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Chemometric study on the trace metal accumulation in the sediments of the Cochin Estuary—Southwest coast of India

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Abstract The distribution and accumulation of trace metals in the sediments of the Cochin estuary during the pre-monsoon, monsoon and post-monsoon periods were investigated. Sediment samples from 14 locations were collected and analysed for the metal contents (Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb), organic carbon, total nitrogen, total sulphur and grain size. The data were processed using statistical tools like correlation, factor and cluster analysis. The study revealed an enrichment of Cd and Zn in the study area particularly at station 2, which is confirmed by enrichment factor, contamination factor and geoaccumulation index. The factor analysis revealed that the source of Cd and Zn may be same. The study indicated that the spatial variation for the metals like Mg, Cr, Fe, Co, Ni, Cu, Zn, Cd and Pb were predominant unlike Mn which shows a temporal variation. The strong association of trace metals with Fe and Mn hydroxides and oxides are prominent along the Cochin estuary. The anthropogenic inputs of industrial effluents mainly control the trace metals enrichment in the Cochin estuary.

Keywords Cochin estuary · Trace metals · Sediments · Factor analysis · Pollution

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Introduction

Trace metal pollution of the natural environment is a universal problem as metals are indestructible and most of them have toxic effect when they exceed the threshold levels (Nuremberg 1984; MacFarlane and Burchett 2000). Estuaries are the most productive ecosystems in the world, serving as breeding and nursery grounds of marine organisms like fishes and shellfishes. They act as a reservoir for trace metals to the oceans and serve as geochemical pollution indicators (Church 1986; Ridgway and Shimmield 2002). Trace metal pollutants transported to estuaries by natural or anthropogenic processes are either in the form of suspended particles or dissolved form that are subsequently removed from the water column by precipitation, adsorbed onto particulate matter and biota and deposited in bottom sediments (Loska and Wiechula 2003). Naturally occurring trace metal levels depend on the geology of the catchment area the anthropogenic loading from point and non-point sources exhibit wide fluctuations with their average values usually higher than normal shale value. Accurate quantification of anthropogenic contamination is important and indispensable for the effective management and remedial action of aquatic environment.

Cochin Estuary is the second largest wetland ecosystem in India. The anthropogenic activities in the region commence from the latter part of the nineteenth century and has been in the increase ever since. The construction of salinity barriers in the upstream south end of the estuary to support agricultural activities during the 1970s brought about a reduction in the flushing characteristics and thereby an increase in sedimentation. The annual dredging volume (about 10×10^6 m^3) from the Cochin harbour region indicated the intensity of sedimentation (Rasheed 1997). Inadequate effluent treatment and discharge from chemical industries on the banks of the rivers Periyar and Chitrapuza eventually have resulted in an accumulation of both organic and inorganic pollutants in the sediments of northern region of the Cochin Estuary (Qasim 2003; Balachandran et al. 2005; Babu et al. 2006). The discharge of industrial effluent has led to an increase in metal contamination in the sediments although the concentration of Fe, Mn, Co, Ni, Cr, Cu, Zn, Cd and Pb have not get reach alarming levels. Zn and Cd show extreme enrichment thereby placing the region among the list of impacted estuaries in the world. Since the Cochin estuary forms part of the vembanadu-Kol wetlands which has been identified as a Ramsar site (no. 1214), the need for protecting the estuary from harmful effect of trace metals pollution cannot be over emphasised (Wetlands 2002). The present study focuses on the spatial and temporal variations of metals like Fe, Ni, Cd, Cr, Co, Cu, Mg, Mn, Pb and Zn in the sediments of Cochin estuary. In order to understand the pollution status, the chemometric techniques like enrichment factor (EF), contamination factor (CF) and geoaccumulation index (I_{geo}) were asserted. The statistical approaches such as factor analysis (principal component analysis (PCA)), Pearson correlation and cluster analysis were used to identify the parameters that help to differentiate the sources.

Materials and methods

Study area

Cochin estuary is a bar-built micro-tidal system connected to the Arabian Sea at two locations—one at Cochin (latitude 9°10′ N) and at Azhikode (latitude 10°10′ N). The estuary is divisible into two parts: the southern arm extending from Cochin to the south and the northern arm extending from Cochin to Azhikode. The Cochin bar mouth is about 450 m wide, whereas the Azhikode inlet is relatively narrow. The Cochin metropolis receives an annual rainfall of 320 cm, of which 60% occurs during the southwest monsoon period, July–Sept (Qasim 2003). The estuary, receives a high volume of fresh water annually (20×10^9 $m^3 year^{-1}$) from the six rivers in the state Kerala (Srinivas et al. 2003). During the months of December to April, construction of a salinity barrier bund at Thanneermukkam virtually cuts off the tidal propagation further towards south and modifies the circulation patterns in the remaining part of the estuary. Sampling was carried at 14 stations spread across the Cochin estuary between May 2007 and May 2008 (Fig. 1).

Sediment collection and analysis

Surface sediments were collected using a Van-veer grab and uncontaminated portions were sampled packed in polyethylene covers and stored at −20°C until analysis Grasshoff et al. (1999).

Textural characteristics (sand, silt and clay) of the sediments were determined by pipette analysis (Krumbein and Petti john 1938). Total carbon (TC), total nitrogen (TN) and total sulphur (TS) were determined using Vario EL III CHNS Analyzer. Organic carbon (OC) was determined according to the method of Gaudette et al. (1974). One gramme of the dried finely powered sediment sample was repeatedly digested using a 1:3 mixture of concentrated $HClO_4$ and HNO_3 then evaporated to dryness (Loring and Rantala 1992). The dry residue was dissolved in 0.1 HNO_3 made up to 25 ml and analysed using flame AAS (Perkin Elmer 3110). The precision of the metal analyses was checked using triplicate analysis of a certified reference material (BCSS-1, National Research Council of Canada) the spiked samples ranged between 96±2% for Cd and 98±2% for Pb.

Multivariate statistical methods

Multivariate statistical approaches- cluster analysis, factor analysis, normalised EF, contamination factor (CF) and I_{geo} were used to differentiate the sources of metals with sediments from anthropogenic inputs, and to quantify the anthropogenic contamination.

