

Assessments of Heavy Metals and Contamination Indices in Surface Sediments of Selected South Gujarat Estuaries at the West Coast of India

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ABSTRACT

The present study is for investigation of sediment in selected South Gujarat estuaries along the west coast of India. In this paper, the assessment of heavy metals in surface sediments with seasonal and annual periods were carried out. The average and range concentration (mg/kg) of heavy metals was 2.95 – 22.03 (7.31) for Cd; 7.2 – 33.1 (15.0) for Cr; 7.2 – 20.33 (13.84) for Cu; 311.2 – 512.5 (385.26) for Fe; 12.52 – 33.21 (19.19) for Mn; 1.84 – 11.69 (7.33) for Ni and 4.93 – 44.5 (19.96) for Pb. Assessment of heavy metals by cluster analysis and Pearson's correlation matrix was done and the results suggested positive and/or negative correlations among heavy metals

and with physico-chemical parameters. Cluster analysis showed that the sources of Cd and Mn were similar and sources of Pb and Cr were similar due to anthropogenic inputs. Enrichment factor (EF) and geo-accumulation index (I_{geo}) showed that the surface sediment of selected estuaries heavily contaminated by the Cd and Pb metals and this reflects the intensity of anthropogenic inputs associated to industrial discharge into the South Gujarat estuarine region.

Keywords: Selected South Gujarat estuaries, Heavy metals, Contamination indices, Cluster analysis.

INTRODUCTION

Coastal area and estuaries are the very productive aquatic ecosystems of the world, which have many ecological and economic values (Mathivaman and Rajaram 2013). Estuarine mangrove is dominant ecosystems that line the coasts of sub-tropical and tropical coastlines around the world and hold with diverse biodiversity (Wolf and Weissing 2012). It is considered the as most productive terrestrials and consequently, it plays a vital role as a primary producer in the estuarine systems, providing foods for inhabitants (the fauna communities) (Zulkifli *et al.* 2012) and also

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adjacent coastal food web (Marchand *et al.* 2011, Zulkifli *et al.* 2014). Mangrove is bio-indicators for different types of environmental pollution including heavy metals, organic pollutants and hydrocarbons.

Heavy metals are naturally occurring compound elements in the environment, which have different concentrations along with the earth's crust. They are non-degradable pollutants, which degraded slowly by the biological or chemical process (Singare *et al.* 2012). It became toxic and carcinogenic when it exceeds the permissible value.

Source of heavy metals in sediments can originate from both natural sources and human activities, it can enter the food web and cause health problems. Heavy metals came from different anthropogenic sources via various industries like i.e. fertilizer, automobiles, pesticides, paints, photographic papers, photo chemicals, textiles, electroplating, ore processing, mining industries (Lohani *et al.* 2008). The major reservoir of pollutants came from estuaries, rivers and their tributaries, which carries a vast amount of industrial and domestic wastage from upper stretches to the coastal region.

Sediment is a key indicator for water pollution (Nobi *et al.* 2010, Harikumar and Nasir 2010, Yang *et al.* 2012, Hui-na *et al.* 2012), especially for heavy metals, which enters from sediment to water column that can incorporate into the aquatic food webs through sediment-water exchanges and then biomagnified in food webs at higher levels (Hosono *et al.* 2011). This process may cause potential damage to mammals, vertebrates as well as to human health. Sediment provides habitations for numerous aquatic organisms that are polluted by various forms of hazardous and toxic substances, including heavy metals and they are carriers of sink heavy metals in the hydrological cycle (Baran and Tarnawski 2015, Ho *et al.* 2010). Most of the investigation in India was focused on heavy metal contamination in marine sediments on estuaries and semi-closed bays (Sugirtha and Sheela 2014, Mitra *et al.* 2012). Present study area, South Gujarat which is a golden corridor for industrialization and fishing activities for the last 20 years. There are many industries located in the bank of South Gujarat Rivers, which have an inversed

impact on the environment.

Several previous studies suggested that at these areas possess the high level of pollution in water and sediment (Zingde *et al.* 1979, Zingde *et al.* 1980, Zingde *et al.* 1986, Nirmal Kumar *et al.* 2009, Saha *et al.* 2017, 2001). Dudani *et al.* (2017) finding that the accumulation of heavy metals by mangroves and results shows high pollution in these areas due to the disposal of industrial effluents. With the help of the present study, we have evaluated the data set of heavy metals present in surface sediments. The aim of this study is to assess and monitoring the distribution of six heavy metal (Cd, Pb, Cu, Ni, Mn, Fe) with contamination indices in surface sediments of these estuaries.

MATERIALS AND METHODS

Study area

The present study area (South Gujarat), which is situated on the west coast of India and categorized as a tropical monsoon climate with strong precipitation mainly from June to November. In this study, four estuaries of South Gujarat were selected for the evaluation of heavy metal contamination in surface sediments. Selected estuaries with GPS co-ordination is: 1) Varoli (latitude 20.21163 N; longitude 72.75619 E), 2) Damanganga (latitude 20.41241 N; longitude 72.84033 E), 3) Kolak (latitude 20.46548 N; longitude 72.8574 E) and 4) Par (latitude 20.5341 N; longitude 72.8881 E) showed in Fig. 1.

