Environment and Ecology 37 (3) : 704—714, July—September 2019
Website: environmentandecology.com ISSN 0970-0420

Assessment of Metal Contamination in Sediment Cores of Zuari and Kushavati Rivers with Reference to Past Mining in Goa, West-Coast of India

Nita Trimbak Rane, Vishnu Murty Matta

Received 14 January 2019; Accepted 19 February 2019; Published on 12 March 2019

Abstract The long-term contamination history of pollutants due to exhaustive iron-ore mining activities in the past was studied for 2 sediment cores collected from the Zuari River (ZR) and Kushavati River (KR) of Goa, West-coast of India. They are analyzed for the texture of the sediment, Organic carbon (OC), Fe, Mn and Al (major elements) and CU, Zn, Pb, Cr and Co (trace metals). The results indicated that ZR core is moderately polluted with Mn while KR core is strongly polluted with Mn and moderately polluted with Fe and Cr. Correlation coefficients are evaluated to understand the interrelationships between major elements and trace metals. The extent of pollution in the 2 rivers was assessed using statistical parameters such as Enrichment Factor, Contamination Factors, Pollution Load Index and Geo-Accumulation Index. The study revealed that iron-ore mining activities in the past have a considerable ecological impact on both the KR and ZR rivers which in turn affect the ecology of aquatic flora and fauna.

Keywords Kushavati river, Zuari river, Sediment core, Texture, Mining impact.

Nita Trimbak Rane, Vishnu Murty Matta*
Department of Marine Science, Goa University, Taleigao Plateau, Goa 403206, India
e-mail : nitags1805@gmail.com
vishnu5678@yahoo.com
*Corresponding author

Introduction

Iron-ore mining is one of the important economic activities in many countries including India, that has produced a tremendous amount of hazardous wastes in the nature (Modabberi et al. 2013). This results in piling up of overburden dumps that are the biggest manmade hillocks seen in the mining region. This causes water and soil contamination due to surface runoff during the monsoon and as they ultimately degrades ecosystem (Luptakova et al. 2012). The State of Goa (India) is well known for its iron and manganese ore production. Iron-ore mining-related activities such as loading of ore, transportation, the release of effluents from beneficiation plants, barge and shipbuilding activities contribute the large quantity of mining material in the catchment area of Zuari river. River sediments are usually derived from loose soils and serve as the major reservoirs of metals (Dessai et al. 2009). Trace metals released into water bodies are generally bound to particulate matter, which finally

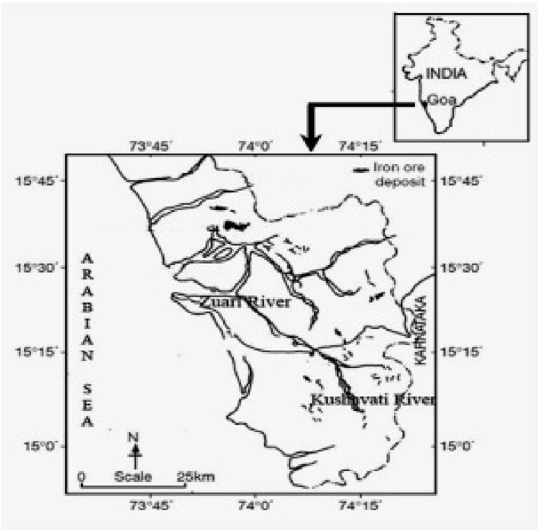

Fig. 1. Station location map.

settles down and get assimilated into sediments, hence the sediment cores are one of the most easily accessed natural archives used to evaluate and reconstruct historical pollution trend in aquatic environments (Liu et al. 2012, Devassy 1983).

The studies carried out on the Mandovi-Zuari riverine basin which mainly focused on biological and geochemical aspects by several researchers (Dessai and Nayak 2009, Rao et al. 2011, Prajith et al. 2015, Kessarkar et al. 2013, Singh et al. 2014). Although, some information is available on metal contamination and their distribution in the sediment core of Zuari river information on Kushavati river is very scanty. Hence, the attempt has been made to understand the impact of past iron-ore mining while evaluating metal concentrations in sediment cores collected from Kushavati river (KR) and Zuari river (ZR) of Goa West-coast of India.

Materials and Methods

Study area

Based on their geographical locations, hydrodynamic conditions and anthropogenic activities, the 2 rivers namely Zuari River (ZR) and its tributary Kushavati River (KR) were selected for the present studies (Fig. 1). KR is one of the major tributaries of KR which brings runoff from the mining dumps in the catchment area of Zuari (Dessai et al. 2009) and it is used for agricultural and drinking water supply. ZR is fed by monsoon precipitation and receives large volume water through land runoff. Geologically catchment area of Zuari is covered by and drains through rocks of the Dharwar Super Group of the Archaean Proterozoic age. Many mining-related activities such as ore loading, transportation of ore, discharge of effluents from beneficiation plants and barge-building activity within the river basin do take place.

