

Research Article

Impact of Past Iron Ore Mining on the Sediment Cores of Rivers of Goa. West-coast of India

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Abstract: In order to assess the long-term contamination history of pollutants due to intense mining activities in the adjoining areas of rivers of northern Goa, sediment core samples collected from three rivers viz, the Bicholim (BR), the Mandovi (MR) and the Terekhol (TR) were analysed for texture, Organic Carbon (OC), major elements (Fe, Al, Ca and Mg) and trace metals (Mn, Cu, Zn, Pb, Ni and Cr). Depositional environment of the cores was assessed based on the color and the distribution of OC. Environmental parameters such as contamination factor, geo accumulation, enrichment factor and pollution load index were used to assess the extent of pollution. In addition, correlation coefficients were calculated to understand their relationships among the major elements and trace metals and their sources. The study revealed that the Bicholim river is strongly polluted with Fe & Mn and moderately polluted with Pb & Cr. Whereas, the Mandovi river is moderately polluted with Mn & Pb. On the other hand, Terekhol River (though unpolluted in the past) is getting polluted with Cu and Cr during recent years because of human interference. The results indicate that mining has a considerable impact on the Bicholim and Mandovi river sediments which in turn affect the ecology of bottom-dwelling organisms.

Keywords: Bicholim, mandovi, major, minor elements, terekhol

INTRODUCTION

Mining, a very important economic activity in many countries today including India, cause significant environmental degradation (IBM, 2002) such as water and soil contamination and biodiversity loss (Bhattacharya *et al.*, 2006; Luptakova *et al.*, 2012). Rivers are the dominant supplier of sediments to estuaries and adjacent seas. The transport and deposition of fine-grained, riverine sediments in estuaries are largely controlled by three factors: estuarine mixing, aggregation (flocculation) and primary particle properties (Rao and Chakraborty, 2016). The anthropogenic input of elements, particularly due to rapid economic development in coastal areas, has caused a severe environmental crisis in aquatic ecosystems (Daskalakis and O'connor, 1995; Ruiz *et al.*, 2005; Xu *et al.*, 2015; Zang and Liu, 2002). Some of metals (e.g., Fe, Mn, Cr, Cu, Ni, Co, Zn and Pb) are of particular concern due to their persistence in the environment, bioaccumulation and high toxicity (Cai *et al.*, 2011; Hu *et al.*, 2013; Simpson and Batley, 2007; Wang and Rainbow, 2008; Wang *et al.*, 2015).

Goa is one of the highest mineral producing states in India and its economy mainly depends on iron and manganese ore mining and export (Goa exports 70.1%

of India's iron ore). Goa is crisscrossed by seven rivers, out of which Mandovi and Zuari are the major drainages. Mining associated activities such as ore loading, transportation of ore to platforms, effluents from beneficiation plants and barge-building activity were taking place for a long time. Mining activity, particularly surface excavations, is affecting soils, surface and groundwater, fauna and flora (Nayak, 2002; Rath and Venkataraman, 1997). Mining in Goa has resulted in an environmental degradation that was first felt in the year 1978 due to large-scale exploitation of mineral resources and as a consequence 287 mining concessions/leases were terminated (Nayak, 2002) and again in the year 2012, that led to a complete ban on mining activities in Goa (Kessarkar *et al.*, 2015).

Earlier studies mostly carried out on the Mandovi-Zuari river systems mainly focuses on biological, geochemical and mineralogical aspects by different authors (Dessai *et al.*, 2009; Dessai and Nayak, 2009; De Sousa, 1999; Kessarkar *et al.*, 2013; Murty *et al.*, 1976; Qasim and Sen Gupta, 1981; Rao *et al.*, 2011; Singh *et al.*, 2014; Upadhyay and Sen Gupta, 1995; Varma and Rao, 1975). However, information on metal contamination and their distribution in sediments of Bicholim and Terekhol rivers are scanty. An attempt has been made to assess the impact of past iron ore

mining by collecting 3 riverine sediment cores from Bicholim and Mandovi rivers running through mine areas and Terekhol river from the non-mining region.

MATERIALS AND METHODS

Study area: Rivers namely Bicholim River (BR), Mandovi RIVER (MR) and Terekhol River (TR) are selected based on their geographical locations, hydrodynamic conditions and anthropogenic activities (Fig. 1). BR a tributary of Mandovi river flows through an iron-ore mining affected area located in Bicholim Taluka of North Goa. The mining area comprises five continuous leases covering an area of 498.10 ha. MR receives abundant river runoff and sediment discharge only during the wet, monsoon season (June-September) and negligible runoff during the dry season (October-May). Estuarine circulation is dominated by tidal and wind-induced currents during the dry season and, the intrusion of saline water has been reported up to 45 km from the mouth of the estuary (Manoj and Unnikrishnan, 2009). Mining of Fe-Mn ores has been an important activity in the drainage basin since 1940. The fine-grained ore deposits stored on the shores flushed into the river during heavy monsoon rains. Ore deposits are also loaded onto barges at several iron-ore loading dock stations along the upper estuary (Prajith *et al.*, 2015). TR in its upper reaches is known as the Banda river and in the lower reaches as the Terekhol. The Redi port (fair weather port) with two working jetties performing lighterage operations for more than 40 years and handles up to one Million Tons Per Annum of iron ore (EIA/EMP, 2012).

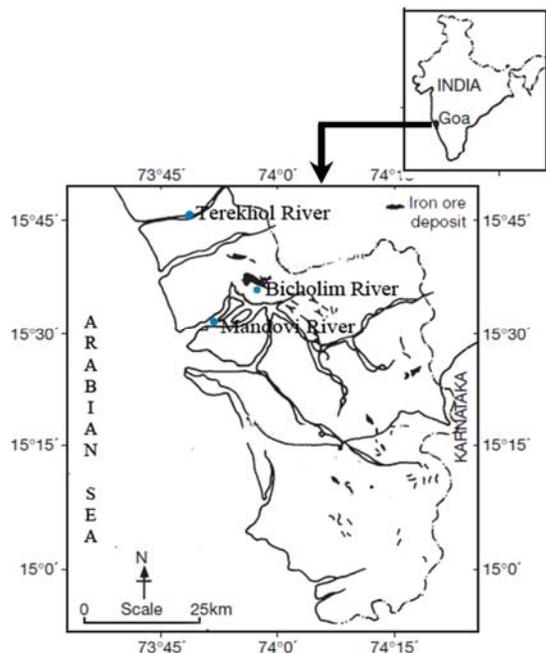


Fig. 1: Station location map

Sampling: The core samples were collected from three rivers using acrylic pipes (50 cm long and 4.5 cm diameter) at a depth of 1 m. Inspection on the field revealed that the cores are intact without any disturbance at the surface. The sediment core collected from BR was in a yellowish brown color whereas; cores collected from MR and TR exhibited grey with dark patches and grey color respectively (Fig. 2). The cores were sliced at 2 cms interval and preserved in the deep freezer until the analyses. The samples were dried at 60°C in a hot air oven and in total, 80 subsamples were analyzed for grain size, organic carbon, major elements and trace metals content. The sediment grain size was analyzed by pipette analysis following Folk (1968). The Organic Carbon (OC) content in the sample was determined following Loring and Rantala (1992).