All these rivers drain to the Arabian Sea at different locations. These rivers are peninsular hence in the summer mostly rivers are dried. In this region, sea presenter has a very high current and high tidal impact. Soil texture from these areas was muddy and salty rocky clay type. During the low tide period, the sea water penetrates up to 45 km from the sea. The opening regions of these estuaries receive a high amount of industrial as well as domestic effluents, which is the main source of various heavy metals. Major industrial wastewater discharged in these rivers, which contain effluent from the pharmaceutical Industries, Chemical Industries and pesticide others in the nearby vicinity. As a consequence of strong precipitation, river sediment transport characteristics



Fig. 1. Map of sampling locations (1) Varoli (2) Damanganga (3) Kolak and (4) Par estuaries of South Gujarat

in the catchment area may be variable.

Sample collection of sediments

Sediment samples were collected from four different located estuaries of South Gujarat with the seasonal collection. Total of 24 surface sediment samples were collected from the four adjacent estuaries of South Gujarat for the analysis of heavy metals. The surface sediment samples were collected from the surface top at the level of 0.5 cm depth and carried out with a Van Veen grab during three consequent seasons i.e., pre-monsoon (May), post-monsoon (November) and winter (March) for the year of 2015-2017. The short symbol S, PM, W for pre-monsoon, post-monsoon and winter respectively are used. Sediment samples were dried in an oven at 60-80°C in the laboratory, passed through a 100-mesh sieve (nylon) and then homogenized and keep in a desiccator until analysis.

Methods for sediment analysis

Heavy metals in sediments were digested and pre-

pared. The analysis of samples using the US EPA method of 3052 was carried out. Metals Cd, Cr, Cu, Ni, Mn, Fe and Pb were determined by inductively coupled plasma mass spectroscopy (ICP-MS, Shimadzu). The detection limits for heavy metals are Cr: 0.06 mg/kg, Cd: 0.1 µg/kg, Mn: 0.02 mg/kg, Cu: 0.1 mg/kg, Ni: 0.2 mg/kg, Fe: 0.2 mg/kg and for Pb: 0.2 µg/kg. Sediment samples were analyzed in three replicates for relative standard deviation (%RSD) which was less than 9.50% and this analysis was done by Coastal Center for Marine Research CCMR, Tuticorin, Tamilnadu. The pH, conductivity and salinity were determined using a standard protocol of Magdoff (1996), Smith and Doran (1996) and using Eutech PCD 650 instrument.

Assessment of metal contamination indices

The latent source and contamination of metal the enrichment indexes like Enrichment Factor (EF) and geo-accumulation index (I_{geo}) are used to assess the occurrence and intensity of anthropogenic contamination deposition on topsoil. These are intending

by normalization of one metal concentration in the topsoil with respect to the reference metal concentration of Earth crust (Turkeian and Woodphool 1967). Enrichment factor (EF) was done by the following equation:

$$EF = \left(\frac{C_m}{C_{fe}} \right)_{\text{sample}} / \left(\frac{C_m}{C_{fe}} \right)_{\text{background}}$$

Whereas, $(C_m/C_{fe})_{\text{sample}}$ is the ratio of the analyzed concentration of heavy metal (C_m) to that of Iron (C_{fe}) is analyzed sediment sample and $(C_m/C_{fe})_{\text{background}}$ is reference ratio in the background sample (Xu *et al.* 2018). Background value for sedimentary rocks (shale) value (mg/kg) were for Fe (47,200), Mn (850), Cu (45), Cr (90), Cd (0.3) and Pb (20) which is given by Turkeian and Woodphool (1967). The degree of metal enrichment is based on Enrichment factor (EF) value as : <2 : depletion to minimal enrichment, 2–5 : moderate enrichment, 5–20 : significant enrichment, 20–40 : very high enrichment, >40 : extremely high enrichment. The geo accumulation index (I_{geo}) is expressed as follows :

$$I_{\text{geo}} = \text{Log}_2 (C_n / 1.5B_n)$$

Where, C_n and B_n are the measured and background values of the analyzed metal. A factor of 1.5 is applied as of lithogenic effects. The I_{geo} is defined as Unpolluted ($I_{\text{geo}} \leq 0$), unpolluted to moderately

polluted ($0 < I_{\text{geo}} \leq 1$), moderately polluted ($1 < I_{\text{geo}} \leq 2$), moderately to strongly polluted ($2 < I_{\text{geo}} \leq 3$), strongly polluted ($3 < I_{\text{geo}} \leq 4$), strongly to extremely polluted ($4 < I_{\text{geo}} \leq 5$) and extremely polluted ($5 < I_{\text{geo}} \leq 6$).

Statistical analyses

In the present study, SPSS (statistical software) was used for cluster analysis (CA) and correlation analysis. For the determination of correlation of all these metals with physico-chemical parameters, the correlation matrix is used. Cluster analysis is performed for an element of different sources and finding the similarities of chemical properties, which could be done automatically by the hierarchical cluster analysis procedure.

RESULTS AND DISCUSSION

Heavy metals in surface sediments

The seasonal variations of heavy metals (Cd, Cr, Cu, Fe, Mn, Ni and Pb) concentrations at the selected locations along the South Gujarat estuaries in the surface sediment are shown in Figs. 2 (a), 2(b), 3(a), 3(b) and 4(a), 4(b). The range and average heavy metals concentrations (mg/kg) were Cd 2.95 – 22.03; (7.31), Cr 7.2 – 33.1; (15.0), Cu 7.2 – 20.33; (13.84), Fe 311.2 – 512.5; (385.26), Mn 12.52 – 33.21; (19.19), Ni 1.84 – 11.69; (7.33) and Pb 4.93 – 44.5; (19.96).