The core samples were collected from 2 rivers using 50 cm long acrylic pipes with a 4.5 cm diameter. The sediment core collected from KR exhibited reddish brown color whereas, core collected from ZR was grey in color (Figs 2a, b). The cores were sliced to obtain a sub-sample at 2 cms interval and it was preserved in the deep freezer in polythene bags until the further analyses. The sub-samples were later dried at 60°C in a hot air oven. In all 32 sub-samples were analyzed for grain size, organic carbon (OC), major elements and trace metals. A pipette analysis technique given by Folk (1968) was adapted to analyzed sediment grain size. A 10 gm sediment sample was treated with 10 ml of 10% sodium hexameta phosphate solution is added to dissolve clay particles and 5 ml of 30% H_2O_2 is added in order to oxidize the organic matter. The sand contents were determined after wet-sieving. The remaining mud fraction was dried in an oven and weighed to calculate silt and clay contents. The organic carbon content in each sub-sample was estimated by Loring and Rantala (1992) method. A known weight of sediment sample was treated with a dichromate solution, this was followed by conc. H_2SO_4, Ag_2SO_4 was added in order to prevent oxidation of chloride ions. H_3PO_4 and NaF were added with ferrous ammonium sulfate using diphenylamine as an indicator.

For element analysis, a known weight of the sediment sample is digested using an acid mixture of $HF:HNO_3:HClO_4$ (7:3:1) and later it was evaporated almost to dryness by using ANALAB hot plate (Jarvis and Jarvis 1985). Supra pure acids of Merck

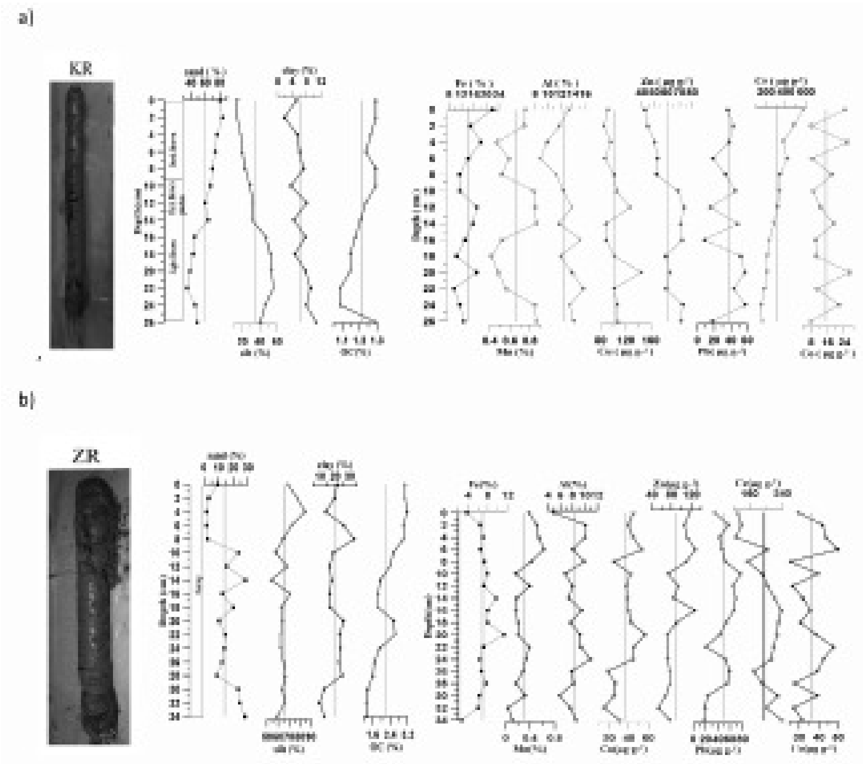

Fig. 2. Down core variation of sand, silt, clay, OC, major elements (Fe, Mn and Al) and trace metals (Cu, Zn, Pb, Ni and Cr) in sediment cores Kushavati river (KR) and Zuari river (ZR).

were used for digestion of the sediment and standard solutions were prepared using Milli Q water. The residue was cooled and dissolved to make 50 ml with 1N HNO_3. A standard stock solution of each metal was prepared using Merck standard solutions. The digested samples were analyzed for major elements (Fe, Mn and Al) using ICP-OES (Model-Agilent 710 series). The calibration of metals was done by using a multi-element standard (23 elements, Merck Germany). While analyzing, the instrument sensitivity was frequently monitored with respect to mixed standard solutions. However, trace metals (Cu, Zn, Pb, Cr and Co) for the study were analyzed by using Atomic Absorption Spectrophotometer (AAS Model GBC 932 AA). The precision and accuracy of the metals analyzed in this study were checked against certified reference Cody Shale (SCO-I) material in triplicate. The recoveries of the major elements and trace metals ontained were good, which lies between 88% to 99% except for Cu (81%).

Evaluation of statistical indices

Enrichment factor : Enrichment factor is one of the indices used to assess the sediment contamination source, which may be contributed either by anthropogenic influence or by the natural sources (Bastami et al. 2012, Taylor and Owens 2009). It is evaluated by normalization of the elements to be studied with Fe or Al. It is calculated according to the following formula :

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

Five contamination categories are used to classify based on the enrichment factor of the metals in the sediment core (Acevedo et al. 2006) :

EF values <2 signifies deficiency to minimal enrichment; EF values 2<5 exhibits moderate enrichment; EF values 5<20 indicates significant enrichment; EF values 20 < 40 signifies very high enrichment and EF values >40 shows extremely high enrichment.

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

$$CF_{(metal)} = C_{(metal\ concentration\ in\ sediment)} / C_{(background\ metal\ concentration)} ....2$$

Four categories of contamination factor have been used for classification :

1 ≤ CF Low contamination, 1 ≥ CF < 3 Moderate contamination, 3 ≥ CF <6 Considerably contaminated and 6≥ CF Highly contaminated.