Major elements and trace metals: For elemental analysis, 0.3 g of each sample was digested using an acid mixture (HF:HNO₃: HClO₄ in the ratio 7:3:1) (Jarvis and Jarvis, 1985) and evaporated almost to dryness by using ANALAB hot plate. Supra pure acids (Merck) were used for digestion and Milli Q water was used for the preparation of standard solutions and dilutions. After cooling the residue was dissolved and diluted to 50 mL with 1N HNO₃. The samples were analyzed for major elements (Fe, Al, Ca and Mg) on ICP-OES (Model: Agilent 710 series). A multi-element standard (23 elements, Merck Germany) was used for calibration. Instrument sensitivity was frequently monitored with respect to mixed standard solutions during the analysis. Trace metals (Mn, Cu, Zn, Pb, Ni and Cr) were analyzed on an Atomic Absorption Spectrophotometer (AAS Model GBC 932 AA). A standard stock solution of each metal was prepared using Merck standard solutions. The precision and accuracy of the metal analysis were checked against certified reference material (SCO-I) in triplicate. The recoveries of all the total metals were good which lie between 88% to 99% except for Cu, for which it was 81%. Pearson's correlation coefficient was employed to understand the interrelationship between metals and other sediment parameters.

Evaluation of statistical parameters:

Enrichment factor: Enrichment factor is one of the indices to compute the sedimentary metal source contributed by anthropogenic activities or by natural sources (Adamo *et al.*, 2005; Bastami *et al.*, 2012; Vald'es *et al.*, 2005). This index is calculated based on a normalization element (Fe or Al) which moderates the variation produced by heterogeneous sedimentation (Landsberger *et al.*, 1982; Loring, 1991). In this index, Al is used as a normalizing element because of its exclusive lithogenic origin, huge availability and its potential minute variations will not affect the significance of the elements to be investigated (Helz, 1976; Rule, 1986). The EF values calculated by using the following formula:

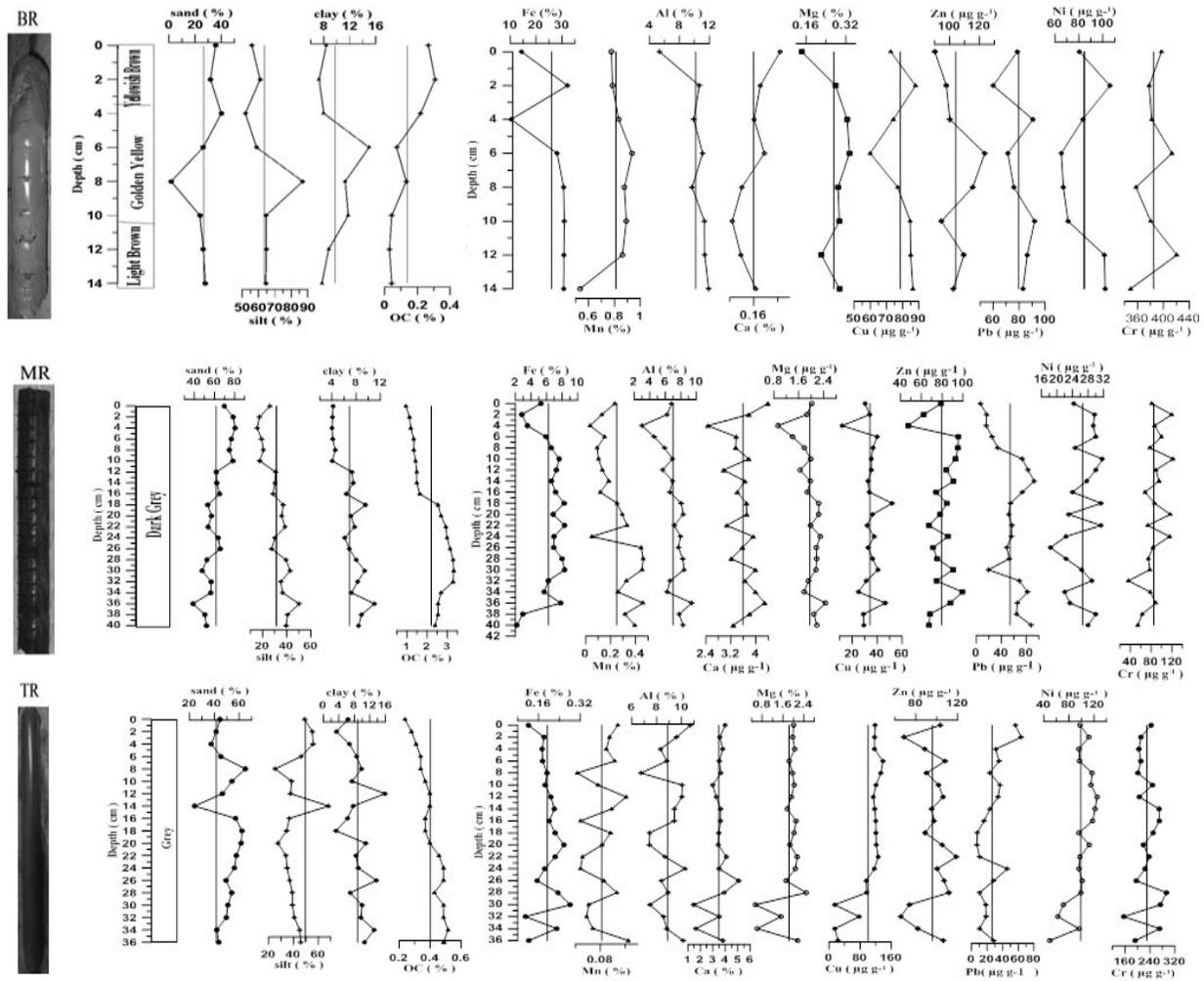


Fig. 2: Down core variation of sand, silt, clay, OC, major elements (Fe, Mn, Al, Ca and Mg) and trace metals (Cu, Zn, Pb, Ni and Cr) in sediment cores of Bicholim river (BR), Mandovi river (MR) and Terekhol river (TR)

$$EF = (Y/X)_{\text{sample}} / (X)_{\text{reference}} \quad (1)$$

where,

Y sample : Trace element concentration in the sample

X Reference : Trace element concentration in the continental crust (Wedepohl, 1995)

Y sample : Al content in the sample

X Reference : Al content in the continental crust (Magesh *et al.*, 2011)

Five contamination categories are recognized based on the enrichment factor (Acevedo-Figueroa *et al.*, 2006).