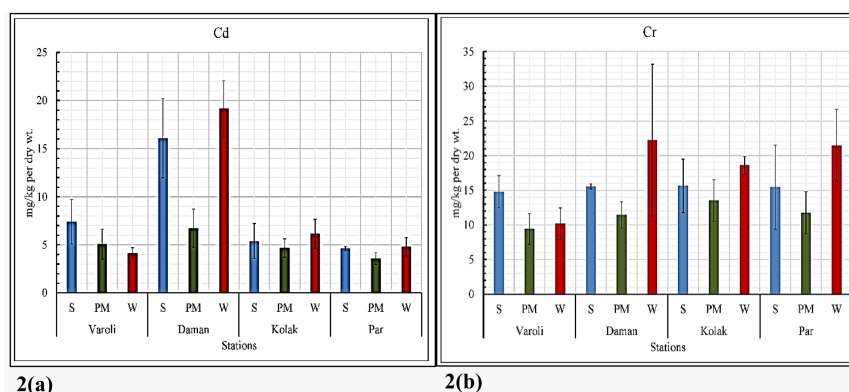


Fig. 2(a) and 2(b). Seasonal distribution of Cd (mg/ kg) and Cr (mg/kg) in the surface sediment samples of selected South Gujarat estuaries. Values expressed are average and vertical bar in each point represents the standard deviation (\pm).

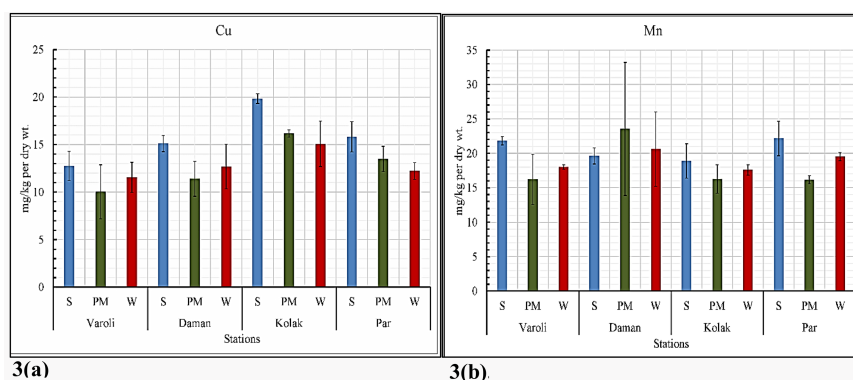


Fig. 3(a) and 3(b). Seasonal distribution of Cu (mg/kg) and Mn (mg/kg) in the surface sediment samples of selected South Gujarat estuaries. Values expressed are average and vertical bar in each point represents the standard deviation (\pm).

The average concentration of Cd (mg/kg) is : Damanganga (13.99) followed by Varoli (5.53), Kolak (5.40) and Par (4.34), which is represented in Fig. 2 (a). The maximum concentration of Cd was recorded in Damanganga (22.03 mg/kg) during the winter season. The minimum Cd was recorded 2.95 (mg/kg) in Par during the post-monsoon season. The average concentration of Cr (mg/kg) order is Damanganga (16.41) followed by Par (16.23), Kolak (15.92) and Varoli (11.46) which is depicted in Fig. 2(b). The maximum concentration of Cr was recorded in Damanganga (33.17 mg/kg) during the winter season. The minimum Cr was recorded 7.2 mg/kg in Varoli during the post-monsoon season.

The average concentration of Cu (mg/kg) order is Kolak (17.02) followed by Par (13.84), Damanganga (13.05) and Varoli (11.44) which is depicted in Fig. 3(a). The maximum concentration of Cu was recorded in Kolak (22.33 mg/kg) during the pre-monsoon season. The minimum Cu was obtained in Varoli (7.2 mg/kg) during the post-monsoon season. The average concentration of Mn (mg/kg) is: Damanganga (21.26) followed by Par (19.27), Varoli (18.67) and Kolak (17.57) which is depicted in Fig. 3(b). The maximum concentration of Mn was documented in Damanganga (33.21 mg/kg) during the post-monsoon season. The minimum Mn was recorded 12.52 mg/kg in Varoli during the post-monsoon season.

The average concentration of Ni (mg/kg) is : Par (8.16) followed by Kolak (8.03), Damanganga (6.78) and Varoli (6.36) which is depicted in Fig. 4(a). The

maximum concentration of Ni was recorded in Kolak (11.69 mg/kg) during the winter season. The minimum Ni was recorded 1.84 mg/kg in Varoli during the pre-monsoon season. The average concentration of Pb (mg/kg) is: Par (20.48) followed by Kolak (20.90), Damanganga (18.61) and Varoli (11.85) which is depicted in Fig. 4(b). The maximum concentration of Pb was recorded in Par (44.5 mg/kg) during the pre-monsoon season. The minimum Pb was recorded 4.93 mg/kg in Varoli during the winter season.

The average concentration of Fe (mg/kg) order is Par (476.7) followed by Kolak (379), Damanganga (357.6) and Varoli (326). The maximum concentration of Fe was recorded in Par (512.5 mg/kg) during the winter season. The minimum Fe was recorded 311 (mg/kg) in Varoli during the winter season.