Pollution load index (PLI) : equation given by Tomilson et al . (1980) was used for evaluating pollution load index in the sediment core as :

$$PLI = n\sqrt{CF1 \times CF2 \times CF3 \times ....CFn}$$

$$LI = n \sqrt{} (CF1 \times CF2 \times CF3 \times CF4 ....CFn) ....3$$

Where, n = total number of metals analyzed and CF = Contamination factor for each metal analyzed.

Index of geo-accumulation (Igeo) : It is calculated in the present study in order to determine the extent of contamination of metals in sediment core (Muller 1979). It was calculated using the following equation (Magesh et al. 2011) :

$$I_{geo} = \log_2 C_n / 1.5\ B_n ....4$$

C_n refers to the concentration of the elements in the sediment core sample and B_n is the shale value of elements in the earth's crust (Wedepohl 1995).

The 6 classses of the geochemical index have been given by Muller (1981) as follows :

Igeo values <0 (class 0) indicates Practically uncontaminated; 0 > Igeo values <1 (class 1) signifies uncontaminated to moderately contaminated; 1> Igeo values <2 (class 2) show moderately contaminated ; 2 > Igeo values <3 (class 3) indicates show moderately to heavily contaminated; 3 > Igeo values <4 (class 4) indicates heavily contaminated; 4> Igeo values <5 (class 5) is heavily to extremely contaminated and Igeo values >5 (class 6) indicates that sediment is extremely contaminated.

Results and Discussion

Sediment composition and texture

KR sediment core recorded (Table 1) high content of sand (59.46%); followed by silt (34.19%) and clay content (6.35%) thus showing silty-sand type texture. While ZR recorded high values of silt (66.25%) followed by clay (19.63%) and sand (4.12%) showing clayey silt type texture. Organic carbon content (%) varied from 1.09-1.29 (1.22) in KR core and from 1.31–3.17 (2.24) in ZR core (Table 1). The down core variation of sand showed an increasing trend in KR and a decreasing trend in ZR (Fig.2) from the bottom up to the surfcae of the core. Organic carbon showed an increasing trend from the bottom of the core up to the surface both in KR and ZR cores. Relatively higher values of organic carbon in few centimeters of the surface core could be an indicator of primary

Table 1. Range and average values for sand, silt clay, OC, major elements and trace metals in cores collected from Kushavati river (KR) and Zuari river (ZR) of Goa, West-coast of India.

Parameters	KR		ZR	
	Range	Average	Range	Average
Sand (%)	35.15 – 84.09	59.46 ± 16.47	1.71 – 28.44	14.12 ± 8.92
Silt (%)	14.05 – 55.76	34.19 ± 15.02	54.01 – 84.67	66.25 7.10
Clay (%)	1.86 – 10.58	6.35 ± 2.34	9.42 – 32.99	19.63 ± 5.94
OC (%)	1.09 – 1.29	1.22 ± 0.08	1.31 – 3.17	2.24 ± 0.67
Fe (%)	9.67 – 22.00	14.23 ± 3.44	2.65 – 11.28	6.98 ± 1.89
Mn (%)	0.41 – 0.86	0.6 ± 0.17	0.04 – 0.62	0.30 ± 0.16
Al (%)	8.80 – 15.71	12.72 ± 1.94	4.93 – 10.91	8.31 ± 1.55
Cu (µ g g^{-1})	85.33 – 144.66	102.19 ± 16.42	14.99 – 56.66	37.18 ± 11.43
Zn (µg g^{-1})	42.24 – 73.57	60.78 ± 11.05	53.24 – 128.90	89.64 ± 22.27
Pb (µ g g^{-1})	8.33 – 57.67	36.9 ± 16.07	17.67 – 77.33	47.48 ± 18.12
Cr (µg g^{-1})	153.67 – 571.66	304.21 ± 123.69	126.67 – 238.66	196.02 ± 36.69
Co (µg g^{-1})	7.67 – 26.33	15.05 ± 7.03	25.67 – 49.67	36.07 ± 7.45

Table 2. Comparison of elemental data in the present study with that of rivers from Goa.

Location	Fe (%)	Mn (%)	Al (%)	Cu (μg-g^{-1})	Zn (μg-g^{-1})	Pb (μg-g)	Cr (μg-g)	Co (μg-g)	Reference
Zuari river	3.0–13.2	0.05-0.54		16.5-169.5	32.3-158.8	nd	22.8-242.0	27.0-110.8	Dessai et al. (2009)
Mandovi river	5.81-13.30	0.08±0.50	5.61 - 10.45	64-96	64-125		183-303	28.25-194	Singh et al. (2014)
Mandovi river	1.39-1.72	0.026 ± 0.03	0.52-0.74	112-117	32-39		37-55	7.00-13.00	Siraswar and Nayak (2011)
Zuari river	10.54	0.21	11.59	42.11	127.38		318.08	23.23	Noronha and Nayak (2015)
Kushavati river	14.23±3.44	0.7 ±0.17	12.72 ± 1.94	102.19 ± 16.42	60.78 ± 11.05	36.9 ± 16.07	304.21 ± 123.69	15.05± 7.03	Present study
Zuari river	6.98 ± 1.89	0.30±0.16	8.31 ± 1.55	37.18 ± 11.43	89.64 ± 22.27	47.48± 18.12	196.02± 36.69	36.07 ± 7.45	

production in the overlying water column of the sediment core influencing the organic carbon content in during their deposition period. It is also supported by grey color with dark patches of the cores indicating lack of oxidation and leaching of the materials (Fig. 2). In general, higher values of organic carbon are observed where silt clay content is high.