- EF < 2 Deficiency to minimal enrichment
- EF = 2 to 5 Moderate enrichment
- EF = 5 to 20 Significant enrichment
- EF = 20 to 40 Very high enrichment
- EF > 40 Extremely high enrichment

Contamination factor: The level of contamination in the sediment core is expressed by Contamination Factor (CF), which was calculated using trace metal data and metal concentration for the world shale average (Wedepohl, 1971) as the background value. The CF is calculated by using the following equation:

$$CF_{\text{metal}} = C_{\text{metal}} / C_{\text{background}} \quad (2)$$

where,

C metal : Metal contamination in polluted sediment

C background : Background value of that metal

Four categories of contamination factor have been distinguished:

- 1 ≤ CF Low contamination
- 1 ≥ CF < 3 Moderate contamination
- 3 ≥ CF < 6 Considerably contaminated
- 6 ≥ CF Highly contaminated

Pollution load index: The Pollution Load Index (PLI) is calculated by using the following equation (Tomlinson *et al.*, 1980):

$$PLI = n \sqrt{(CF1 \times CF2 \times CF3 \times \dots \times CFn)} \quad (3)$$

where,

CF = Contamination factor

n = Number of metals

Index of Geo-accumulation: Geo-accumulation Index (Igeo) (Muller, 1979) is calculated in order to determine the extent of metal contamination in sediments by comparing current concentrations with pre-industrial levels. The Index was computed using the following equation (Loska *et al.*, 2004; Magesh *et al.*, 2011; Muller, 1981; Selvaraj *et al.*, 2004):

$$I_{geo} = \log_2 C_n / 1.5B_n \quad (4)$$

where, C_n is the measured concentration of the element in the core sediment and B_n is the geochemical background value (average shale) in the earth's crust (Wedepohl, 1995). Factor 1.5 allows for natural fluctuations in the content of a given substance in the environment with very small anthropogenic influences. Six classes of the geochemical index have been distinguished (Muller, 1981).

Class Value Sediment Quality

- 0 $I_{geo} < 0$ Practically uncontaminated
- 1 $0 < I_{geo} < 1$ Uncontaminated to moderately contaminated
- 2 $1 < I_{geo} < 2$ Moderately contaminated
- 3 $2 < I_{geo} < 3$ Moderately to heavily contaminated
- 4 $3 < I_{geo} < 4$ Heavily contaminated
- 5 $4 < I_{geo} < 5$ Heavily to extremely contaminated
- 6 $5 < I_{geo}$ Extremely contaminated

RESULTS AND DISCUSSION

Sediment composition and texture: The sediment core collected at BR recorded the highest silt content (63.6%) followed by sand (26.7%) and clay content (9.8%) (Table 1). However, MR recorded higher values of sand (61.7%); moderate silt (31.4%) and low values of clay (6.9%), whereas TR showed a high percentage of sand (49.6) and silt (41.55) and low clay content (8.85%) (Table 1). Based on the sand, silt and clay composition, the texture of the sediment was assessed as sandy silt in BR core, while silty sand in MR and TR cores.

The down core variation of sand in BR core showed a decreasing trend from the bottom up to the 8 cm depth and thereafter showed an increasing trend up to the surface of the core. Distribution of silt and clay compensates the sand throughout the length of the core (Fig. 2). Sand showed a decreased and silt showed an increased peak at 8 cm depth in BR core. On the other hand, the down core variation of sand showed a fluctuating increasing trend from bottom to the surface of the core, whereas the distribution of silt and clay compensates the variation of sand throughout the length of the MR core (Fig. 2). The down core variation of sand in TR core showed an increasing trend from the bottom up to the 16 cm depth and showed a decreased value at 14 cm and thereafter it showed an increasing trend up to the 8 cm depth and further it showed decreasing trend up to the surface of the core (Fig. 2). Distribution of silt compensates the variation of sand throughout the length of the core. Clay showed almost a decreasing fluctuating trend from bottom to the surface of the core. Higher silt content in BR core may be due to the settling of particles during river mixing resulting in faster settling of fine colloidal aggregates in the region (Dessai and Nayak, 2007).

Organic carbon (%) content varied from 0.03-0.31 (0.14) in BR core; 0.95-3.32 (2.21) in MR core and from 0.24-0.52 (0.40) in TR core (Table 1). Down core variation of OC (Fig. 2) showed an increasing trend

Table 1: Range and average values for sand, silt, clay, OC, major elements and trace metals in cores collected from Bicholim river (BR), Mandovi river (MR) and Terekhol river (TR) of Goa, West coast of India