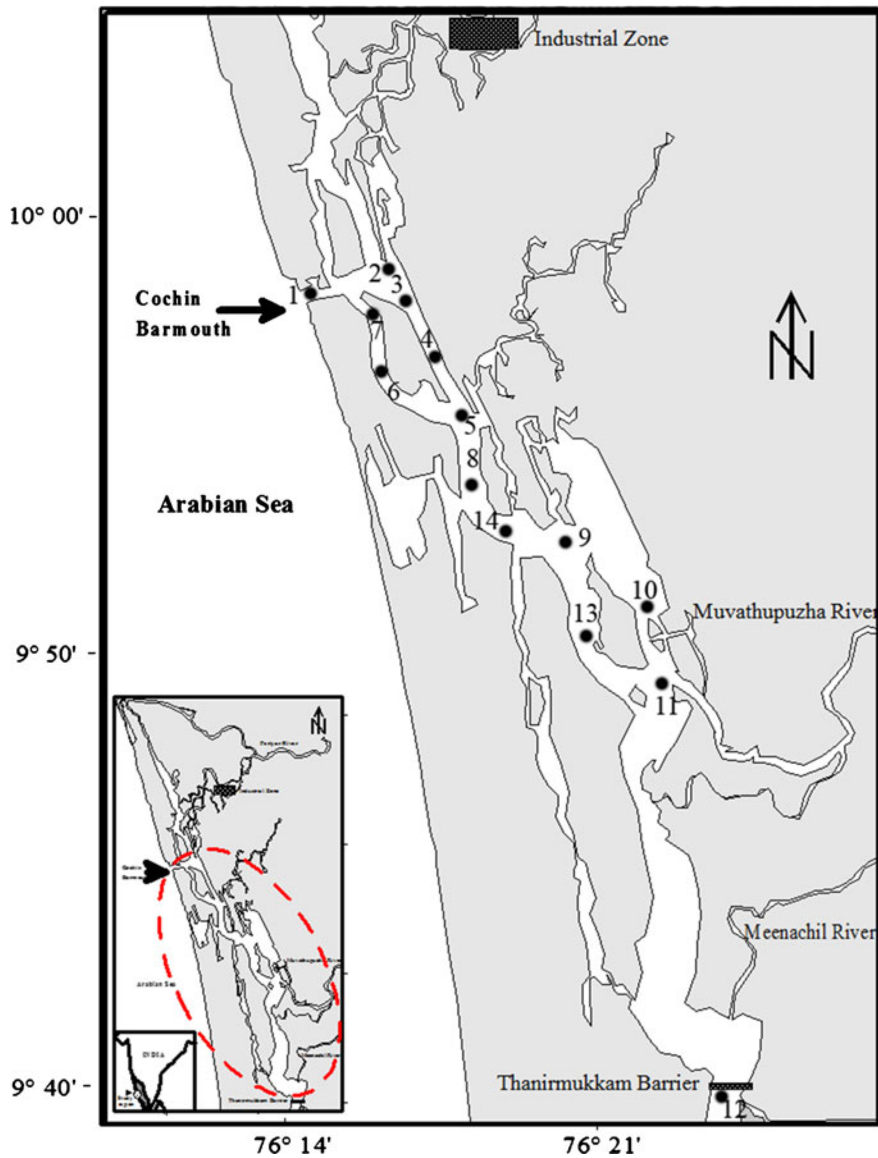

Fig. 1 Map of the Cochin estuary showing sampling locations

Cluster analysis

Cluster analysis is a multivariate statistical technique used to classify the objects of a system into categories or clusters based on their similarities. The most similar objects are first grouped and these initial groups are merged according to their similarities. Eventually, as the similarity decreases all subgroups are fused together into a single cluster, which resulted a hierarchical clustering procedure (Richard and Dean 2002; Alvin 2002).

Factor analysis

Factor analysis is a data-reduction technique used to explain the variances and relationships among the variables in the observed data (Bartolomeo et al. 2004; Glasby et al. 2004; Ghrefat and Yusuf 2006). Original variables are transformed into newly uncorrelated variables called factors, which are a linear combination of the original variables. PCA was used for an extraction of different factors. The axis defined by PCA is rotated to reduce the contribution of less significant variables (Richard and Dean 2002; Alvin 2002). This treatment provides a small number of factors that usually account for approximately the same amount of information as the original set of observations.

Enrichment factor of metals

To detect and quantify the anthropogenic contribution of metals over natural inputs, the conservative elements such as Al or Fe, whose levels are unaffected by anthropogenic input is employed to identify the anomalous metal concentrations in the sediments and it is generally defined as the observed metal concentration to Al or Fe ratio in the sample divided by the background metal concentration Al or Fe ratio. The following equation was used to estimate the EF of metals from each sediments samples using Fe as a normalizer to correct for differences in sediments grain size and mineralogy: (Covelli and Fontolan 1997; Simeonov et al. 2000; Zhang et al. 2007).

$$\mathrm{EF} = (M/X)_{\mathrm{sample}}/(M/X)_{\mathrm{background}}$$

Where M is the target metal, X is the selected normalizer (reference metal) and $(M/X)_{\mathrm{sample}}$ and $(M/X)_{\mathrm{background}}$ are the ratios of target metal and the normalizer in the interest and background sediments, respectively.

A five-category ranking system is used to denote the degree of anthropogenic influence on the metal concentration levels in the estuarine sediments (Sutherland 2000; Kartal et al. 2006).

An EF of <2 represents a deficiency to minimum enrichment whereas an EF of ~2–5 shows a moderate enrichment. An EF of ~5–20 represents a significant enrichment whereas an EF of (~20–40 and >40) shows a very high and extremely high enrichment, respectively.

Contamination factor

Contamination factor express the level of contamination of sediment by a metal, and it denoted as:

$$\mathrm{CF}\frac{\text{metal concentration in sediment}}{\text{background value of metal}}$$

Where CF of <1 refers to low contamination, $1 \leq \mathrm{CF} \leq 3$ means moderate contamination, $3 \leq \mathrm{CF} \leq 6$ indicates considerable contamination, and CF of >6 indicates very high contamination.

Geoaccumulation index

The I_{geo} quantify and assess the extent of trace metal contamination as well as pollution associated with the estuarine sediments.

The I_{geo} was calculated as,

$$I_{\mathrm{geo}} = \log_2 \frac{C_{\mathrm{n}}}{1.5 \times B_{\mathrm{n}}}$$

(Muller 1969)

Where, C_{n} represents the measured total metal concentration in the fine-grained sediment fraction (clay or silt; in mg/kg), B_{n} represents the geochemical background concentration of the metal (in mg/kg), and 1.5 is the background matrix correction in factor due to lithogenic effects. For the analysis of the geochemical background values of metals (B_{n}), world crustal average metal concentration as reported by Wedephol (1995) is taken.

The pollution free, less polluted, moderately polluted and strongly polluted zones are classified according to the I_{geo} values. $I_{\mathrm{geo}}<0$ means pollution free, $0 \leq I_{\mathrm{geo}}<1$ means pollution free to moderately polluted, $1 \leq I_{\mathrm{geo}}<2$ means moderately polluted, $2 \leq I_{\mathrm{geo}}<3$ means moderately to strongly polluted, $3 \leq I_{\mathrm{geo}}<4$ means strongly polluted, $4 \leq I_{\mathrm{geo}}<5$ means strongly to very strongly polluted and $I_{\mathrm{geo}} \geq 5$ means very strongly polluted.