Metal geochemistry

The range and average values of different chemical elements (major and trace metals) are given in Table 1. KR core exhibited abnormally high concentrations of Fe (14.23 ±3.44) and Mn (0.66 ±0.17) as compared to ZR core for Fe (6.98 ±1.89) and Mn (0.4 ±0.16). KR and ZR cores are enriched with Mn when compared with the shale values. While Al (12.72±1.94) recorded slight enrichment in KR core however it did not show any enrichment in ZR core. Metals such as Cu (102.19 ±16.42) and Cr (304.21 ±123.69) in KR core and Pb (47.48 ± 18.12) and Co (36.07 ± 7.45) in ZR core are enriched when compared with shale values. However, Zn did not show any enrichment in both the cores (Table 1). Higher concentration of metals in the KR core could be related to the release of material directly from mining actvities as it is highly influenced by mining and associated acttivities. The iron ore mining activity along the central portion of the state involves open cast mining largely for iron and manganese in the southern sector and this region is largely controlled by southwest monsoon, it is expected that the large quantity of material flow from open cast mining to Zuari river is through tributaries such as the Kushavati river (Dessai and Nayak 2009). The observed values for Fe and Mn are much higher compared with other reports from Coastal waters of Goa (Table 2).

Pearson's correlation

The correlation matrix identified the relationships

Table 3. Correlation matrix for metals, sand, silt, clay and organic carbon of (a) Kushavati river (N=14) and (b) Zuari river (N=17).
(a).

	Sand	Silt	Clay	Oc	Fe	Mn	Al	Cu	Zn	Pb	Cr	Co
Sand	1.00											
Silt	-0.75	1.00										
Clay	-0.61	-0.07	1.00									
OC	-0.73	0.51	0.48	1.00								
Fe	-0.07	-0.14	0.28	0.11	1.00							
Mn	-0.76	0.64	0.38	0.76	-0.12	1.00						
Al	-0.44	0.30	0.30	0.21	0.22	0.24	1.00					
Cu	-0.31	0.17	0.26	0.60	0.32	0.40	0.19	1.00				
Zn	-0.65	0.59	0.27	0.63	-0.09	0.62	0.13	0.40	1.00			
Pb	-0.14	-0.05	0.27	0.20	0.52	0.03	0.11	0.18	0.30	1.00		
Cr	0.63	-0.60	-0.23	-0.65	0.24	-0.54	-0.02	0.07	-0.39	-0.11	1.00	
Co	-0.29	0.27	0.12	0.34	0.08	0.52	0.29	0.52	0.12	-0.07	0.00	1.00

Table 3. Continued.

(b).

	Sand	Silt	Clay	Oc	Fe	Mn	Al	Cu	Zn	Pb	Cr	Co
Sand	1.00											
Silt	-0.99	1.00										
Clay	-0.66	0.57	1.00									
OC	0.80	-0.82	-0.36	1.00								
Fe	0.53	-0.55	-0.23	0.41	1.00							
Mn	0.22	-0.24	-0.02	0.27	0.12	1.00						
Al	-0.67	0.65	0.54	-0.43	-0.18	0.18	1.00					
Cu	-0.50	0.48	0.45	-0.26	0.05	-0.03	0.37	1.00				
Zn	-0.62	0.61	0.47	-0.38	-0.38	0.40	0.48	0.37	1.00			
Pb	-0.15	0.22	-0.34	-0.39	-0.12	-0.06	-0.05	0.21	-0.13	1.00		
Cr	0.91	-0.89	-0.64	0.68	0.65	0.07	-0.49	-0.43	-0.75	-0.15	1.00	
Co	0.08	-0.09	0.01	-0.12	0.58	-0.16	-0.08	0.31	-0.21	0.45	0.12	1.00

among metals and major process governing the release of metals. The correlation coefficient matrix (Tables 3a and b) exhibited a significant positive correlation between organic carbon and silt, Mn, Zn and Cu indicating the metals are derived from finer fractions of sediments in KR core. Similarly, ZR core also exhibited a significant positive correlation between organic carbon and Co, Zn and Cu indicating that these are derived from the finer fractions of sediment (Table 3b). It is well established fact that organic carbon content, as well as fine sediments, are one of the important controlling factors in the abundance of trace metals in the sediment core (Rubio et al. 2000). Taking into account its high specific surface area, organic matter can form complexes with metals and conseqeuntly influence their distribution (Loomb 2001). Further flocculation of organic matter leads to more adsorption surfaces, thus resulting in an increase of adsorption rates. It is interesting to note that Fe showed a significant positive correlation with Pb, which indicates their common source of origin in both the cores since Fe-oxyhydroxide phase is a good scavenger of Pb and it is one of the major controlling factors for its distribution in the sediment cores.

