23	19.16	31.89	0.08	0.63	9.61	3.62	16.17	30.10
S.t5	0.10	1.80	9.08	4.32	21.08	36.38	0.08	1.00	10.44	4.54	16.52	32.58	0.11	0.93	9.74	5.28	19.64	35.70
S.t6	0.05	1.82	10.06	3.94	21.71	37.57	0.06	0.69	10.55	3.35	14.83	29.48	0.08	0.64	8.66	3.60	18.79	31.77
S.t7	0.04	1.32	9.81	3.21	18.58	32.96	0.05	0.57	9.22	2.96	12.00	24.79	0.05	0.60	6.99	3.27	18.50	29.40
S.t8	0.09	1.45	8.12	3.70	19.08	32.44	0.06	0.95	9.34	4.54	11.56	26.45	0.06	0.76	7.18	5.00	22.41	35.42
S.t9	0.23	1.60	7.65	3.30	24.14	36.93	0.05	1.06	11.13	3.53	11.81	27.58	0.05	0.66	7.57	4.17	21.58	34.03
S.t10	0.25	1.58	6.20	3.09	24.64	35.77	0.07	0.60	5.56	3.74	14.56	24.54	0.08	0.76	7.11	4.46	21.54	33.95
S.t11	0.08	1.41	9.91	4.17	18.62	34.19	0.06	1.02	5.56	3.82	13.71	24.16	0.13	0.93	5.40	6.19	23.35	36.01
Mean	0.11	1.53	8.19	3.75	21.24		0.07	0.88	8.00	3.93	15.87		0.08	0.80	7.44	4.52	18.35	

Table 3 Factor loadings on elements in surface sediments from the Mandovi estuary

Variable	Monsoon			Postmonsoon		Premonsoon		
	F1	F2	F3	F1	F2	F1	F2	F3
Eigen values	4.25	2.75	1.28	5.35	2.79	4.85	3.50	1.02
Variance %	42.49	27.50	12.76	53.45	27.92	48.49	34.97	10.16
Sand	−0.91	−0.12	−0.35	−0.94	−0.19	0.98	−0.01	0.11
Silt	0.87	−0.12	0.36	0.94	0.05	−0.99	0.08	0.05
Clay	0.83	0.35	0.27	0.87	0.34	−0.94	−0.07	−0.25
OC	0.86	−0.02	−0.13	0.34	0.87	−0.75	0.51	−0.27
Fe	0.01	0.87	−0.08	−0.47	0.81	0.52	0.79	0.10
Mn	0.06	−0.03	0.93	0.46	0.68	0.04	0.86	0.20
Zn	0.22	0.88	0.25	0.13	0.89	−0.37	0.88	−0.19
Cr	−0.34	0.69	−0.51	−0.74	0.07	0.15	0.03	0.98
Cu	0.07	0.70	−0.11	0.09	0.94	0.09	0.99	−0.07
Pb	0.37	−0.08	0.88	0.68	0.56	0.91	0.35	0.05

Note: Entries in bold are significant

postmonsoon season, and three factors in premonsoon season which is thus explained by 82.75%, 81.37%, and 93.62% of the total variance. During monsoon season, factor one (F1) explained 42.49% of the total variability and was positively loaded by finer particles (silt, clay) and OC. It suggested organic matter adsorption on finer sediments. Factor two explaining 27.50% of the variance was strongly positively correlated with Fe, Zn, Cr, and Cu. It indicated scavenging nature of Fe-Mn oxyhydroxides in the estuary that regulated the distribution of metals in sediments. Similarly, third factor explained for 12.76 % of the variability that exhibited strong positive loading for Mn and Pb and suggested role of Mn oxyhydroxides as a host phase for Pb. During postmonsoon season, factor one (F1) explained 53.45% of variance. The strong positive loading of Pb, silt, and clay in first component indicated the association of Pb with fine fraction of sediments. Factor two (F2) explained 27.91% of the variability with high positive loadings for OC, Fe, Mn, Zn, Cu, and Pb. It highlighted role of OC and Fe-Mn oxyhydroxides as a major host phase for the abundance of Zn, Cu, and Pb. In premonsoon season, factor one (F1) explained 48.49% of variability with strong positive loading for sand and Pb. It also indicated good loading for Fe. It supported the role of Fe oxide coatings on the sand grains in the adsorption of Pb as discussed under the correlation analysis. Factor two (F2) accounted for 34.97% of variance with positive loadings for Fe, Mn, Zn, and Cu. It indicated role of oxides of Fe-Mn in sediments. Similarly, factor three accounted for 10.16 % of the variability with strong positive association for Cr. It might be due to the differential anthropogenic source in the Mandovi estuary.

Conclusions

The distribution of grain size in the lower estuary particularly during the monsoon season showed abundant of sand, whereas finer sediments (silt and clay) were low in concentration and vice versa during non-monsoon periods. Such a grain size sorting was attributed to waves and tidal energy-regulated processes. Moreover, high sand fractions at the upper estuarine region during monsoon season indicated coarser sediment input to the upper estuary carried by the heavy riverine runoff. The open-cast mining activities have been the principal assets of Fe, Mn, Zn, Cr, Cu, and Pb within the Mandovi estuary, in addition to fishing, industrial, and agricultural activities. Mn, Zn, and Pb exhibited high concentration during monsoon season which suggested their additions by heavy freshwater runoff. The use of statistical factor and correlation matrix analysis showed that geochemical distribution of trace metal in surface sediments was mainly controlled by fine-grained sediment particle, OC and Fe-Mn oxy-hydroxides. Further, an application of the pollution indices, viz, Igeo, CF, and Cp, showed high degree of contamination by Cr and Pb in the sediments as compared to rest of the metals. Additionally, Cd and mCd highlighted moderate level of metal contamination in the Mandovi estuary.

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Availability of data and materials Raw data will be made available on request.

Declarations

Ethics approval Not applicable

Consent to participate Not applicable

Consent for publication All the authors agree with the present submission of this paper.

Competing interests The authors declare no competing interests.

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