Results

Sediment geochemical parameters

Textural parameters like sand, silt and clay showed a significant spatial variation throughout all stations (Table 1). This is indicated by the variation of sand (2.26–95.86%), silt (0.06–72.13%) and clay (4.08–50.44%). contents in sediments during pre-monsoon. Sand, silt and clay contents in the monsoon season varied between 0.37% and 96.11%, 0% and 92.61% and 3.11% and 47.28%, respectively. Similarly, for the post-monsoon season sand, silt and clay contents varied between 0.73% and 91.77%, 3.27% and 58.22%, and 4.96% and 67.80%, respectively.

Table 1 Seasonal distribution of concentration of trace metals, texture and organic component along the Cochin estuary

	Station	Cd	Co	Cu	Cr	Fe (%)	Mg (%)	Mn	Ni	Pb	Zn	Sand (%)	Silt (%)	Clay (%)	OC (%)	TN (%)	TC (%)	TS (%)
Pre-monsoon	1	0.69	8.24	8.83	15.66	2.84	1.01	85.63	19.38	11.50	71.25	85.47	2.13	12.40	0.55	0.21	1.64	0.34
	2	4.28	15.94	26.21	36.58	5.93	2.13	188.75	49.38	26.13	333.75	5.05	50.83	44.11	2.59	0.25	2.85	1.33
	3	1.45	14.44	21.38	36.24	5.93	2.25	184.38	48.98	20.50	101.25	5.16	72.13	22.72	2.30	0.25	2.55	1.13
	4	1.05	18.13	23.85	30.38	7.64	1.06	263.75	44.49	17.25	58.13	10.30	40.38	49.32	2.16	0.22	2.69	0.51
	5	1.70	13.64	23.18	36.60	6.94	2.33	183.13	59.96	16.63	86.88	12.68	42.09	45.23	2.21	0.26	1.13	0.53
	6	1.03	12.43	18.90	29.88	4.75	1.84	136.88	41.63	16.63	93.75	6.02	46.25	47.73	2.48	0.27	2.79	1.19
	7	1.86	15.39	24.38	64.90	7.57	2.33	191.25	59.03	19.50	106.88	2.26	48.69	49.04	2.51	0.26	2.58	1.18
	8	1.50	14.01	26.44	48.39	8.22	2.15	196.88	61.93	20.63	93.75	15.04	34.52	50.44	2.32	0.27	2.85	1.13
	9	0.79	4.90	20.59	47.45	6.54	0.95	158.75	38.61	13.50	54.38	48.92	32.55	18.53	1.80	0.16	2.07	0.53
	10	0.16	4.38	7.69	13.11	2.16	0.25	48.75	10.89	4.38	3.13	95.86	0.06	4.08	0.47	0.03	0.64	0.00
	11	0.19	7.16	4.40	7.53	1.48	0.15	61.25	6.83	3.88	5.63	74.04	13.40	12.56	0.72	0.13	1.36	0.00
	12	0.65	13.03	10.48	18.86	4.47	0.60	175.63	21.84	10.00	21.88	69.06	13.41	17.53	0.98	0.07	0.98	0.00
	13	1.06	17.40	21.48	15.23	6.53	1.75	244.38	49.83	18.13	70.00	26.17	30.97	42.86	2.00	0.24	2.38	0.68
	14	1.03	10.74	11.30	23.44	4.39	0.98	186.88	26.26	12.38	65.00	65.27	18.66	16.07	0.98	0.12	1.26	0.36
monsoon	1	1.53	12.96	20.80	22.09	5.66	2.13	163.75	49.35	17.50	103.75	9.83	68.91	21.26	2.00	0.21	2.56	1.13
	2	5.13	17.01	29.94	31.83	7.46	2.21	232.50	60.33	25.25	390.63	21.29	52.18	26.53	2.64	0.28	3.23	1.21
	3	1.41	14.38	22.55	32.99	6.54	2.10	233.13	49.80	18.88	90.63	8.55	72.30	19.15	2.14	0.29	2.92	1.02
	4	0.68	5.88	46.88	13.91	2.39	0.75	67.50	18.18	8.75	27.50	79.47	13.84	6.69	0.42	0.08	1.35	0.00
	5	1.79	18.18	25.38	46.31	6.84	2.22	316.25	62.54	28.00	103.75	5.07	92.61	2.32	2.67	0.31	3.15	1.07
	6	1.21	12.78	17.39	21.05	5.28	1.95	170.00	42.50	16.63	88.13	5.00	59.32	35.68	2.40	0.30	3.26	1.22
	7	1.30	18.41	26.55	42.31	7.65	2.16	364.38	59.71	22.63	100.63	0.37	59.83	39.80	2.69	0.34	3.41	1.29
	8	1.41	19.54	29.63	66.09	8.30	2.39	332.50	72.53	21.50	99.38	14.26	38.46	47.28	2.77	0.32	3.29	1.15
	9	0.90	10.35	14.61	13.53	5.18	0.67	143.13	27.34	12.25	31.88	61.39	19.13	19.48	0.89	0.11	1.37	0.31
	10	0.68	11.19	4.44	13.30	4.14	0.54	146.88	20.73	1.88	26.25	88.39	0.00	11.61	0.70	0.01	1.12	0.44
	11	0.31	5.44	8.00	13.06	2.45	0.22	657.50	12.43	7.25	16.25	96.11	0.77	3.11	0.39	0.04	0.69	0.00
	12	1.04	24.09	15.74	22.33	7.71	0.88	433.13	35.88	16.88	55.00	35.93	43.18	20.89	1.27	0.16	1.86	0.33
	13	1.68	17.84	25.69	38.00	7.41	2.21	315.63	61.25	24.50	100.00	51.40	25.13	23.46	1.38	0.19	1.91	0.48
	14	0.99	13.74	16.75	28.20	5.76	1.26	302.50	38.69	18.63	60.00	75.81	18.46	5.72	0.51	0.07	0.85	0.00
Post-monsoon	1	0.99	12.13	19.43	59.16	4.25	2.01	134.38	46.90	20.50	68.75	19.50	47.92	32.58	1.95	0.21	2.49	1.15
	2	5.96	17.21	32.05	61.54	7.60	2.32	201.25	60.84	26.75	433.13	2.00	58.22	39.78	2.99	0.26	2.97	1.26
	3	1.29	15.16	23.74	37.81	6.65	2.26	223.75	55.26	26.50	118.13	10.16	50.56	39.27	2.62	0.28	2.78	1.17
	4	0.98	6.45	7.70	14.61	2.77	0.94	73.13	18.85	7.13	75.00	84.61	8.60	6.79	0.34	0.14	1.01	0.00

Table 1 (continued)