Enrichment factor

The enrichment factor (EF) is used to assess metal contamination in the sediments of Kushavati (KR) and Zuari (ZR) rivers. Mn showed moderate to significant enrichment, Fe and Cr exhibited moderate enrichment, whereas trace metals Cu, Zn, Pb and

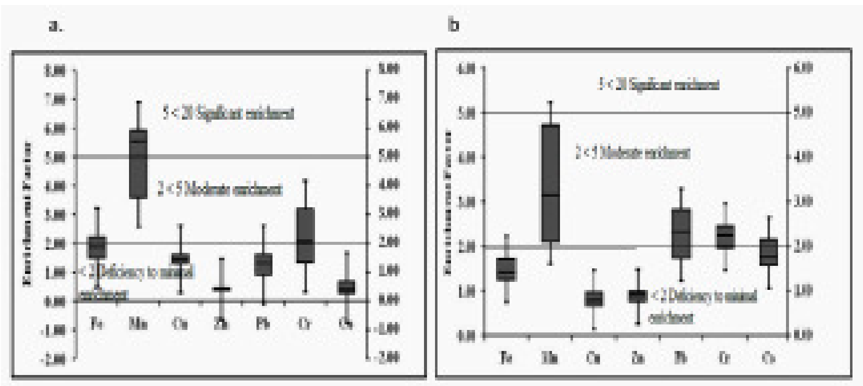

Fig. 3 . Enrichment factor for major elements and trace metals in cores collected from Kushavati river (a) and Zuari river (b) of Goa, West-coast of India.

Co showed deficiency to minimal enrichment in KR core (Fig.3a). In ZR core, Mn, Pb and Cr showed moderate enrichment, whereas, Fe, Cu, Zn and Co exhibited deficiency to minimal enrichment (Fig. 3b). Moderate enrichment of Mn, Pb and Cr can be attributed to anthropogenic inputs. According to Zang and Liu (2000), if EF values are between the range of 0.05 and 1.5 then it indicates that the metal is entire of crustal origin or is due to natural processes, whereas if EF values obtained are higher than 1.5 suggests that the sources are more likely to be due to anthropogenic influence. An overall higher EF value for Pb shows atmospheric deposition of Pb from fly ash and other industries and also from the constant movement of fishing boats and barges (Stephen-Pichaimani et al. 2008). Domestic and industrial effluents and atmospheric deposition may be the major anthropogenic sources of the observed high level of Pb. This element is used in industry in plumbing (pipes), solder, gasoline, drying agent for oils, glass, plumber's cement, covering of steel to prevent rust, batteries, as a pigment in paint. The main anthropogenic sources of Cr is pesticides and herbicides and used in alloys with lead and copper, oxidizing agents, Cr-plating, corrosion inhibitors, ceramics, glass (Hall et al. 2014).

Contamination factor (CF)

Contamination factors of KR core revealed that Mn is very highly contaminated; considerably contaminated with Fe and Cr; moderately contaminated with Al, Cu and Pb, while low contamination is shown by Zn and Co are (Fig. 4a).Contamination factors of metals in ZR core revealed considerable contamination of Mn; moderate contamination for Fe, Al, Pb, Cr and Co and low contamination for Cu and Zn (Fig. 4b). High contamination for Mn and considerable contamination for Fe and Cr in KR sediment core can be attributed to exhaustive iron-ore mining activities and discharge of mining wastes in this region. Moderate contamination of Al in the core may probably be due to the use of aluminium salts in the treatment of wastes from the mining pits. Considerable contamination of Mn in ZR core sediment may probably be due to run-off from mining waste dumps which include trace elements and minerals which are often associated with iron deposits and dumps piled along the shore (Chaturvedi and Patra 2016).

Pollution load index

PLI values for KR and ZR cores varied from 2.30 to 5.52 (3.78) and 3.88 (2.42) respectively. KR and ZR exhibited higher pollution load index values that can be attributed to the enrichment of pollutants due to exhaustive iron-ore mining activities along the shores of Kushavati and Zuari rivers. The down core variation of PLI values (Fig.5) in KR core showed an irregular trend from the bottom of the core up to the surface, whereas ZR core showed an increasing trend up to the 6 cm depth of the core and thereafter

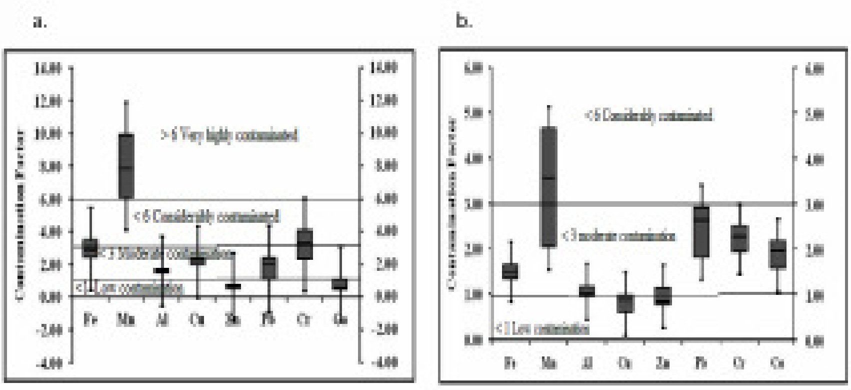

Fig. 4. Contamination factor and enrichment factor for major elements and trace metals in cores collected from Kushavati river (a) and Zuari river (b) of Goa, West-coast of India.