	BR core		MR		TR	
	Range	Average	Range	Average	Range	Average
Sand (%)	1.67-40.07	26.66±11.48	38.66-80.52	61.7±11.51	24.07-64.95	49.60±9.89
Silt (%)	51.90-87.02	63.56±10.54	15.48-50.32	31.40±9.51	25.19-68.23	41.55±10.30
Clay (%)	7.31-14.96	9.79±2.66	4.00-11.02	6.90±2.09	3.28-15.92	8.85±3.23
OC (%)	0.03-0.31	0.14±0.11	0.95-3.32	2.21±0.83	0.24-0.52	0.40±0.08
Fe (%)	10.40-32.11	25.98±8.54	2.19-8.33	6.26±1.89	0.11-0.28	0.19±0.05
Mn (%)	0.53-0.94	0.81±0.12	0.03-0.46	0.25±0.14	0.04-0.12	0.08±0.03
Al (%)	5.32-11.90	10.16±2.10	3.00-9.41	6.99±1.45	6.74-10.71	8.90±1.11
Ca (%)	0.12-0.20	0.16±0.03	2.46-4.38	3.58±0.45	1.47-5.08	3.47±0.08
Mg (%)	0.14-0.33	0.27±0.06	0.93-2.46	1.96±0.34	0.54-2.49	1.83±0.49
Cu (µg/g)	59.99-87.99	78.49± 9.47	11.99-52.00	34.23±7.87	14.66-138.66	100.10±39.16
Zn (µg/g)	90.24-123.57	104.28± 11.21	47.24-99.57	79.57±13.04	65.47-118.90	95.80±14.87
Pb (µg/g)	60.00-92.00	79.75± 10.69	6.33-92.67	53.76±25.62	7.00-63.67	26.58±16.17
Ni (µg/g)	65.33-106.00	84.54± 16.59	18.33-31.67	26.60±3.85	49.33-125.33	99.10-19.95
Cr (µg/g)	349.33± 420.33	384.70± 24.71	36.33-122.33	85.25±21.69	156.00-292.66	230.35±35.42

from bottom to surface of the BR core. The down core variation of organic carbon in MR core showed a decreasing trend from the bottom up to the surface of the core. Similarly, the down core variation of OC in TR core also showed a decreasing trend from bottom to the surface of the core (Fig. 2). Relatively lower values in the top few cms of the core are due to oxidation of OC and higher values at the bottom are due to lack of oxygen for decomposition of organic matter. Low organic carbon content in BR core could be due to oxidation of organic matter above the sediment-water interface. Constant flushing by tidal activities along with the impact of waves causes the oxidation of organic matter in the water column (Sundararajan and Natesan, 2010). This is also supported by the yellowish brown color of the BR core (Fig. 2) indicating the organic material has been oxidized and leached to some degree. The dissolved oxygen concentration in the bottom water also plays an important role in the decomposition of OC. Relatively higher values of OC in MR core indicates that primary production in the overlying water column influences the organic carbon content in the sediment core during their deposition period (Devassy, 1983). This is also supported by grey color with dark patches. Moderate OC values in TR core indicate that the sediments are collected from reducing environments. This was also supported by the grey color of the TR core (Fig. 2). Relatively high concentrations of OC in the top few sections of the core indicate the adsorption and incorporation of organic matter from the overlying water column. Lower values at the bottom may probably due to the dominance of decomposition overproduction of organic matter (Sundararajan and Natesan, 2010). The composition of the sediment affects the retention of trace metals since trace metals are strongly correlated with certain constituents. The constituents are able to bind trace metals chemically to their structure by means of adsorption, surface complexation and (co-)precipitation. The compounds most able to retain trace metals are characterized by large specific surface areas, high surface charges and high cation exchange capacities, which are generally related to the smaller grain sizes. The most common materials meeting these criteria are clay minerals, organic matter, hydrous manganese oxides and hydrous iron oxides (Horowitz, 1991).

Their ability to concentrate heavy metals in descending order is manganese (hydr)oxides, organic matter, iron (hydr)oxides and clay minerals (Forstner, 1982). Clay minerals also act as substrates for the precipitation and flocculation of organic matter and secondary minerals, such as hydrous iron and manganese oxide (Zhang and Yu, 2002; Lion *et al.*, 1982). Thus rather than the metal adsorbs on to the clay mineral it is carried by the clay mineral on its coating of secondary minerals and organic matter. Therefore grain size is by far the parameter to help to interpret the data as it integrates all the other parameters (Horowitz, 1991).

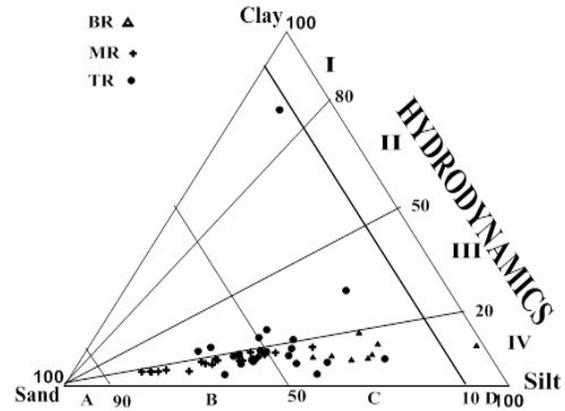


Fig. 3: Triangular diagram for the classification of hydrodynamics of cores BR, MR and TR (Pejrup, 1988)

To understand the hydrodynamic conditions in which sediment deposition took place, the ternary diagram proposed by Pejrup (1988) were employed (Fig. 3). Sediment samples of BR core fell in section IVC indicating the deposition of finer sediments under the very violent condition, whereas sediment in MR core fell in IV B and IVC indicating the deposition of finer to coarser sediment in very violent hydrodynamic conditions. However, sediments of TR core fell in section IIIB, IIIC, IVB and IVC indicating that grain size varies from finer to coarser and deposited in violent hydrodynamic condition.

Geochemistry of major elements: Among the major elements, Fe exhibited abnormally high percentage (25.98 ± 8.45) in BR core compared to MR core (6.26 ± 1.98) and TR core (0.19 ± 0.005) (Table 1). In the case of TR core, the percentage of Fe is much lower than that of shale value. Hence, the lower value of Fe in TR core cannot be explained except dilution by other minerals containing Ca and Mg (Table 1). Similarly, Mn (%) also showed higher concentration in BR core (0.81 ± 0.12) and lower values in MR core (0.25 ± 0.14) and in TR core (0.08 ± 0.03). While the first two cores (BR and MR) were enriched with Mn compared to the shale value, no such enrichment was observed in case of TR core (Table 2). Other major elements (%) Al (10.16 ± 2.1), recorded slight enrichment while Ca (0.16 ± 0.03) and Mg (0.27 ± 0.006) reported depletion in BR core. On the other hand, Ca showed enrichment in MR (3.58 ± 0.45) and TR (3.47 ± 0.08) sediment cores (Table 1).