Station	Cd	Co	Cu	Cr	Fe (%)	Mg (%)	Mn	Ni	Pb	Zn	Sand (%)	Silt (%)	Clay (%)	OC (%)	TN (%)	TC (%)	TS (%)
5	1.20	13.58	21.10	37.69	5.69	2.03	155.63	50.26	20.13	90.63	14.63	32.89	52.48	2.39	0.26	2.87	1.13
6	1.80	16.20	28.00	33.06	7.12	2.42	224.38	62.56	28.75	137.50	2.21	29.99	67.80	2.95	0.32	3.03	1.29
7	1.63	14.96	23.89	79.16	5.89	2.36	182.50	60.90	25.63	102.50	0.73	35.03	64.24	2.90	0.35	3.20	1.49
8	0.79	4.43	5.25	11.24	1.70	0.48	65.00	10.50	6.75	27.50	88.62	4.08	7.30	0.26	0.25	0.36	0.00
9	0.59	6.71	8.24	11.48	3.59	0.41	72.50	16.58	8.38	26.88	84.75	8.95	6.30	0.26	0.05	0.30	0.00
10	0.35	7.43	9.78	20.88	3.31	0.31	88.75	16.25	9.13	30.00	91.77	3.27	4.96	0.40	0.03	1.28	0.00
11	0.46	5.73	7.58	14.51	2.81	0.29	95.00	13.64	7.00	23.13	80.35	10.79	8.86	0.12	0.07	0.61	0.00
12	1.18	24.61	15.54	31.03	7.84	1.11	428.13	36.74	18.00	45.63	40.37	44.58	15.05	1.17	0.17	2.40	0.00
13	0.54	12.11	14.10	19.89	4.88	1.10	201.88	32.25	14.75	44.38	74.52	7.88	17.59	0.44	0.10	1.46	0.58
14	0.69	11.79	10.93	20.95	4.33	0.97	182.50	26.35	13.50	39.38	67.42	17.30	15.28	0.40	0.12	1.09	0.39

OC distribution indicates a significant spatial variation in the study area with values varying from 0.39% to 2.77%, 0.26% to 3% and 0.47% to 2.59%, respectively, for pre-monsoon, monsoon and post-monsoon seasons. Total nitrogen, total carbon, and total sulphur content in sediments indicated a trend similar to that observed for texture and OC during the three seasons. There is a significant spatial variation of TN, TC and TS in the study area. TN varied from 0.03% to 0.27%, 0.01% to 0.34% and 0.03% to 0.35% during the three seasons. Similarly, TC varies from 0.64% to 2.85%, 0.85% to 3.41% and 0.30% to 3.20%, respectively, for the pre-monsoon, monsoon and post-monsoon seasons. In the case of TS, the values ranged between 0% and 1.33%, 0% and 1.29% and 0% and 1.49%, respectively, for three seasons.

Trace metal concentrations in sediments

Cd, Co, Cu, Cr, Fe, Mg, Ni, Pb and Zn showed significant spatial variation indicating a predominance of anthropogenic inputs. Fe concentration during the pre-monsoon, monsoon and post-monsoon ranges from 1.48% to 8.22%, 2.45% to 8.30% and 1.70% to 7.84%, respectively; Mg values ranged from 0.15% to 2.33%, 0.22% to 2.39% and 0.41% to 2.42% during the pre-monsoon, monsoon and post-monsoon (Table 1). Mn is the only metal which did not show any spatial variation and gives only significant temporal variation. Mn showed values in the ranges 48.8–263.8, 67.5–657.5 and 65–428 μg/g during the pre-monsoon, monsoon and post-monsoon seasons. The enrichment of Mn during the monsoon was high when compared with pre-monsoon and post-monsoon. The spatial variation of Co ranged from 4.38 to 18.13, 5.44 to 24.09 and 4.43 to 24.61 μg/g, respectively, during pre-monsoon, monsoon and post-monsoon. For Cu, the spatial variation ranged from 4.40 to 26.44, 4.44 to 46.88 and 5.25 to 32.05 μg/g during the three seasons. The spatial variations of Zn ranged from 3.13 to 333.75, 16.25 to 390 and 23.13 to 433.13 μg/g during pre-monsoon, monsoon, post-monsoon and seasons respectively, while that of Cr ranged from 7.5 to 65, 13 to 66 and 11 to 79 μg/g, respectively. Ni concentrations varied between 18.2 and 72.5, 18.9 and 62.5 and 6.8 and 62 μg/g, respectively, during the seasons while Cd varied between 0.32 and 5.13, 0.35 and 5.96 and 0.16 and

4.28 μg/g. Pb concentration varied from 3.88 to 26, 1.88 to 28 and 6.75 to 28.75 μg/g during the seasons.

Discussion

Comparison of spatial and seasonal variability with average shale values

The 14 sampling stations were grouped into two zones on the basis of their geographical proximity. Zone I included stations 1 to7 broadly within the Cochin port area. Zone II included stations 8 to 14, which are outside the port, and are largely influenced by non-point out puts.

Comparison of spatial variation of trace metals with respective average shale values indicated Cd, Fe and Zn were below the average shale metals values. Cd, Fe and Zn concentrations exceeded respective shale average indicating the influence of land-based inputs.

Rock-forming Fe, Mg and are land based, and their abundances show regional variations. Fe, Mg and Mn concentrations were compared with shale average values (4.32%, 2.20% and 716 ppm respectively) reported by Wedephol (1995). During pre-monsoon stations, Fe values from zone I (except station 1), were higher than the world shale average while zone II with stations 10 and 11showed values lower than world shale average. During monsoon, Fe displayed higher values irrespective of zones but had lower values than shale at stations 4, 10 and 11. For post-monsoon, zone II had lower concentration of Fe at stations 8, 9, 10, 11 and stations 1 and 4 in zone I. The spatial variability was prominent during the monsoon season mainly because of point sources from industries along the banks of estuary. In the case of Mn during all three seasons both zones gave a concentration well below world average. However, there was higher enrichment in monsoon season when compared with pre-monsoon and post-monsoon season. This higher concentration of Mn during the monsoon was mainly due to flocculation at low salinities. Adsorption of soluble Mn compounds into sediments depend their cation exchange capacity and organic composition (Garrison et al. 1995). During monsoon season the possibility of untreated effluent being discharged into the estuary could be higher as the increased monsoonal water flow would facilitate quick dilution. This could be the reason for high concentrations being observed during monsoon compared with post- and pre-monsoon. The anova results also indicate the temporal variation.

Co showed prominent regional variation during the three season's concentrations during pre-monsoon being below the average shale value at all stations. However during monsoon and post-monsoon, zone I gave lower values at all stations, but in zone II stations 12 gave slightly higher than shale average. The higher concentration at station 12 (near Thanneermukkam Bund) was mainly due to agricultural activity in the vicinity.

The world shale average of Cu is 25 ppm. Zones I and II generally recorded Cu concentrations lower than the world averages in all seasons. However stations 2 and 8 during pre-monsoon, stations 2 and 6 in post-monsoon and stations 2, 4, 5 and 8 during monsoons were exceptions and exhibited values higher than the world averages. This could have been due to the leaching of antifouling paints used on marine vessels frequenting the Cochin port area which is a land mark of zone I.

The main sources of Cr in the estuary are from tanning, textile and steel industries that abound on its northern side while hexavalent chromium is widely known for its toxic effect on man and animals are considered as essential trace metal. Although concentrations in both zones are well within the world average, zone I showed higher values than zone II reflecting its industrial environment.