The seasonal distribution of heavy metals in the pre-monsoon season with average concentration (mg/kg) follow order: Mn (20.61 ± 1.69) > Pb (20.33 ± 10.45) > Cu (15.87 ± 1.12) > Cr (15.36 ± 3.15) > Cd (8.37 ± 2.11) > Ni (4.95 ± 0.694). In the post-monsoon season, the order of average concentration of metals was: Mn (18.04 ± 3.99) > Pb (15.91 ± 5.82) > Cu (12.76 ± 1.60) > Cr (11.54 ± 2.54) > Ni (6.92 ± 0.86) > Cd (5.0 ± 1.27). In the winter season, average concentration of metals was Pb (23.61 ± 6.40) > Mn (18.92 ± 1.76) > Cr (18.11 ± 4.93) > Cu (12.88 ± 1.8) > Ni (8.71 ± 1.54) > Cd (8.55 ± 1.47).

The results of heavy metals showed that the Damanganga and Par estuaries were possessed a

Table 1. Pearson's correlation matrix for heavy metals and physico-chemical parameter of sediments (n=24). * Correlation is significant at the 0.05 level (2-tailed). ** Correlation is significant at the 0.01 level (2-tailed).

	Cd	Ni	Mn	Cu	Pb	Cr	pH	EC	Salinity	OM
Cd	1									
Ni	-0.001	1								
Mn	0.329*	-0.078	1							
Cu	0.054	0.095	0.258	1						
Pb	0.061	0.173	0.047	0.278	1					
Cr	0.383*	0.222	0.374*	0.370*	0.720**	1				
pH	-0.141	0.149	-0.421*	0.218	0.399*	0.207	1			
EC	-0.190	-0.051	-0.093	-0.527**	-0.244	-0.464*	-0.201	1		
Salinity	-0.202	-0.042	-0.048	-0.505*	-0.271	-0.468*	-0.251	0.995**	1	
OM	0.180	0.025	0.077	-0.199	-0.334*	-0.257	-0.313*	0.481*	0.494*	1

higher Pb, Cd and Cr concentration than other selected estuaries. The Varoli estuary has the lowest metal concentration in comparison to other selected estuaries. The seasonal distribution of heavy metals in selected estuaries showed that the highest metal concentration was found during the pre-monsoon followed by winter and post-monsoon season respectively. During the post-monsoon seasons, the high evaporation rate of water and low availabilities of freshwater leads to the high deposition of heavy metals in sediments. In post-monsoon, the effect of dilution and freshwater lead transfer the metals into oceans hence the deposition of metals is less compare to other seasons.

The concentration of Fe was highest and Cd was lowest at all stations except in Damanganga. The assessment of heavy metals study suggested that the

Varoli estuary was less contaminated as compared to other estuaries but in Varoli estuary the concentration of Cd found higher than acceptable limits of earth crust. Varoli estuary is adjacent to Damanganga, which is heavily contaminated by Cd. The Cd has low penetration power and high mass density, which allowed to present in sediments for a long time. The results of Damanganga estuary showed that the average concentrations of Cd, Mn and Cr were found higher. Par estuary was contaminated by the Pb, which is supported by a previous study (Zingde *et al.* 1981). Kolak estuary has the highest average concentration of Cu, which is an essential metal to the survival of living things. The results showed that seasonal, anthropogenic activity and weathering have an influence on the variation of these metals.

Industries were discharged effluent into the rivers

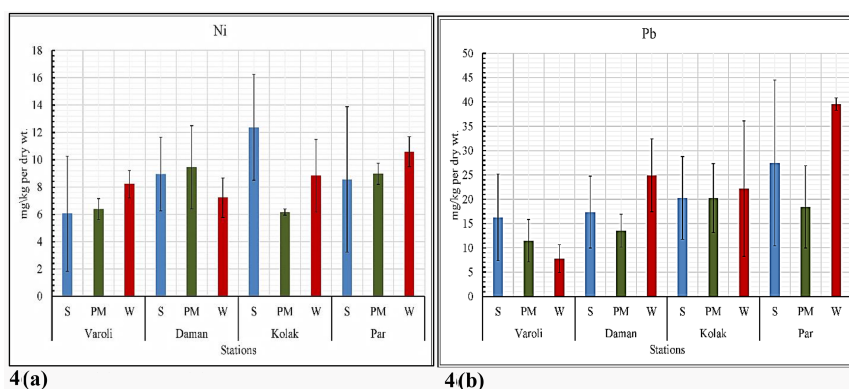


Fig. 4(a) and 4(b). Seasonal distribution of Ni (mg/ kg) and Pb (mg/kg) in the surface sediment samples of selected South Gujarat estuaries. Values expressed are average and vertical bar in each point represents the standard deviation (\pm).