In general, the down core variation showed a decreasing trend for Fe (up to 4 cm), Al and Mg in BR core; Fe, Mn, Al and Mg in MR core and Fe in TR core sediments (Fig. 2). However, Mn and Ca showed an increasing trend from the bottom up to the surface in BR core sediments. On the other hand, down core variations showed an irregular trend for Ca in MR core; Ca and Mg showed an irregular trend from the bottom

Table 2: Data on Pearson's correlation between different sediment components sand, silt, clay and OC, major elements (Fe, Mn, Al, Ca and Mg) and trace metals (Cu, Zn, Pb, Ni and Cr) in sediment core of a. Bicholim river (BR), b. Mandovi river (MR) and c. Terekhol river (TR) (n = 8), MR (n = 21) and TR (n = 19)

Parameters	Sand	Silt	Clay	OC	Fe	Mn	Al	Ca	Mg	Cu	Zn	Pb	Ni	Cr
a.														
sand	1.00													
silt	-0.97	1.00												
clay	-0.46	0.24	1.00											
OC	0.40	-0.31	-0.47	1.00										
Fe	-0.60	0.58	0.26	-0.50	1.00									
Mn	-0.24	0.10	0.65	-0.03	-0.03	1.00								
Al	-0.21	0.17	0.19	-0.63	0.66	-0.05	1.00							
Ca	0.52	-0.52	-0.18	0.61	-0.51	-0.26	-0.66	1.00						
Mg	-0.17	0.09	0.40	-0.29	0.24	0.13	0.73	-0.40	1.00					
Cu	-0.03	0.20	-0.66	-0.04	0.43	-0.47	0.33	-0.47	-0.15	1.00				
Zn	-0.53	0.41	0.66	-0.47	0.37	0.38	0.43	-0.17	0.50	-0.50	1.00			
Pb	0.11	-0.11	-0.04	-0.51	-0.33	-0.01	0.09	-0.47	0.00	0.11	-0.24	1.00		
Ni	0.42	-0.25	-0.81	0.17	0.17	-0.63	0.23	0.08	-0.22	0.71	-0.35	-0.16	1.00	
Cr	0.34	-0.44	0.30	-0.08	-0.15	0.59	-0.13	0.18	-0.29	-0.41	0.21	0.01	-0.08	1.00
b.														
Sand	1.00													
Silt	-1.00	1.00												
Clay	-0.96	0.95	1.00											
OC	-0.73	0.73	0.71	1.00										
Fe	-0.29	0.28	0.30	0.36	1.00									
Mn	-0.78	0.78	0.74	0.72	0.19	1.00								
Al	-0.77	0.77	0.72	0.64	0.33	0.70	1.00							
Ca	-0.31	0.33	0.23	0.16	0.13	0.28	0.58	1.00						
Mg	-0.67	0.68	0.62	0.58	0.34	0.60	0.98	0.65	1.00					
Cu	-0.38	0.36	0.42	0.23	0.60	0.26	0.59	0.44	0.62	1.00				
Zn	-0.12	0.12	0.09	0.02	0.52	-0.03	0.20	0.49	0.24	0.55	1.00			
Pb	-0.42	0.41	0.47	0.26	0.14	0.12	0.31	-0.04	0.30	0.06	0.23	1.00		
Ni	0.19	-0.20	-0.09	-0.35	-0.19	-0.31	-0.34	-0.32	-0.36	-0.01	-0.16	0.02	1.00	
Cr	0.44	-0.44	-0.44	-0.35	0.14	-0.45	-0.06	0.16	0.00	0.22	0.22	-0.22	0.00	1.00
c.														
sand	1.00													
silt	-0.95	1.00												
clay	-0.03	-0.28	1.00											
OC	0.09	-0.27	0.58	1.00										
Fe	0.22	-0.23	0.04	0.19	1.00									
Mn	-0.48	0.45	0.02	-0.28	-0.21	1.00								
Al	-0.43	0.43	-0.04	-0.12	-0.47	0.37	1.00							
Ca	0.05	0.00	-0.14	-0.25	-0.52	0.22	0.15	1.00						
Mg	0.20	-0.07	-0.39	-0.43	-0.32	0.27	0.30	0.77	1.00					
Cu	0.21	-0.09	-0.38	-0.65	-0.08	-0.03	0.03	0.58	0.68	1.00				
Zn	0.18	-0.24	0.21	0.01	0.03	0.28	0.26	0.49	0.56	0.35	1.00			
Pb	-0.36	0.41	-0.20	-0.52	-0.53	0.26	0.62	0.19	0.20	0.24	-0.11	1.00		
Ni	0.04	-0.02	-0.06	-0.48	0.35	-0.05	0.03	0.14	0.26	0.68	0.24	0.12	1.00	
Cr	-0.02	0.11	-0.28	0.01	0.66	-0.05	0.05	-0.40	-0.15	-0.12	0.15	-0.29	0.29	1.00

up to 30 cm and thereafter the values remained nearly constant up to the surface in TR core. The high Fe content in the former case (BR) can be explained due to intense iron ore mining activities as the river flows through mining area comprises of five major mining leases covering an area of 498.10 ha. The ore stored at different points on the shores of the river gets flushed into the river during heavy monsoon rains. While in the latter case (MR) discharge of ore residues during transport of iron ore by barges resulted in high concentration. The very high contents of Fe and Mn in sediment cores from the BR core indicate that they were sourced from ore material which accumulated at the core sites due to anthropogenic activity on the shores of the river (Prajith *et al.*, 2016). In general, the surface enrichment can be attributed to anthropogenic (mining) flux and its incorporation in sediments. The

observed values for major metals are in broad agreement with those reported earlier except Fe and Mn in BR core which showed somewhat higher values than that reported from other Indian rivers (Biksham and Subramanian (1988) Shah *et al.* (2013) Subramanian *et al.* (1985) Biksham and Subramanian (1988) Sundararajan and Natesan, 2010: Karabassi and Shankar, 2005: Magesh *et al.*, 2011: Achyuthan *et al.*, 2002: Alagarsamy, 2006: Singh *et al.*, 2014: Siraswar and Nayak, 2011: Veerasingam *et al.*, 2014: Nasnodkar and Nayak, 2015: Noronha-D'Mello and Nayak, 2015).

Geochemistry of trace metals: Trace metals such as Cu, Zn, Pb and Cr (except Ni) were enriched in BR core when compared with those of shale values, while only Pb in MR core whereas, all trace metals (Cu, Zn, Pb, Ni and Cr) were enriched in TR core (Table 1).