Cd concentration in all three seasons showed higher values than world average irrespective of the zones. Station 2 of zone I showed very high values during all the three seasons. This was only to be expected in view of the leaching of treated/untreated effluence from the industrial units located in this zone. Cd is one of the main products of the zinc industry located close to station 2.

Zn also reported gave values much higher than world shale average in zone I during all the three seasons. This was onto to be expected in view of an annual loading of ~80 T of Zn in ~250 chemical industries situated upstream of the northern (Shibu et al. 1995) of which the Zn manufacturing industry in the prominent unit. Zone II shows lower values at stations 9, 10, 11, and 12 during pre-monsoon and monsoon and all stations in post-monsoon.

Ni may be deposited in sediments by precipitation, complexation and adsorption on clay particles and via uptake by biota. The release of Ni from sediment may occur as a result of microbial activity or changes in physical and chemical parameters such as pH, ionic strength and sorption processes (Di Toro et al. 1991). Nickel showed enrichment at station, 5, 7 and 9 during pre-monsoon. Monsoon recorded slight enrichment of Ni at stations 2, 5, 7 and 8 in zone I and at station 13 in zone II. During post-monsoon, stations from zone I showed higher values at stations 2, 6 and 7.

Pb reaches the aquatic system from manufacturing industries, smelting and refining and from sewage/ domestic waste (Fergusson 1990). Sorption of Pb by sediments has been reported to be processes correlated with organic content, grain size and anthropogenic pollutants (Muniz et al. 2004). Zone I yielded concentrations higher than world average at all stations except at station 1. All stations in Zone II showed higher values than shale value. Zone I in monsoon and post-monsoon had similar trend they have higher range than world average. Zone II was less enriched in Pb compared with zone I during all three seasons. Therefore, the spatial variation was very prominent in zone I.

Statistical analysis

Geochemistry and inter-metal relationships

Pearson correlation matrix was calculated for the analysed sediment geochemical parameters and metals and the results are presented in Tables 2, 3 and 4. Intermetallic relationship in the sediments revealed a high degree of correlation among certain metals, indicating their identical behaviour during transport in the estuarine environment. This matrix provided clues for the interaction of various carrier phases with trace metals and for their geochemical association which in turn led to their incorporation into the sediments.

Metal–metal correlation

The seasonal correlation matrix indicated that Fe has highly significant positive correlation with all the metals during post-monsoon. However, the high Fe correlation with Mn, Cu, Zn and Cd during the monsoon and Zn and Cd during the pre-monsoon periods weakens.

Mn showed a significant correlation with Mg, Fe, Co, Ni, Cu and Pb but insignificant with Cr, Zn and Cd. During post-monsoon, Mn again showed significant correlation with Fe, Co and Pb but insignificant Mg, Cr, Ni, Cu, Zn and Cd. During monsoon, Mn was insignificantly correlated with Mg. Cr, Fe, Co, Ni, Cu, Zn, Cd and Pb.

Mg exhibited highly significant correlation with all the metals investigated during all the seasons. However during post-monsoon its correlation with Mn suffered a weakening, during monsoon its correlation with Mn and Co also suffered a similar weakening.

Co displayed significant correlation with Mg, Mn, Ni, Cu, Cd and Pb during pre-monsoon; with Mg, Cr, Fe, Ni and Pb during monsoon and with Mg, Cr, Mn, Fe, Ni, Cu and Pb during post-monsoon. The correlation was weakening or insignificant with Cr and Zn with Mn, Cu, Zn and Cd and with Zn and Cd, respectively, during the above three seasons.

During pre-monsoon Cu showed significant correlation with all other metals. But in monsoon, it did not show any significant correlation with other metals. For post-monsoon, it gave significant correlation with all metals except Mn.

Zn showed significant correlation during pre-monsoon with Mg, Cu, Cd and Pb but weak correlations with Cr, Mn, Fe, Co and Ni during pre-monsoon. Zn displayed significant correlations with Mg, Ni, Cd and Pb but weak correlations with the metals Cr, Mn, Fe, Co and Cu during the monsoon. During post-monsoon Zn exhibited significant correlations with Mg, Cr, Fe, Ni, Cu, Cd and Pb but correlations with Mn and Co.

During the pre-monsoon, Ni revealed significant correlations with the metals Mg, Cr, Mn, Fe, Co, Cu, Cd and Pd, and gave weak correlation with the metal Zn. In the post-monsoon, Ni has significant correlations with the metals Mg, Cr, Fe, Co, Cu, Zn, Cd and Pb, but gives weak correlation with the metal Mn. In the case of Ni, it exhibited significant correlations with Mg, Cr, Fe, Co, Zn, Cd and Pb during the monsoon and gives weak correlations with the metals Cu and Mn.

For the pre-monsoon season, Cr showed significant correlations with Mg, Fe, Ni and Cu but also showed weak correlations with the metals Mn, Co, Zn and Cd.

Table 2 Correlation matrix of trace metals, texture and organic component during pre-monsoon season

	Cd	Co	Cu	Cr	Fe%	Mg%	Mn	Ni	Pb	Zn	Sand (%)	Silt (%)	Clay (%)	OC (%)	TN (%)	TC (%)	TS (%)
Cd	1.00																
Co	*0.55*	1.00															
Cu	**0.68**	**0.70**	1.00														
Cr	0.49	0.32	**0.77**	1.00													
Fe%	0.48	**0.69**	**0.94**	**0.78**	1.00												
Mg (%)	**0.68**	**0.67**	**0.85**	**0.69**	**0.74**	1.00											
Mn	0.43	**0.85**	**0.76**	0.44	**0.86**	*0.56*	1.00										
Ni	*0.61*	**0.71**	**0.96**	**0.78**	**0.93**	**0.93**	**0.74**	1.00									
Pb	**0.83**	**0.76**	**0.92**	*0.66*	**0.80**	**0.89**	**0.72**	**0.88**	1.00								
Zn	**0.97**	0.46	*0.60*	0.39	0.36	*0.62*	0.32	0.51	**0.79**	1.00							
Sand (%)	*−0.64*	**−0.78**	**−0.91**	**−0.68**	**−0.81**	**−0.87**	**−0.71**	**−0.91**	**−0.88**	*−0.57*	1.00						
Silt (%)	*0.60*	*0.63*	**0.80**	*0.65*	**0.68**	**0.81**	*0.59*	**0.79**	**0.82**	*0.55*	**−0.92**	1.00					
Clay (%)	*0.56*	**0.80**	**0.86**	*0.58*	**0.81**	**0.77**	**0.70**	**0.87**	**0.78**	0.48	**−0.89**	*0.65*	1.00				
OC (%)	**0.67**	**0.71**	**0.94**	**0.73**	**0.84**	**0.87**	**0.68**	**0.92**	**0.89**	*0.61*	**−0.98**	**0.91**	**0.88**	1.00			
TN (%)	*0.55*	**0.65**	**0.79**	*0.56*	**0.67**	**0.88**	0.51	**0.84**	**0.82**	*0.54*	**−0.86**	**0.75**	**0.82**	**0.83**	1.00		
TC (%)	*0.54*	*0.61*	**0.77**	*0.57*	*0.66*	*0.66*	*0.56*	**0.69**	**0.82**	*0.57*	**−0.81**	**0.73**	**0.74**	**0.82**	**0.80**	1.00	
TS (%)	**0.72**	*0.57*	**0.82**	**0.70**	*0.65*	**0.88**	0.46	**0.80**	**0.90**	**0.72**	**−0.86**	**0.83**	**0.73**	**0.88**	**0.84**	**0.87**	1.00