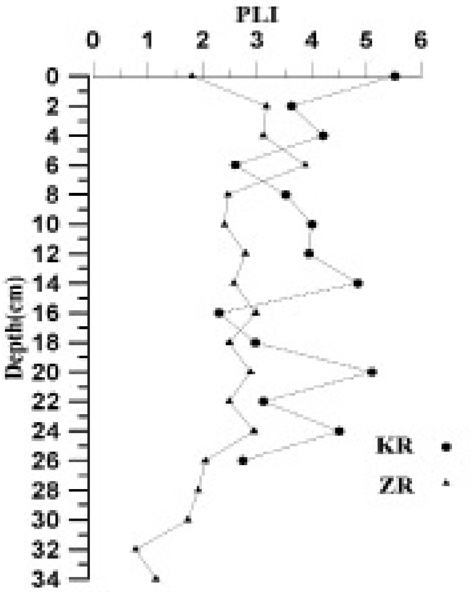

Fig. 5. Downcore variation of PLI in sediment cores of Kushavati river (KR) and Zuari river (ZR).

it showed a decreasing trend from 6 cm up to the surface of the core. The down core variation of PLI values in KR and ZR sediment cores revealed that enrichment of pollutants is higher by 1—2 times in bottom sections compared to the surface section of the core (Fig. 5).

Geo-Accumulation Index (I-geo)

Geo-accumulation Index values in KR core indicated that the sediments are moderately to strongly polluted with Mn (class 2); moderately polluted with Fe and Cr (class 1) ; whereas unpolluted to moderately polluted with Cu and Pb and however unpolluted with Al, Zn and Co (Fig. 6a). The Igeo values for ZR sediment core showed (Fig. 6b) moderate pollution for Mn; unpolluted to moderately polluted by Fe, Pb,Cr and Co and unpolluted for Cu and Zn. The moderate pollution (class 2) of Fe and Mn in sediment cores of the Kushavati and Zuari river is directly related to Fe-Mn ore deposits on the banks of the river, loading and transportation of it through the riverine system of Goa (Shynu et al. 2012). The moderate contamination of Cr in the sediment core might be associated with the presence of barge building and boatyards . I-geo values >1 in the present study, which suggests that the metals are mainly derived from mining related

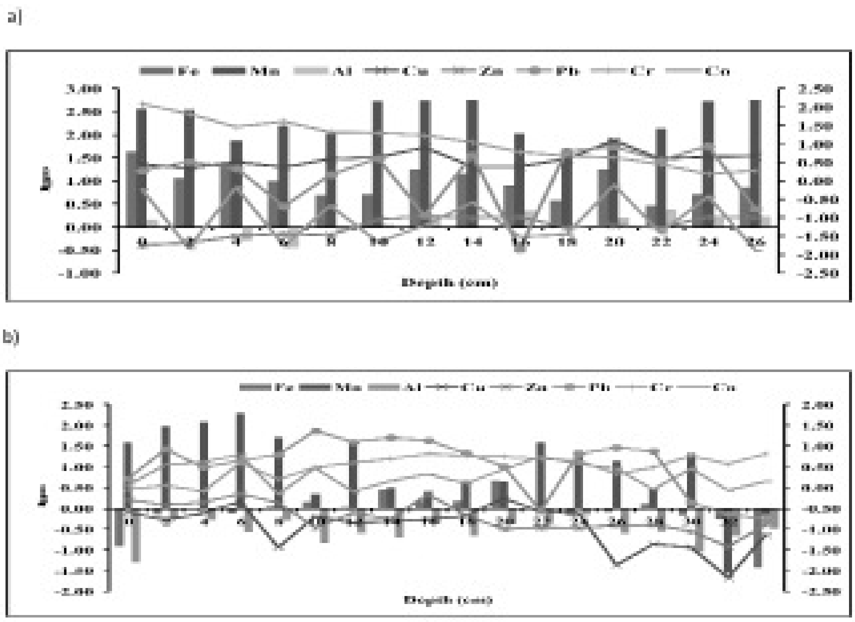

Fig. 6. Geo-accumulation (Igeo) for major elements and trace metals in cores collected from Kushavati river (a) and Zuari river (b) of Goa, West-coast of India.

anthropogenic activities, while values<1 indicates that they could have been derived from natural weathering processes. Ore processing units operate all along the banks of these 2 rivers and the industries also release associated elements to the waters of the river. In addition, the loading jetties in the upstream of Zuari and Kushavati river are also expected to release a considerable amount of Fe, Mn and Cr. Chromium may have been released as leachates from loading of mining ores and shipping activities at the Mormugao harbor located nearby in addition to effluents from treated domestic sewage and industrial discharges and corrosion of uncoated steels from ships in the harbor at the mouth and shipbuilding industries located along the river.

Factor analysis

Factor analysis is a technique commonly used to analyze geochemical matrices by creating one or more factors, each representing a cluster of interrelated variables within the data set. The identification of metal groups and their interrelations is important for source evaluation. Four factors with eigen values

Table 4. Factor analysis matrix after varimax rotation for core (a) KR and (b) ZR.