On the other hand, Ni in BR; Cu, Ni and Cr in MR sediment cores were impoverished compared to those of the shale values. Though the down core variation of trace metals was irregular, they showed a decreasing trend from bottom to the surface indicating surface enrichment due to leaching of metal from mine tailings and their subsequent incorporation in sediments (Fig. 2). This is particularly evident in case of Pb which has an additional atmospheric input apart from land as it is used in petrol as an additive. But in recent years this has been reduced to a greater extent by the use of leaded gasoline. Lead aerosols are carried to rivers and seas in rain and snow and are greatly scattered. The observed values of trace metals are in broad agreement with those reported earlier from other rivers (Biksham and Subramanian (1988) Shah *et al.* (2013); Subramanian *et al.* (1985); Biksham and Subramanian (1988) Sundararajan and Natesan, 2010; Karabassi and Shankar, 2005; Magesh *et al.*, 2011; Achyuthan *et al.*, 2002; Alagarsamy, 2006; Singh *et al.*, 2014; Siraswar and Nayak, 2011; Veerasingam *et al.*, 2014; Nasnodkar and Nayak, 2015; Noronha-D'Mello and Nayak, 2015).

The capacity of the sediment to retain heavy metals is large under oxidized conditions and is controlled by adsorption and precipitation processes due to the affinity of these metals with many solids. In oxic conditions, the precipitation of trace metals with manganese and an iron (hydr) oxide is the dominant process and high correlations of trace metals with these (hydr) oxides can be expected (Luoma and Rainbow, 2008). The mobility of most metals under reducing conditions is further decreased due to the formation of barely soluble sulfide minerals (Du Laing *et al.*, 2009; Van der Perk, 2006), which microorganisms are able to catalyze (Burkhardt *et al.*, 2010).

Correlation coefficients of elements: To understand the influence of sediment components on metal distribution in the sediment, Pearson's correlation among the grain size, organic carbon and metals were performed. In BR core (Table 2a), Al showed good association with Mg and Cu showed a good association with Ni indicating their common source in the sediment core. The correlation coefficient of metals in MR core (Table 2b) showed a positive correlation between sand

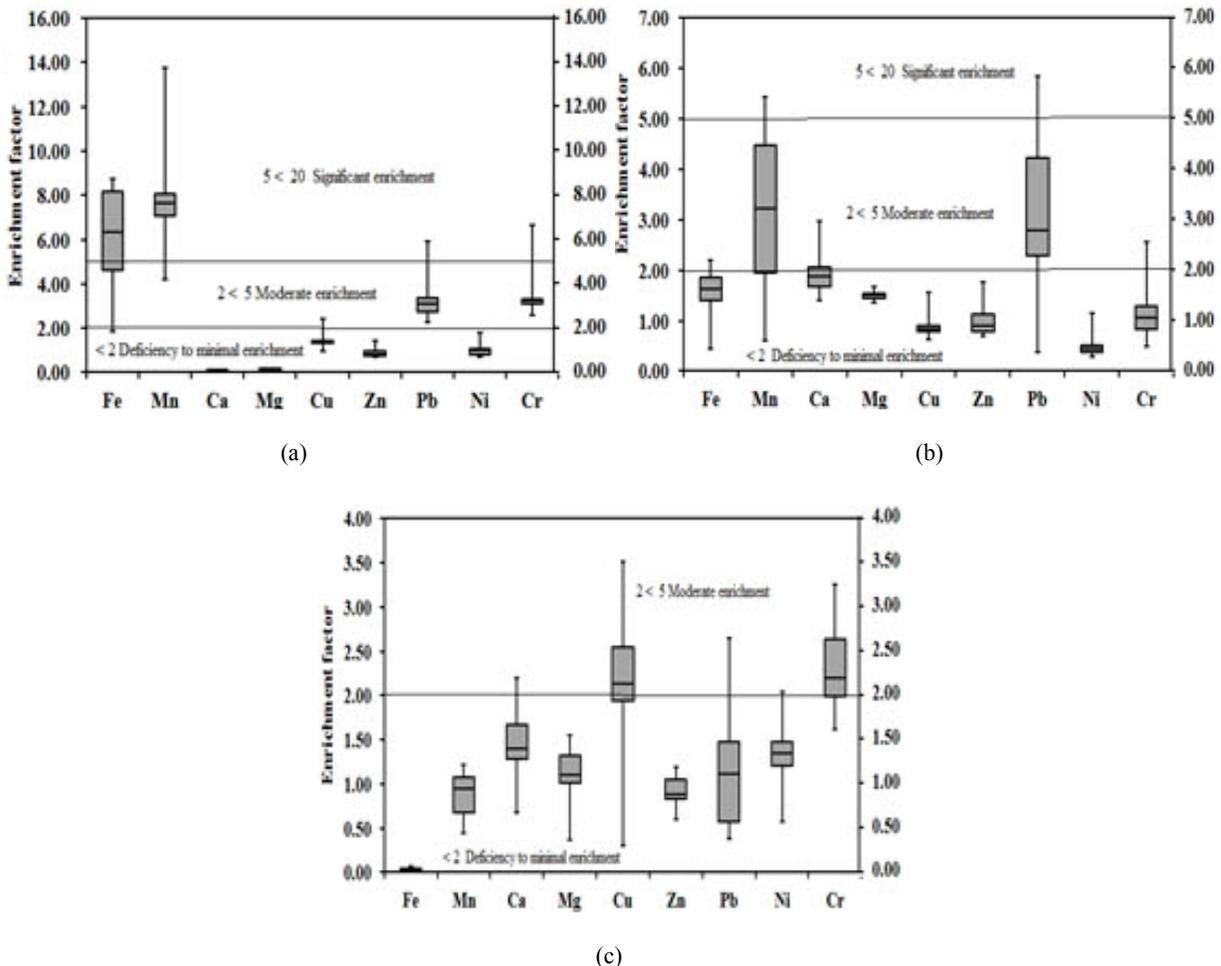


Fig. 4: (a) Enrichment factor for major elements and trace metals in cores collected from Bicholim river, (b) Mandovi river, (c) Terekhol river of Goa, West coast of India

and Cr indicating it is derived terrigenous. Whereas, silt, clay and OC showed a positive correlation with Mn, Al and Mg indicating that their association with finer sediments (Abílio *et al.*, 2006). Iron showed a strong positive correlation with Cu and Zn indicating their common source of origin in sediments. Fe-Mn is known to scavenge metals from the water column (Venkatramanan *et al.*, 2014). Significant relation of Al with Ca, Mg indicating their common source of origin in the sediment core. In TR core Fe showed significant correlation with Cr and Al showed good association with Pb (Table 2c) indicating that they must have originated from the same source. Ca and Mg showed significant positive correlation with Cu and Zn indicating their common source of origin.