Correlation significant at 0.05 levels are set in italics. Correlation significant at 0.01 levels are set in bold

Table 3 Correlation matrix of trace metals, texture and organic component during monsoon season

	Cd	Co	Cu	Cr	Fe%	Mg (%)	Mn	Ni	Pb	Zn	Sand (%)	Silt (%)	Clay (%)	OC (%)	TN (%)	TC (%)	TS (%)
Cd	1.00																
Co	0.37	1.00															
Cu	0.32	0.08	1.00														
Cr	0.31	**0.66**	0.38	1.00													
Fe%	0.49	**0.94**	0.15	**0.77**	1.00												
Mg%	*0.55*	*0.59*	0.43	**0.78**	**0.75**	1.00											
Mn	−0.14	0.19	−0.34	0.19	0.11	−0.14	1.00										
Ni	*0.56*	**0.74**	0.37	**0.89**	**0.88**	**0.95**	0.00	1.00									
Pb	*0.60*	**0.71**	0.41	**0.75**	**0.81**	**0.86**	0.11	**0.90**	1.00								
Zn	**0.99**	0.36	0.32	0.32	0.49	*0.57*	−0.10	*0.56*	*0.59*	1.00							
Sand (%)	−0.43	*−0.62*	−0.29	*−0.61*	**−0.71**	**−0.86**	0.11	**−0.80**	**−0.74**	−0.45	1.00						
Silt (%)	0.40	0.52	0.27	0.49	*0.57*	**0.77**	−0.10	**0.69**	**0.73**	0.40	**−0.92**	1.00					
Clay (%)	0.26	0.50	0.19	*0.54*	*0.62*	*0.58*	−0.08	*0.61*	0.37	0.32	*−0.62*	0.28	1.00				
OC (%)	*0.56*	*0.61*	0.30	**0.73**	**0.73**	**0.88**	−0.05	**0.86**	**0.75**	*0.59*	**−0.94**	**0.83**	**0.67**	1.00			
TN (%)	0.49	*0.60*	0.39	**0.73**	**0.72**	**0.90**	−0.02	**0.86**	**0.80**	0.52	**−0.96**	**0.85**	**0.67**	**0.97**	1.00		
TC (%)	*0.53*	*0.56*	0.39	**0.67**	**0.68**	**0.87**	−0.14	**0.82**	**0.71**	*0.56*	**−0.95**	**0.84**	**0.69**	**0.98**	**0.98**	1.00	
TS (%)	0.52	0.48	0.19	0.58	*0.62*	**0.84**	−0.17	**0.77**	*0.61*	*0.56*	**−0.92**	**0.80**	**0.67**	**0.96**	**0.91**	**0.96**	1.00

Correlation significant at 0.05 levels are set in italics. Correlation significant at 0.01 levels are set in bold

Table 4 Correlation matrix of trace metals, texture and organic component during post-monsoon season

	Cd	Co	Cu	Cr	Fe (%)	Mg (%)	Mn	Ni	Pb	Zn	Sand (%)	Silt (%)	Clay (%)	OC (%)	TN (%)	TC (%)	TS (%)
Cd	1.00																
Co	0.44	1.00															
Cu	**0.73**	**0.71**	1.00														
Cr	*0.56*	*0.55*	**0.79**	1.00													
Fe (%)	*0.58*	**0.95**	**0.85**	*0.59*	1.00												
Mg (%)	*0.57*	*0.64*	**0.94**	**0.81**	**0.75**	1.00											
Mn	0.24	**0.95**	0.48	0.31	**0.84**	0.41	1.00										
Ni	*0.59*	**0.73**	**0.97**	**0.83**	**0.84**	**0.98**	0.51	1.00									
Pb	*0.58*	**0.76**	**0.97**	**0.79**	**0.87**	**0.96**	*0.57*	**0.99**	1.00								
Zn	**0.99**	0.41	**0.76**	*0.56*	*0.58*	*0.61*	0.20	*0.63*	*0.62*	1.00							
Sand (%)	*−0.58*	**−0.72**	**−0.95**	**−0.84**	**−0.81**	**−0.97**	−0.50	**−0.98**	**−0.97**	*−0.61*	1.00						
Silt (%)	*0.65*	**0.78**	**0.84**	**0.77**	**0.81**	**0.82**	*0.61*	**0.83**	**0.84**	*0.65*	**−0.88**	1.00					
Clay (%)	0.42	*0.54*	**0.87**	**0.75**	*0.67*	**0.92**	0.32	**0.92**	**0.89**	0.46	**−0.92**	*0.62*	1.00				
OC (%)	*0.63*	*0.64*	**0.96**	**0.83**	**0.78**	**0.96**	0.40	**0.97**	**0.96**	*0.66*	**−0.98**	**0.83**	**0.93**	1.00			
TN (%)	0.46	0.47	**0.73**	**0.68**	*0.53*	**0.84**	0.30	**0.79**	**0.78**	0.46	**−0.83**	0.63	**0.85**	**0.85**	1.00		
TC (%)	0.53	**0.79**	**0.93**	**0.83**	**0.85**	**0.94**	*0.58*	**0.96**	**0.95**	*0.56*	**−0.95**	**0.84**	**0.88**	**0.95**	**0.76**	1.00	
TS (%)	0.51	0.49	**0.91**	**0.83**	*0.63*	**0.96**	0.25	**0.94**	**0.91**	*0.57*	**−0.92**	**0.72**	**0.93**	**0.93**	**0.79**	**0.87**	1.00

Correlation significant at 0.05 levels are set in italics. Correlation significant at 0.01 levels are set in bold

Cr also leads significant correlations with the metals Mg, Fe, Co, Ni and Pb and gives weak correlations with the metals Mn, Cu, Zn and Cd during the monsoon. The post-monsoon has significant correlations with Mg, Fe, Co, Ni, Cu, Zn, Cd and Pb and weak correlations with the metal Mn.

During the pre-monsoon, Cd exhibits significant correlations with the metals Mg, Co, Ni, Cu, Zn and Pb but the correlation gets weakened for the metals Fe, Mn and Cr. In the case of Cd, correlations has high significance with the metals like Mg, Ni, Zn and Pb during the monsoon, and correlations gets weakened for Cr, Mn, Fe, Co and Cu. For the post-monsoon season, Cd gives significant correlations with the metals Mg, Cr, Fe, Ni, Cu, Zn and Pb but the correlations gets declining for the metals Mn and Co.