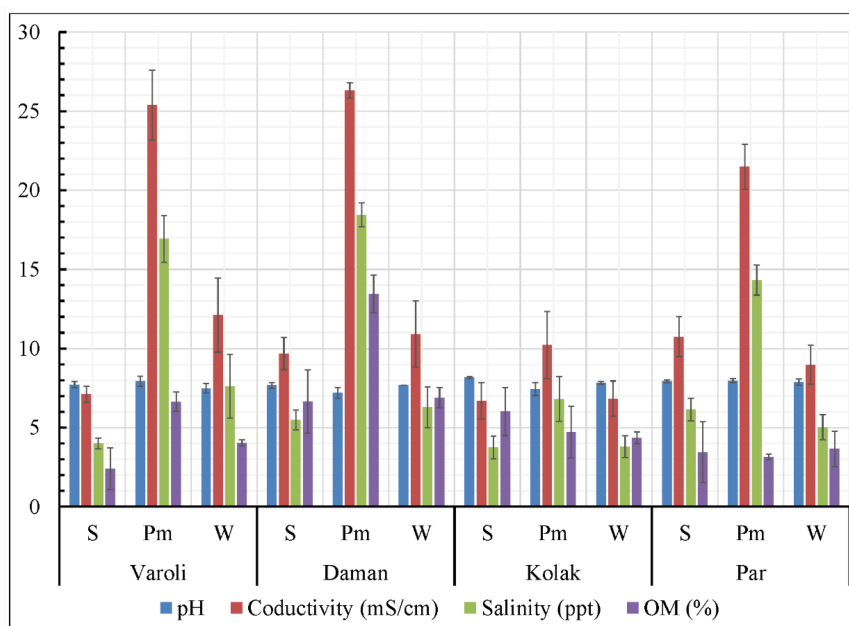


Fig. 5. Seasonal distribution of pH, conductivity (mS/cm), salinity (ppt) and organic matter (%) in the surface sediment samples of selected South Gujarat estuaries. Values expressed are average and vertical bar in each point represents the standard deviation (\pm).

streams and directly into the estuaries is the chief cause for the higher concentration of heavy metals especially the toxic metals in the study areas. The results of sediments in particularly the high content of Cd and Pb is a major concern for the study area due to the presence of recyclers of Pb and Cd based industries in this region.

Physico-chemical parameters of sediment

The results of physico-chemical parameters of sediment fluctuated with the seasonal change and are depicted in Fig. 5. The range and average value were for pH 6.86 – 8.26; (7.75), conductivity 5.54 – 27.6; (13.04) mS/cm, salinity 3.02 – 19.21; (8.22) ppt and organic matter (%). 1.1 – 14.65; (5.45).

The average pH was found maximum in Varoli (8.26) and a minimum in Damanganga (6.86). The average pH was found higher in pre-monsoon (7.87) and lower in post-monsoon (7.64). The average conductivity (mS/cm) was found maximum in Varoli (27.6) and a minimum of 5.54 in Kolak. The average conductivity (mS/cm) was found higher in 20.84 in a

post-monsoon decreased to 9.70 in winter and 8.56 in pre-monsoon. The distribution of organic matter varied from 1.1 to 14.65 (%) in the sediments. The highest concentration of organic matter was found at Damanganga 14.65 % and the lowest was 1.1 % in Varoli. The average organic matter (%) was found higher in post-monsoon (6.98) followed by a slight decrease in winter (4.73) and lowest in pre-monsoon (4.63).

In the post-monsoon season, average conductivity and salinity were found much higher as compared to other seasons because of mudflat well mixing of saline water with the sediment. In the pre-monsoon season, the deposition of salt was found higher. Water salinity of these regions is much higher in the all-seasons due to these rivers are peninsular and dry almost in all seasons. The results of average organic matter were found higher in post-monsoon (6.98 %) and similar results were observed by Sobha (2016), George *et al.* (2012). During post-monsoon, the river discharge was brought a large amount of organic matter to these estuaries. It also brings nutrients and suspended particulate matter (SPM), which leads to the high organic matter in post-monsoon.

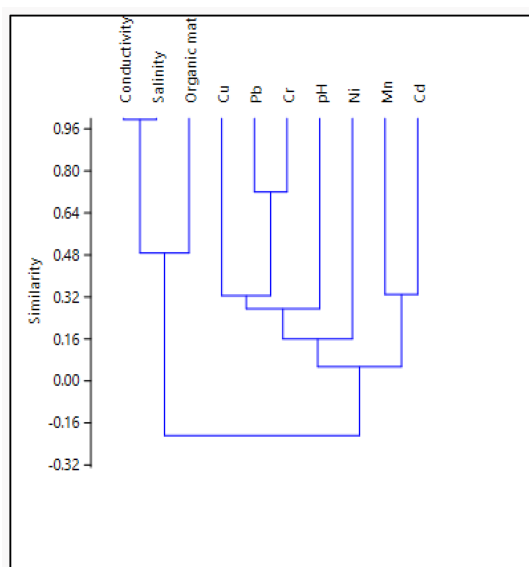


Fig. 6. Cluster of parameters by paired group-correlation method.

Pearson's correlation matrix for heavy metals in surface sediments

Table 1 shows Pearson's correlation matrix for the determination of the relationships between heavy metals (Cd, Cr, Mn, Ni, Pb) and physico-chemical parameters. Cd showed positive correlation with Mn ($r = 0.329$, $p < 0.05$) and Cr ($r = 0.383$, $p < 0.05$). Ni was not correlated with any metal, which suggests that the source of Ni was individual and comes from natural availability.