Evaluation indices:

Enrichment factor: The Enrichment Factor (EF) is used to assess the metal contamination in the sediments of Bicholim, Mandovi and Terekhol rivers. In BR core Fe and Mn showed significant enrichment, Pb and Cr showed moderate enrichment, whereas Ca, Mg, Cu, Zn and Ni showed deficiency to minimal enrichment (Fig.

4a). Mn and Pb exhibit moderate enrichment, whereas Fe, Ca, Mg, Cu, Zn, Ni and Cr showed deficiency to minimal enrichment in the MR core (Fig. 4b). Enrichment factor in TR core recorded moderate enrichment for Cu and Cr, whereas Fe, Mn, Ca, Mg, Zn, Pb and Ni showed deficiency to minimal enrichment (Fig. 4c). Significant moderate enrichment of Fe, Mn, Pb, Cr and Cu in the three cores can be attributed to anthropogenic inputs while other elements (Ca, Mg, Zn and Ni) may be of crustal origin. According to Zang and Liu (2000), EF values between 0.05 and 1.5 indicate that the metal is entirely from crustal materials or natural processes, whereas EF values higher than 1.5 suggest that the sources are more likely to be anthropogenic.

Contamination Factor (CF): Contamination factor for BR core indicates that Fe and Mn are highly contaminated; Pb and Cr are considerably contaminated; Al, Cu, Zn and Ni are moderately contaminated whereas, Ca and Mg are low contaminated (Fig. 5a). Contamination factor of metals in MR core revealed considerable contamination for

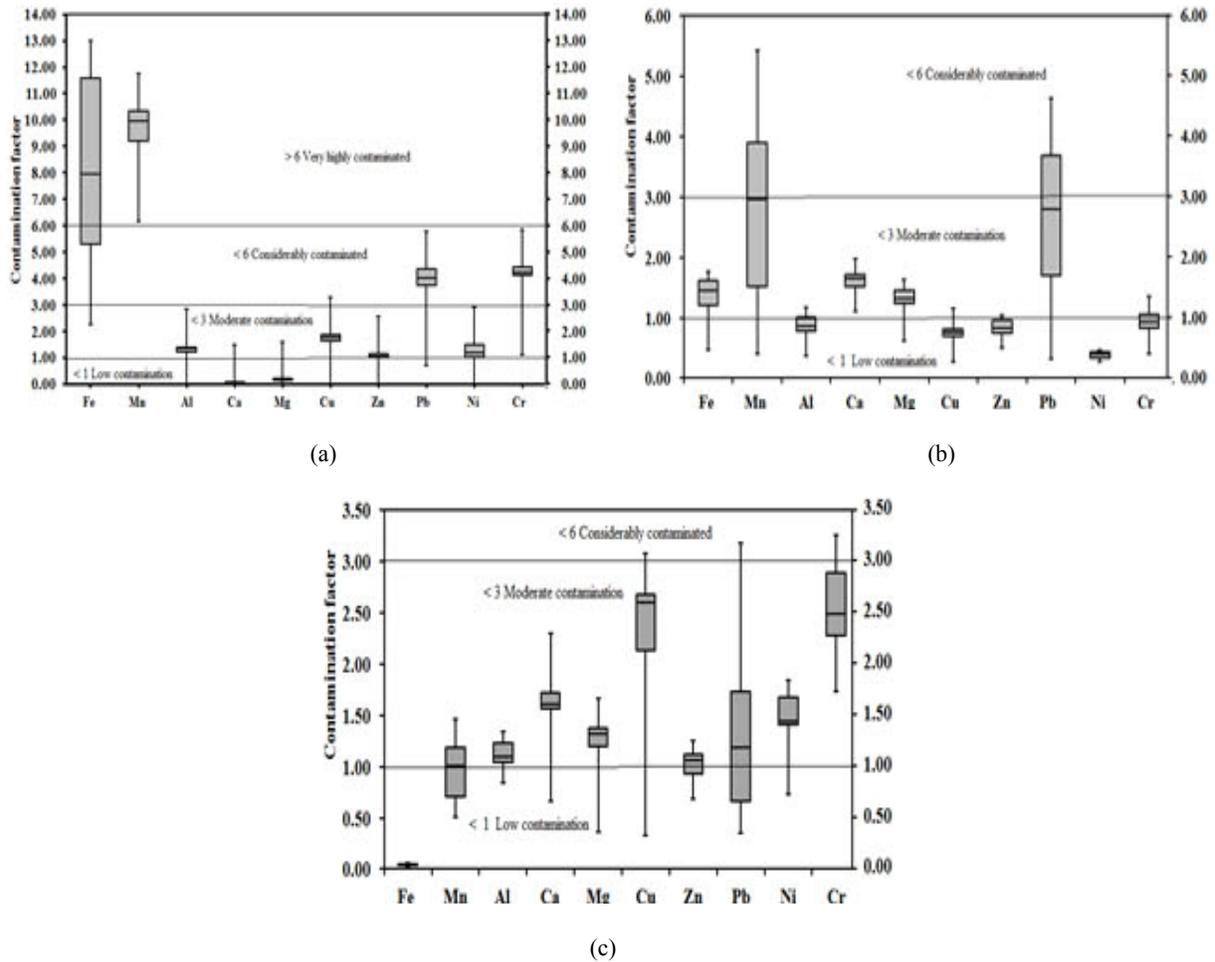


Fig. 5: (a) Contamination factor for major elements and trace metals in cores collected from Bicholim river, (b) Mandovi river, (c) Terekhol river of Goa, West coast of India

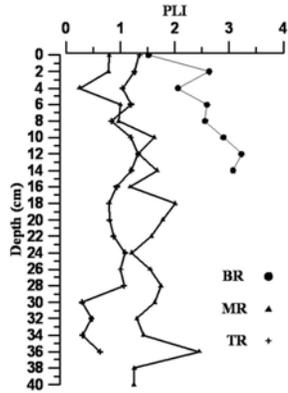


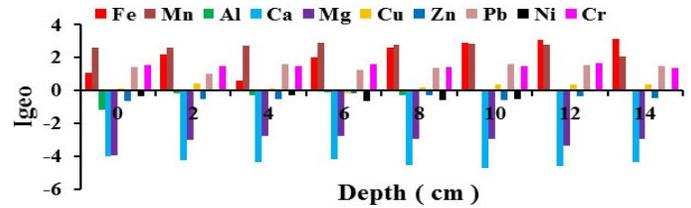
Fig. 6: Downcore variation of PLI in sediment cores of Bicholim river (BR), Mandovi river (MR) and Terekhol river (TR)

Mn and Pb; moderate contamination for Fe, Ca and Mg and low contamination for Al, Cu, Zn, Ni and Cr (Fig. 5b). Contaminator factor for TR core indicated moderate contamination for Mn, Al, Ca, Mg, Cu, Zn, Pb; and low contamination of Fe (Fig. 5c).