The post- and pre-monsoon seasons, Pb indicated significant correlations with all the metals Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn and Cd. However, except Mg, Cr, Fe, Co, Ni, Zn and Cd, the metals Cu and Mn showed weak correlations with Pb during the monsoon.

Trace metal enrichment in sediments is linked to scavenging mechanisms involving hydrous oxides. Fe and Mn being the abundant elements in the study region exert a major control on the distribution of other elements in the sediments. The hydrous oxides of Fe and Mn constitute significant sink to trace metal in estuaries through adsorption/co-precipitation of other trace metals and formation of complexes with a verity of organic ligands. The highly significant Fe and Mn correlation observed during post-monsoon revealed the formation of stable Fe–Mn oxyhydroxides, while the significant correlation of Fe with all other metals indicated their adsorption and incorporation into the sediment matrix. The weakening of Fe–Mn correlation during monsoon indicated the precipitation of Fe–Mn oxyhydroxides, while the insignificant of correlation of Mn vis-à-vis other metals revealed their near association. Co-precipitation of Cd and Zn with Fe–Mn hydroxides along with scavenging of other metals could account for the net accumulation of trace metals in the sediments of the Cochin estuary. The results of the seasonal correlation matrix thus indicated that a substantial fraction of the trace metal were co-precipitated with or adsorbed onto Fe and Mn geochemical phases in the sediments.

Correlation metals with other sedimentary parameters

During the present study, Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb are all well correlated with silt, clay and organic carbon during the pre-monsoon period. However, significant deviations in these correlations are noted during the monsoon and post-monsoon periods. During monsoon, clay showed well-defined significant correlations with Mg, Cr, Fe and Ni weak correlation with Mn, Co, Cu, Zn, Cd and Pb. Silt was significantly correlated with Mg, Fe, Co, Ni and Pb during the monsoon, but weakly with Mn, Cr, Cu, Zn and Cd. In the post-monsoon season, while silt showed well-defined correlations with Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, and Cd, clay showed significant correlations only with Mg, Cr, Fe, Co, Ni, Cu, and Pb while in Mn, Zn and Cd, the correlations diminished. Weak correlations were noted for Mn and Cu with organic carbon during monsoon. However, such weak correlations were noted only for Mn during the post-monsoon period.

Organic matter contents and grain size are important controlling factors influencing the abundance of trace metals in sediments (Rubio et al. 2000; Aloupi and Angelidis 2001; Liaghati et al. 2003). Adsorption of metal increases with order: sand<silt<clay, due to an increase in their superficial area and in their mineral/organic matter contents (Haque and Subramanian 1982). The significant positive correlations observed for the metals with OC indicating their role as geochemical carriers of these metals in the study region. Fe and Mn have fairly close spatial distribution patterns and correlations in sediments during post-monsoon and pre-monsoon seasons indicating their strong association in the geochemical matrix and the dependence of their seasonal variations on differences in estuarine hydrodynamics. The very strong correlations of Fe, Mg, Mn, Co, Ni, Cu, Zn, Cr, Cd and Pb with silt, clay and OC during the pre-monsoon period implies that these metals can be accumulated either by clay minerals that adsorb these trace metals directly or by organic matter, which is mounted on the clay surface and hence interrelated to the fine-grained fraction (Wang and Chen 2000). The strong relationship of Fe with OC, silt and clay during all points suggests its presence as a constituent of clay minerals and on coatings on the surface of clay particles. However, the weak relationship of Mn with organic carbon, silt and clay content during monsoon and post-monsoon suggests that other factors also control their distribution. The present study authenticates the effective relation of organic carbon with most of the elements (except Mn and Cu during the monsoon) and endorses the role of sediment organic matter as metal carrier and of complexation with organic matter playing an important role in defining their distribution patterns. Thus silt, clays and hydrous iron oxides exert a major influence on the adsorption properties of sediments on trace metals. The strong correlation of trace metals with mud (silt and clay) in all seasons indicates that they are concentrated to the fine-grained particles and are hosted by clay phases.

Cluster analysis

The results of cluster analysis reveals the existence of three major groups of stations during the pre-monsoon and of four major groups of stations during the monsoon and post-monsoon periods (Fig. 2). The first group cluster during the pre-monsoon period consisted of stations 3, 4, 5, 6, 7, 8, 9, 12, 13 and 14 characterised with moderate to high levels of Fe, Co, Mg, Mn, Cu, Cr, Cd, Ni, Pb and Zn and enriched with organic carbon contents in the sediments. The second group of stations 1, 10 and 11 showed lesser anthropogenic inputs as evidenced by low levels of Fe, Mn, Mg, Co, Cu, Ni, Zn, Cr, Cd and Pb and high sand content probably due to higher rate of water renewal at these locations. The third cluster formed during the pre-monsoon consisted of only at station 2, which was subject to heavy industrial contamination and hence characterised by very high concentrations of Zn, Cu, Cd and Pb. Organic carbon, total carbon and total sulphur contents were also found at highly elevated concentrations.

The first group cluster during the monsoon period consisted of stations 1, 3, 4, 6, 9 and 10 characterised by moderate levels of Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb. The second group consisted of stations 5, 7, 8, 12, 13 and 14 characterised by high levels of Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb and the third group cluster consisted of only station 2 characterised by highest levels of Cd and Zn in the sediments. A fourth group cluster formed during the monsoon, consisted of only station 11 characterised by highest levels of Mn and lowest levels of Mg, Cr, Fe, Co, Ni, Cu, Zn, Cd and Pb.