(a)

	Factor 1	Factor 2	Factor 3	Factor 4
Sand	-0.974430	0.074790	0.106462	0.125337
Silt	0.951141	-0.160248	-0.138220	-0.132818
Clay	0.751156	0.502093	0.138011	-0.029404
OC	-0.747684	0.398937	0.067589	0.246868
Fe	-0.468415	0.179175	0.783576	0.086035
Mn	-0.098372	0.030109	-0.006808	0.968270
Al	0.713618	0.173631	0.082870	0.244260
Cu	0.599727	-0.037610	0.530752	0.088131
Zn	0.702451	0.075638	-0.184925	0.539962
Pb	0.096761	-0.955580	0.177385	-0.039968
Cr	-0.913368	0.110536	0.236642	-0.028511
Co	-0.011883	-0.332011	0.857139	-0.157332
Expl Var	5.412644	1.548398	1.813007	1.426261
Prp Totl	0.451054	0.129033	0.151084	0.118855
% Variance	45.82	16.61	13.12	9.44

Table 4. Continued.

(b)

	Factor 1	Factor 2	Factor 3	Factor 4
Sand	-0.838345	-0.173601	-0.119781	-0.429034
Silt	0.779661	-0.259967	0.118586	0.206025
Clay	0.326675	0.571747	0.038075	0.398020
OC	0.788699	0.273708	0.382738	0.035684
Fe	-0.244622	0.755756	0.213203	0.219708
Mn	0.795153	-0.048729	0.407358	0.167357
Al	0.109492	0.111285	0.142450	0.878632
Cu	0.197274	0.316729	0.848806	-0.052888
Zn	0.766087	0.203544	0.214860	-0.148039
Pb	0.121323	0.831077	-0.055440	-0.097452
Cr	-0.846623	0.030103	0.269363	-0.010208
Co	0.129703	-0.158452	0.806349	0.293686
Expl Var	4.117673	1.943906	1.900501	1.355049
Prp Totl	0.343139	0.161992	0.158375	0.112921
%Variance	40.53	16.82	11.72	8.56

>1 were obtained for both the core. The loadings between principal factors and metals, as well as the positions of metals in the coordinates of the principal factors, are given in Tables 4a, b. In KR core, factor 1 accounted for 45.82% of the total variance shows significant positive loadings for silt, clay, Al and Zn and suggesting that these metals are derived from finer fractions of sediments. Factor 3 with 13.12% of the total variance shows significant positive loadings for Fe and Co represents a mixture of dust and pollutant mixed. Factor 4 with 9.4% of the total variance shows significant positive loadings for Mn representing dust dominated (Table 4a). Similarly, in ZR core four factors are drawn (Table 4b). Factor 1 has significant positive loadings for silt, organic carbon, Mn and Zn suggesting these are mostly derived from finer fractions of sediment. Factor 2 shows significant positive loading for Fe and Pb indicating that these are derived from a mixture of dust dominated and anthropogenic input. Factor 3 shows a significant loading on Cu and Co representing that these are derived from industrial emission. Factor 4 shows a significant loading for Al indicating its terrestrial origin.

Conclusion

The depositional environment of KR core is assessed as oxidizing while that of ZR core is from reducing environment based on the color of the core. This is also supported by the silty sand texture of KR core and its relative lower organic carbon content and clayey silt type texture with relatively high organic carbon in ZR core. Kushavati river is more enriched with respect to Fe, Mn, Al and Cr of the 2 rivers, due to large-scale extraction of minerals from Fe-Mn ores mines and dumping of their mine wastes. Enrichment of Pb, Cr and Co in ZR might be associated with the presence of and barge building and boatyard. Contamination factors revealed that KR and ZR core are highly contaminated with Mn due to runoff from adjacent mining activities. Geo-accumulation Index (I-geo) of metals in KR core indicated that it is moderately polluted by Fe, Mn and Cr and which may probably due to anthropogenic input; whereas ZR core is moderately polluted by Mn as it receives the runoff from Kushavati river which is the tributary of Zuari. The results of PLI studies indicated that KR (PLI = 3.78) and ZR (PLI =2.42) sediment cores are polluted. Factor loading revealed that the texture of the sediment and intensity of mining activities and anthropogenic input are major factors responsible for trace elements accumulation in both the rivers. However, the difference in the accumulation of pollutants in the 2 rivers can be related to the difference in the mining activities and the anthropogenic input of metal. It is therefore concluded that exhaustive iron-ore mining had a considerable impact on the sediment quality of KR and ZR.

Acknowledgement

The author (Nita Trimbak Rane) is grateful to the Department of Marine sciences, Goa University for providing the nescessary facilities to carry out the Research work. The author also thanks the Head, Department of Marine Sciences, Goa University, Goa for providing the necessary facilities to carry out this work.

References

Acevedo-Figueroa D, Jimenez BD, Rodriguez-Sierra CJ (2006) Trace metals in sediments of 2 estuarine lagoons from Puerto Rico. Environ Poll 141 : 336—342.

Bastami KD, Bagheri H, Haghparast S, Soltani F, Hamzehpoor A, Bastami MD (2012) Geochemical and geo-statistical assessment of selected heavy metals in the surface sediments of the Gorgan Bay Iran. Mar Poll Bull 64 : 2877-2884.

Chaturvedi N, Patra HK (2016) Iron-ore mining, waste generation, environmental problems and their mitigation through phytoremediation technology. Int J Sci Res Meth 5 (1) : 397—420.

Dessai DVG, Nayak GN, Basavaiah N (2009) Grain size geochemistry, magnetic susceptibility : Proxies in identifying sources and factors controlling distribution of metals in tropical estuary, India. Estuarine and Coastal Shelf Sci 85 (2) : 307—318.