Mn showed a positive correlation with Cr ($r = 0.374$, $p < 0.05$) and negatively correlated with pH ($r = -0.421$). Cu showed a positive correlation with Cr ($r = 0.370$, $p < 0.05$) and negative correlation with conductivity ($r = -0.527$, $p < 0.01$) and salinity ($r = -0.505$, $p < 0.01$). Pb showed a positive correlation with Cr ($r = 0.720$, $p < 0.01$), pH ($r = -0.399$, $p < 0.05$) and negatively correlated with organic matter ($r = -0.334$, $p < 0.05$). The pH showed a negative correlation with organic matter ($r = -0.313$, $p < 0.05$). Correlation matrix showed that the Cr was positively correlated with all-metals except with Ni, which suggested that sources of Cr were the same for all these estuaries either natural or anthropogenic. The effect of soil pH was not very much influenced on all metals except

Pb. The organic matter (OM) showed a positive correlation with salinity and conductivity. The positive correlation between Cr and Pb was due to both were coming from a common anthropogenic source. There is an influence of pH on the availability of Cu concentration. Organic matter is not correlated with any heavy metals except with Pb. OM is also positively correlated with dissolved inorganic salts.

Spatial distributions and sources of heavy metals by cluster analysis

Fig. 6 showed the sediment cluster, which suggested that cluster 1 formed by conductivity, salinity and organic matter. The reason behind these estuaries is well dominant on the tidal and seasonal influence. Cluster 2 formed by Cd and Mn and result of correlation matrix showed a positive correlation of both these metals, which suggested that the sources of these metals were similar. Cluster 3 formed by Cr and Pb, which is furthered co-clustered by Cu, which showed that sources were from an industrial and domestic discharge. CA is also suggesting that Ni has no direct association with any other heavy metals and physico-chemical parameters.

Assessment of sediment contamination

The average value of enrichment factor (EF) for Cd: (309.9), Pb: (119.7), Cu: (38.1), Cr: (20.5), Ni: (15.38) and Mn: (2.82). The EFs showed the following order: $Cd > Pb > Cu > Cr > Ni > Mn$. The average EF for Mn is of suggestive that a moderate enrichment and source of this metal is a natural continental shelf. The average EF for Cd and Pb is suggested that extremely high enrichment and sources of these metals from industrial and also comes from domestic waste. The EF for Cu and Cr values suggested a very high enrichment of such metals, which is due to a natural and anthropogenic source. The elevated EF values in Damanganga suggested the highest enrichment of Cd, Mn and Cr is due to the effluent discharge channel of industries and domestic waste inputs in the catchments of this river. The EF value for Cd in all selected estuaries had very much higher than the natural enrichments. The metallic properties of Cd and all these estuaries are adjacent to each other leads to pollution of Cd in these regions. The Par River contaminated by Pb and Kolak

Table 2. Average concentration of heavy metals in sediments of South Gujarat estuaries and other estuaries of the world in mg/kg.

Estuary Location	Cd	Cr	Pb	Cu	Ni	Fe	Mn	Reference
Dhamara, India	1.63	347	31.90	29.40	64.20	-	652.3	Asa <i>et al.</i> (2013)
Sundarbans of West Bengal	2.84-5.78	-	36.81-61.38	43.61-79.87	-	1.9% 25%	200- 445	Saha <i>et al.</i> (2001)
Gizri Creek	9.94	346	50.28	88.33	18.50	1.45%	10.66	Siddique <i>et al.</i> (2009)
Gomti, India	2.42	8.15	40.33	5.00	15.17	2662	-	Singh <i>et al.</i> (2005)
Manakudy, India	-	78	29.54	17.14	94.0	-	103.70	Sugirtha <i>et al.</i> (2014)
Rupnarayan, West Bengal	1.6	-	14.30	15.10	22.40	1.72%	-	Kumar <i>et al.</i> (2011)
Feni, Nigeria	-	35.28	6.47	-	33.27	-	37.85	Islam <i>et al.</i> (2018)
Minho, Iberia	-	22.2	14.60	5.60	-	-	0.03	Mil-Homens <i>et al.</i> (2013)
Karnaphuli, Banladesh	0.63 3.56	11.56 -	21.98 73.42	-	-	-	-	Ali <i>et al.</i> (2016)
Average earth shale abundance	0.3	90	20	45	68	4.72%	850	Turkeian and Woodphool (1961)
Earth crust abundance	0.2	100	12.5	55	75	5.63%	950	Taylor (1964)
Varoli	5.53	11.46	11.85	11.44	6.36	326.6	18.67	
Daman	13.99	16.41	18.61	13.05	6.78	357.6	21.26	Present selected
Kolak	5.40	15.92	20.90	17.02	8.03	379.9	17.57	South Gujarat
Par	4.34	16.23	28.48	13.84	8.16	476.7	19.27	estuaries

estuary has the highest enrichment for Ni and Cu.

The average I_{geo} values for heavy metals is given in decreasing order: Cd: (3.77), Pb: (-0.86), Cu: (-2.32), Cr: (-3.27), Ni: (-3.72) and Mn: (-6.09). The average I_{geo} value of Cd in Damanganga was five and it was four for other estuaries, which recommends a strong to extreme pollution by Cd metal. I_{geo} values for Cr, Pb, Cu, Mn and Ni ≤ 0 indicate that the metals in the surface sediment are originated from natural crustal contributions and do not represent contamination by anthropogenic sources. During the pre-monsoon season in the Par estuary, the I_{geo} value of Pb found ≤ 1 indicating it is originated from anthropogenic sources. The previous study by Zingde (1980) showed that the Par River was contaminated by Pb metal.