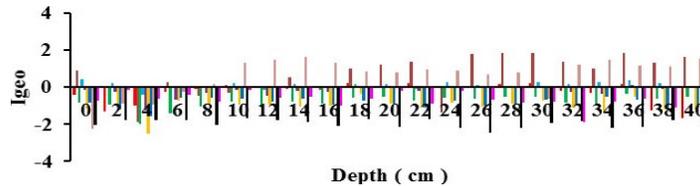
High contamination of Fe and Mn and considerable contamination for Pb and Cr in BR sediment core can be attributed to enormous mining activities and discharge of wastes in this region. Moderate

contamination of Al may probably due to using aluminum salts in treating wastes from the mining pits. Considerable contamination of Mn and Pb in MR sediment core may probably be due to runoff from mining waste which includes trace elements and minerals often associated with iron deposits (Chaturvedi and Patra, 2016). On the other hand, low contamination of Fe in TR core reveal that this area is not affected by mining activities (Kessarkar *et al.*, 2015).

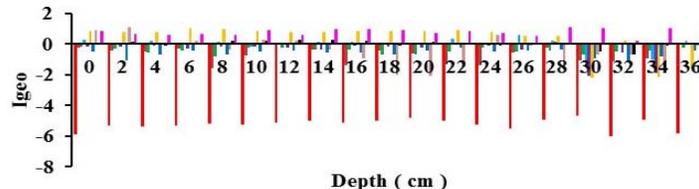
Pollution Load Index (PLI): PLI values in BR, MR and TR cores varied from 1.51 to 3.23 (2.57); 0.24 to 2.45 (1.37) and 0.29 to 1.35 (0.92) respectively. These results indicated that BR and MR cores are polluted (PLI >1) and TR core is unpolluted (<1). The down core variation of PLI (Fig. 6) in BR core showed a decreasing trend from bottom up to the surface of the core, in MR core it showed an irregular trend up to 16 cm depth and thereafter it showed a decreasing trend up to 4 cm depth and in TR core it showed a decreasing trend up to 30 cm depth and thereafter it showed an irregular trend up to 8 cm depth. On the other hand, TR core though showed an irregular trend, recorded surface enrichment of pollutants (up to 14 cm depth of the core). The down core variation of PLI values in BR and MR core revealed that enrichment of pollutants by one



(a)



(b)



(c)

Fig. 7: (a) Geo-accumulation (Igeo) for major elements and trace metals in cores collected from Bicholim river, (b) Mandovi river, (c) Terekhol river of Goa, West coast of India

to two times higher in bottom section compared to a surface section of the core. Higher PLI values of BR and MR cores can attribute to the enrichment of pollutants due to intense mining activities along the shores of Bicholim and Mandovi rivers.

Geo-accumulation Index (Igeo): Igeo is used for the quantification of metal accumulation in the study area (Fig.7a to c). Igeo grades in the study area varied from metal to metal and site to site (across metals and sites) (Rabee *et al.*, 2011). Igeo values in BR core is moderate to strongly polluted with Fe and Mn, moderately polluted with Pb and Cr, unpolluted to moderately polluted with Cu, whereas unpolluted with Al, Ca, Mg, Zn and Ni (Fig.7a). Igeo values for MR sediment core showed moderate pollution for Mn and Pb, unpolluted to moderately polluted by Fe and Ca and unpolluted for Al, Mg, Cu, Zn, Ni and Cr (Fig.7b). Igeo values for TR sediment core showed unpolluted to moderately polluted by Cu and Cr, whereas Fe, Mn, Al, Ca, Mg, Zn, Pb and Ni did not show any pollution (Fig.7c). The moderate pollution of Fe and Mn in sediment cores is directly related to Fe-Mn ore deposits and human-induced activity in handling and transportation of these ores through the river. Shynu *et al.* (2012) and Alagarsamy (2006) also observed a high value of Fe and Mn in suspended matter and surface sediments, respectively in the Mandovi river. The moderate contamination of Cu and Cr might be associated with the presence of boatyard and small vessel building yards. The increase of Pb in sediments is caused by the use of anti-fouling paints, combustion of petroleum and diesel in the boat, ferry and other traffic activities (Veerasingam *et al.*, 2014). Igeo values greater than 1 suggest that the metals (Fe, Mn, Pb and Cr) are derived from anthropogenic activities, while values less than 1 indicates that metals (Cu and Ca) are entirely derived from natural weathering processes.

CONCLUSION

The color of the cores was used to assess the condition of the environment accordingly BR core is collected from the oxidizing environment and MR and TR core are collected from reducing environment. The sandy silt texture of BR core and its relative lower organic carbon content also supports this view. On the other hand, MR and TR cores are of silty sand texture with relatively high organic carbon content supports that these derived from reducing environments. Of the 3 rivers, Bicholim river is more enriched with respect to Fe, Mn, Al, Zn, Pb and Cr due to large-scale extraction of minerals from Fe-Mn ores and dumping of their mine wastes. Enrichment of Ca and Mg in MR core may be due to larger marine input in addition to the diagenetic precipitation. On the other hand, enrichment of Cu and Ni in TR core may be due to anthropogenic input. Contamination factors revealed that Bicholim

and Mandovi river areas are highly contaminated for Mn due to the runoff from of the mining-related activities. High contamination of Cu in TR core could be due to the operation phase of cargo vessels and domestic wastes. Geo accumulation index (Igeo) of metals indicated that BR core is moderately polluted by Fe, Mn and Pb and it is believed to be due to anthropogenic input; MR core is moderately polluted by Fe, the ore deposits brought from the mines are stored and loaded onto barges at several shore stations in the upper/middle part of the river and transported through the river to the port for export and also due to natural weathering process and TR core is unpolluted to moderately polluted by Cu. Pollution load index indicated that BR and MR sediment cores were polluted (PLI>1) whereas only the upper few centimeters of the TR core showed pollution. Hence, our study showed that past mining has an adverse impact on the sediment quality of Bicholim and Mandovi rivers.

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