Dessai D, Nayak GN (2009) Distribution and speciation of selected metals in surface sediments, from the tropical Zuari estuary, Central West-coast of India. Environ Monit Assess 158 : 117—137.

Devassy VP (1983) Plankton production associated with cold water incursion into the estuarine environment. Mahasagar 16 (2) : 221—233.

Folk RL (1968) Petrology of Sedimentary Rocks. Hemphil Publishing, Austin, pp 44—50.

Hall M, Sar E, Kurt MA (2014) Assessment of arsenic and heavy metal pollution in surface sediments of the Ergene River, Turkey. Poll J Environ Stud 23 (5) : 1581—1590.

Jarvis IJ, Jarvis K (1985) Rare earth element geochemistry of standard sediments : A study using inductively coupled plasma spectrometry. Chem Geol 53 : 335—344.

Kessarkar PM, Shynu R, Rao VP, Feng C, Tanuja N, Jing Z (2013) Geochemistry of the suspended sediment in the estuaries of the Mandovi and Zuari Rivers, Central West coast of India. Environm Monit and Assess 185 : 4461—4480.

Liu LY, Wang JZ, Wei GL, Guan YF, Zeng ET (2012) Polycyclic aromatic hydrocarbons (PAHs) in continental shelf sediment of China : Implications for anthropogenic influences on coastal marine environment. Environm Poll 167 : 155—162.

Loomb CAM (2001) Muddy Sedimentation in a Sheltered Estuarine Marina, West Park Marina, Auckland, New Zealand (Doctoral dissertation, University of Waikato).

Loring DH, Rantala RTT (1992) Manual for the geochemical analysis of marine sediments and suspended particulate matter. Earth Sci Rev 32 : 235—283.

Luptakova A, Ubaldini S, Macingova E, Fornari P, Giuliano V (2012) Application of physical-chemical and biological-chemical methods for heavy metals removal from acid mine drainage. Process Biochem 47 : 1633—1639.

Magesh NS, Chandrasekar N, Vetha Roy D (2011) Spatial analysis of trace element contamination in sediments of Tamiraparani estuary, Southeast coast of India. Estuar Coast Shelf Sci 92 : 618—628.

Modabberi S, Alizadegan A, Mirnejad H, Esmaeilzadeh E (2013) Prediction of AMD generation potential in mining waste piles in the sarcheshmeh porphyry copper deposit. Iran Environ Monit Assess 185 : 9077—9087.

Muller G (1979) Schwermetalle in den sedimenten des Rheins e Vera nderungen seit 1971. Umschau 79 : 778—783.

Muller G (1981) Die Schwermetallbelastung der sedimenten des Neckars und Seine Nebenflusse. Chemiker-Zeitung 6 : 157—164.

Noronha-D'Mello CA, Nayak GN (2015) Geochemical characterization of mangrove sediments of the Zuari estuarine system, West-coast of India. Estuarine Coastal and Shelf Sci 167 : 313-325.

Prajith A, Rao VP, Kessarkar PM (2015) Controls on the distribution and fractionation of yttrium and rare earth elements in core sediments from the Mandovi estuary. Western India Continental Shelf Research 92 : 59—71.

Rao VP, Shynu R,Kessakar PM, Sundar D, Michael GS, Narvekar T (2011) Suspended sediment dynamics on a seasonal scale in the Mandovi and Zuari estuaries, Central West-coast of India. Estuarine Coastal and Shelf Sci 91 : 78—86.

Rubio B, Nombela MA, Vilas F (2000) Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain) : An assessment of metal pollution. Marine Poll Bull 40 (11) : 968—980.

Singh KT, Nayak GN, Fernande LL, Borole DV, Basavaiah N (2014) Changing environmental conditions in recent past-reading through the study of geochemical characteristics, magnetic parameters and sedimentation rate of mudflats, Central West coast of India. Palaeogeogr Palaeo climato Palaeocol 397 : 61—74.

Shynu R, Rao VP, Kessarkar PM, Rao TG (2012) Temporal and spatial variability of trace metals in suspended matter of the Mandovi estuary, Central West-coast of India. Environ Earth Sci 65 : 725—739.

Stephen-Pichaimani V, Jonathan MP, Srinivasalu S, Rajeshwara Rao N, Mohan SP (2008) Enrichment of trace metals in surface sediments from the Northern part of Point calimere, SE coast of India. Environm Geol 55 : 1811—1819.

Taylor KG, Owens PN (2009) Sediments in Urban river basins : A review of sediment-contaminant dynamics in an environmental system conditioned by human activities. J Soils Sediments 9 : 281—303.

Tomilson DC, Wilson JG, Harris CR, Jeffrey DW (1980) Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Helgoland Mar Res 33 : 566—575.

Wedepohl KH (1971) Environmental influences on the chemical composition of shales and clays. Physics and Chemistry of the Earth 8 : 307—333.

Wedepohl KH (1995) The composition of the continental crust. Geochimica et cosmochimica Acta 59 : 1217—1232.

Zang J, Liu CL (2000) Riverine composition and estuarine chemistry of particulate metals in China Weathering features anthropogenic impact and chemical fluxes. Estuarine Coastal Shelf Sci 54 : 1051—1070.