Heavy metals comparison with Earth crust and other parts of the world

The concentration of heavy metals was evaluated in the surface sediment of our study area and is in accordance with the other part of the world. A comparison

is shown in Table 2. The average concentration of Cd in surface sediments in the study area was found higher than the average Earth crust and shale value. The average concentration of Cd in Damanganga is comparatively high as compared to other reported studies. While, the average concentration of Mn, Cr, Ni and Fe were found lower than the average Earth shale (Table 2). The concentration of Cr found lower in the present study as compared to other reported studies except for the Gomti River. The average concentration of Cu was found comparatively lower than other reported studies except for Gomti and Minho River (Singh *et al.* 2005, Mil-Homens *et al.* 2013). The concentration of Mn and Ni was found lower as compared to other studies except for Mn in Minho River. The average concentration of Pb was found slightly higher in Kolak and Par than the average Earth shell and crust. Pb was found lower in the present study than other reported studies except for Rupnarayan, Feni and Minho River.

CONCLUSION

The results of this study are exposed that heavy metals

in sediment are the result of their accumulation over a long period. But estuaries are under the active dynamics with tidal and monsoon flushing is changing availabilities of metals in sediment of the estuaries. The results from this study indicated that the surface sediment is highly contaminated by the Cd metal followed by Pb and Cr. Cluster analysis is indicated that the sources of Pb, Cd and Cr are mainly derived from coastal industrial effluents, whereas Mn, Ni and Fe are mainly formed Earth crust and natural weathering. The pollution contamination indices EF and I_{geo} showed that the metals Cd, Pb and Cr have moderate to high enrichment in the present study area and it is primarily due to anthropogenic pollution, whereas the other heavy metals Fe, Mn, Ni and Cu in the study area may originate mainly in Earth crustal materials or natural weathering processes. Cluster analysis is also suggesting that the physico-chemical parameters of sediment are correlated to each other and not influenced by availabilities of heavy metals. It is concluded that heavy metal contamination in the marine environment of the Damanganga, Kolak and Par estuary region is caused mainly by anthropogenic activities.

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REFERENCES

- Ali MM, Ali ML, Islam MS, Rahman MZ (2016) Preliminary assessment of heavy metals in water and sediment of Karnaphuli River, Bangladesh. *Environ Nanotech Monit Man* 5 : 27—35.
- Asa SC, Rath PU, Panda C, Parhi PK, Bramha S (2013) Application of sequential leaching, risk indices and multivariate statistics to evaluate heavy metal contamination of estuarine sediments: Dhamara Estuary, East Coast of India. *Environ Monit Assess* 185 : 6719—6737.
- Baran A, Tarnawski M (2015) Assessment of heavy metals mobility and toxicity in contaminated sediments by sequential extraction and a battery of bioassays. *Ecotoxicology* 24 (6) : 1279—1293.
- Dudani S, Lakhmapurkar J, Gavali D Patel T (2017) Heavy metal accumulation in the mangrove ecosystem of South Gujarat Coast, India. *Turk J FishAqua Sci* 17 : 755—766.
- George B, Nirmal Kumar JI, Kumar RN (2012) Study on the influence of hydrochemical parameters on phytoplankton distribution along Tapi estuarine area of Gulf of Khamhat, India. *J Egy Aqua Res* 38 (3) : 157—170.
- Harikumar PS, Nasir UP (2010) Ecotoxicological impact assessment of heavy metals in core sediments of a tropical estuary. *Ecotox. Environ Saf* 73 : 1742—1747.
- Ho HH, Swennen R, Damme AV (2010) Distribution and contamination status of heavy metals in estuarine sediments near Cuaong Harbor, Ha Long Bay, Vietnam. *Geologica Belgica* 13 : 37—47.
- Hosono T, SuC, Siringan F, Amano A, Onodera S (2010) Effects of environmental regulations on heavy metal pollution decline in core sediments from Manila Bay. *Mar Poll Bull* 60 (5) : 780—785.
- Hui-na Z, Xing-zhong Y, Guang-ming Z, Min J, Jie L, Chang Z, JuanY, Hua-jun H, Zhi-feng L, Hong-wei J (2012) Ecological risk assessment of heavy metals in sediments of Xiawan Port based on a modified potential ecological risk index. *Trans Non-ferrous Met Soc China* 22 : 1470—1477.
- Islam MS, Hossain MB, Matin A Islam, Sarker MS (2018) Assessment of heavy metal pollution, distribution and source apportionment in the sediment from Feni River estuary, Bangladesh. *Chemosphere* 202 : 25—32.
- Kumar B, Sajwan KS, Mukharjee DP (2012) Distribution of heavy metals in valuable coastal fishes from the North East Coast of India. *Turk J Fish Aqua Sci* 12 (1) : 81—88.
- Lohani MB, Singh A, Rupainwar DC, Dhar DN (2008) Seasonal variations of heavy metal contamination in river Gomti of Lucknow. *Environ Monit Assess* 147 (1-3) : 253—263.
- Magdoff FR, Tabatabai MA, Hanlon (1996) Soil Organic Matter: Analysis and Interpretation. *Soil Sci Spec Publ* 46 : 21—31.
- Marchand C, Allenbach M, Lallier-Vergès E (2011) Relationship between heavy metals distribution and organic matter cycling in mangrove sediments (Conception Bay, New Caledonia). *Geoderma* 160 (3-4) : 444—456.
- Mathivaman K, Rajaram R (2013) Anthropogenic influences on toxic metals in water and sediment samples collected from industrially polluted Cuddalore coast, Southeast coast of India. *Environm Earth Sci* 72 (4) : 997—1010.
- Mil-Homens M, Costa AM, Fonseca S, Trancoso MA, Lopes C, Serrano R, Sousa R (2013) Characterization of heavy-metal contamination in surface sediments of the Minho River estuary by way of factor analysis. *Arch. Environ Contam Toxicol* 64 : 617—631.
- Mitra A, Saha SB, Bikash S, Bhattacharyya S, Choudhury A (2012) Status of sediment with special reference to heavy metal pollution of a brackishwater tidal ecosystem in Northern Sundarbans of West Bengal. *Trop Ecol* 42 (1) : 127—132.
- Nirmal Kumar JI, George B, Kumar RN, Sajish PR, Viyol S (2009) An assessment of heavy metal distribution at lower reaches of three permanent tropical estuaries of Gulf of Khamhat, India. *Int J Poll Res* 4 : 597—601.

- Nobi EP, DilipanE, Thangaradjou T, Sivakumar K, Kannan L (2010) Geochemical and geo-statistical assessment of heavy metal concentration in the sediments of different coastal ecosystems of Andaman Islands, India. *Estu Coast Shelf Sci* 87 : 253—264.
- Saha J, Rajendiran S, Vassanda C, Dotaniya M, Kundu S, Patra A (2017) Status of Soil Pollution in India.
- Saha SB, Mitra A, Bhattacharyya SB, Choudhury A (2001) Status of sediment with special reference to heavy metal pollution of a brackishwater tidal ecosystem in Northern Sundarbans of West Bengal. *Trop Ecol* 42 (1) : 127—132.
- Siddique A, Mumtaz M, Zaigham NA, Mallick KA, Saied S, Zahir E, Khwaja HA (2009) Heavy metal toxicity levels in the coastal sediments of the Arabian Sea along the urban Karachi, Pakistan region. *Mar Poll Bull* 58 (9) : 1406—1414.
- Singare PU, Mishra RM, Trivedi MP (2012) Sediment contamination due to toxic heavy metals in the Mithi River of Mumbai. *Adv Anal Chem* 2 (3) : 14—24.
- Singh KP, Mohan D, Singh VK, Malik A (2005) Studies on distribution and fractionation of heavy metals in Gomi River sediments—A tributary of Ganges. *Ind J Hydrol* 312 : 14—27.
- Smith JL, Doran JW (1996) Measurement and use of pH and electrical conductivity for soil quality analysis. In Methods assessing soil quality. *Soil Sci Soc Am* 49 : 169—182.
- Sobha R (2016) Seasonal changes in physico-chemical characteristics of the water of Gosthani estuary in Visakhapatnam District Andhra Pradesh, India. *J Eur Acad Res* 3 (6) : 12805—14.
- Sugirtha KK, Sheela MS (2014) Heavy and trace metals in manakudy estuarine core sediments, Southwest coast of India. *Poll Res Paper* 1 : 7—15.
- Taylor (1964) Abundance of chemical elements in the continental crust: A new table. *Geochimica Cosmochimica Acta* 28 : 1273—1285.
- Turkeian KK, Woodphool DH (1961) Distribution of the element in some major units of the earth's crust. *Bull Geol Soc Am* 72 : 175—192.
- Wolf M, Weissing FJ (2012) Animal personalities: Consequences for ecology and evolution. *Trends Ecol Evol* 27 (8) : 452—461.
- Xu F, Hu B, Dou Y, Song Z, Liu X, Yuan S, Sun Z, Li A, Yin X (2017) Prehistoric heavy metal pollution on the continental shelf off Hainan Island, South China Sea: From natural to anthropogenic impacts around 4.0 kyr BP. *The Holocene* 28 (3) : 455—463.
- Yang Y, Chen F, Zhang L, Liu J, Wu S, Kang M (2012) Comprehensive assessment of heavy metal contamination in the sediment of the Pearl River estuary and adjacent shelf. *Mar Poll Bull* 64 : 1947—1955.
- Zingde MD, Sharma RV, Desai BN (1979) Pollution in river Par and its abatement. *J Int Mar Sci* 8 : 266—270.
- Zingde MD, Narvekar PV, Sharma RV, Desai B.N. (1980) Water quality of the River Damanganga, Gujarat. *J Int Geo-Mari Sci* 9 : 94—99.
- Zingde MD, Chandar S, Rokade MA, Desai BN (1981) Base-line water quality of the river Narmada (Gujarat). *J Int Mar Sci* 10 : 161—164.
- Zingde MD, Narvekar PV, Sharma P, Sabnis MM (1986) Environmental studies of the Ambika and associated river estuaries. *Mari Poll Bull* 17 : 267—274.
- Zulkifli SZ, Ismail A, Mohamat-Yusuff F (2012) Bioaccumulation of Selected Heavy Metals in Soldier Crabs, *Dotilla myctiroides* (Decapoda: Ocypodidae) from Bagan Lalang, Selangor, Malaysia. *Acta Biologica Malaysiana*, pp 94—100.
- Zulkifli SZ, Mohamat-Yusuff F, Mukhtar A, Ismail A, Miyazaki N (2014) Determination of food web in an intertidal mudflat of tropical mangrove ecosystem using stable isotope markers: A preliminary study. *Life Sci J* 11 (3) : 427—431.