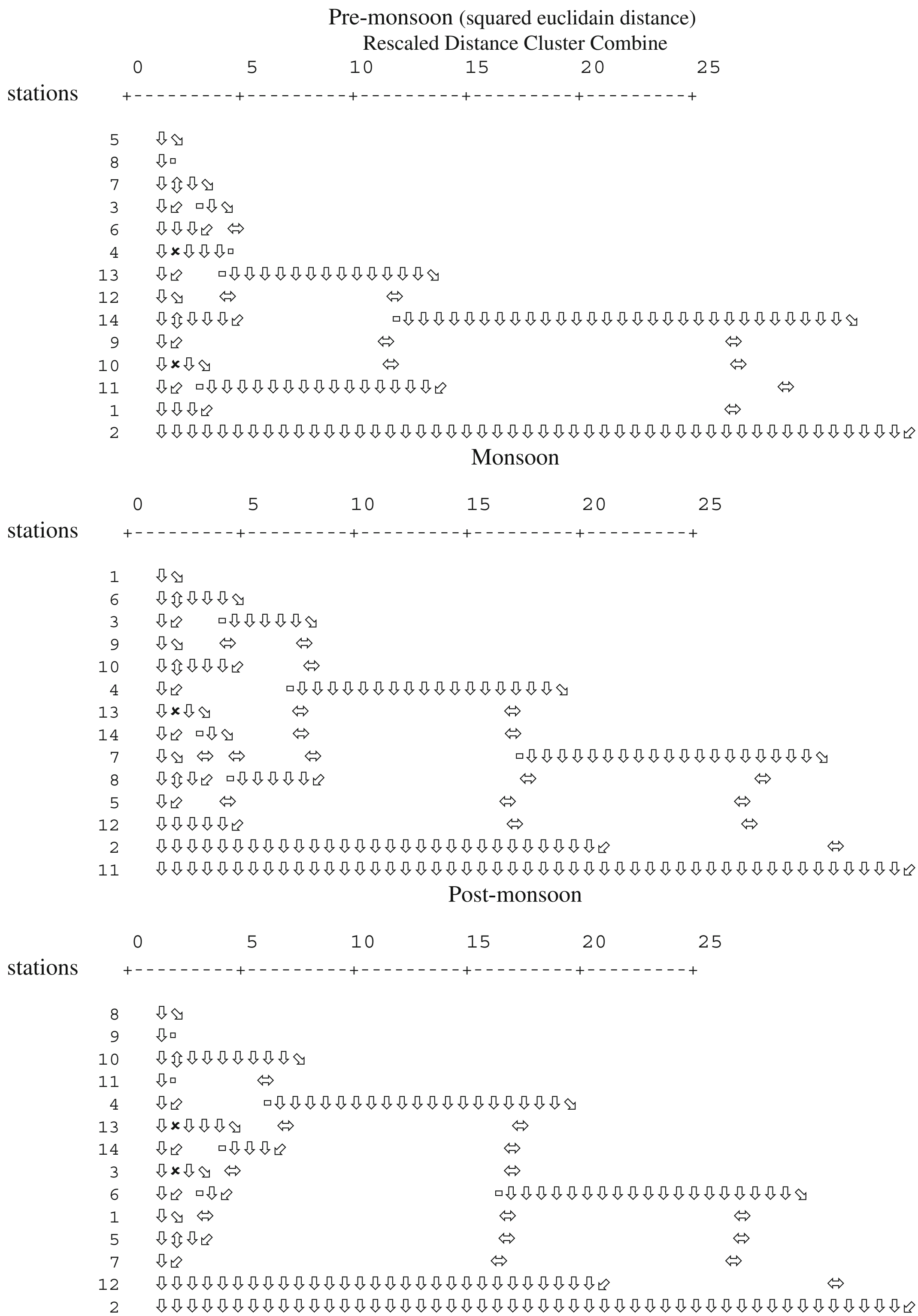

Fig. 2 Dendrogram showing station groups formed by group averaging cluster analysis of elemental concentration during three seasons

The first group cluster during the post-monsoon period consisted of stations 4, 8, 9, 10 and 11 characterised by lowest levels of trace metals Fe, Co, Mg, Mn, Cu, Cr, Cd, Ni, Pb and Zn. The second group consisted of stations 1, 3, 5, 6, 7, 13 and 14 characterised by moderate to high levels of trace metals Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb while the third group consisted of only station 2 characterised by highest levels of Cu, Zn and Cd. The fourth group cluster formed during the post-monsoon period consisted of only station 12 characterised by highest levels of Fe, Mn and Co in the sediments.

Principal Component Analysis

In multivariate statistical analysis, PCA was used to establish the possible factors that contribute to trace metal concentration and source characterization. PCA has been employed to find out the possible linear combination of original variables of trace metals, which could account for the largest part (80%) of the total variance.

Table 5 showed the varimax component of two factors in sediment during the pre-monsoon period. Two significant components, whose eigenvalues of >1.0 and accounting for 83% of cumulative variance, were distinguished from the analytical data. Factor 1 accounted for 50.66% of the total variance characterised by of high loading of silt, clay, OC, TN, TC including Mg, Cr, Mn, Fe, Co, Ni and Cu in the sediments. Factor 2 accounted for 32.51% of the total variance which includes a strong coupling of high loading TS with high loading of metals Zn, Pb and Cd.

The monsoon period exhibited four significant components with a cumulative variance of 87% which accounted for eigenvalues of >1. Factor 1 explains 41.235% of total variance accounting the grouping of very high loading silt, clay, OC, TN, TC and TS with the high loading of the metals like Mg and Ni in sediments. Factor 2 explains the 22.37% of the total variance characterised with high loading of Fe and Mn, indicating an association of Fe–Mn oxides, which couples with the strong very high positive loadings of the metals like Co, Cr, Ni and Pb. Factor 3 accounted for 15.03% of the total variance which accounted for the grouping of high loading of Cd and Zn indicating their common origin. Factor 4 explained the 9.2% of the total variance characterising the high content of Cu. Here, high negative loadings of Fe and Mn coupled with high positive loading of Cu probably indicate some degree of continental influence. The spatial segregation/loading of the anthropogenic metals Zn, Pb and Cd in association with the loading of natural metals Fe and Mn, during the monsoon season indicated co-precipitation whereas during the post-monsoon and pre-monsoon indicated adsorption with Fe–Mn oxide geochemical phases controlling other trace metals in sediments. Accordingly, co-precipitation of Pb, Cd and Zn with Fe–Mn hydroxides along with scavenging of other metals could account for the net accumulation of trace metals in the sediments of the Cochin estuary.

Three significant components have occurred with a cumulative variance of 93.89% which accounted for eigenvalues of >1during the post-monsoon period. Factor 1 accounts for the 51.79% of the total variance characterised with grouping of high amount of silt, clay, OC, TN, TC and TS along with high Mg, Cu, Cr, Ni and Pb. Factor 2 accounted for 23.97% of the total variance characterised by strong positive loading of Fe and Mn, indicating an association of Fe–Mn oxides, which again couples with the strong positive loadings of the metal Co. Factor 3 accounted for the 18.13% of the total variance characterised by the high loading only for Zn and Cd.

During the pre-monsoon period, high levels of trace metals coupled with higher enrichment silt, clay, OC, TN and TC indicated that organic matter fluxes derived from anthropogenic sources in the Cochin estuary has a higher capacity to bind most metals during its transport and export to the bottom sediments and (Murray et al. 1999; Reimann and de Caritat 2005) also support these factors in their correlation studies. The associations of Fe and Mn in factor 1 during the pre-monsoon period and also in factor 2 during the monsoon and post-monsoon periods suggest their common occurrence in the basic rock. The shifting or spatial segregation of Fe–Mn associations in the factor loadings during the monsoon, post-monsoon and pre-monsoon periods were possibly as a result of their flocculation properties attributed to seasonal differences in pH, salinity and organic matter fluxes from anthropogenic origin (Balachandran et al. 2005, 2006). The distribution of Zn, Pb and Cd in the factor 2 in the period has shifted to all other factors with low or high intensity during the monsoon and post-monsoon periods which suggests this metal contribution is from both natural and anthropogenic sources.

Table 5 Factor analysis of Cochin estuarine sediment loading with chemical parameters during three seasons

Variable	Pre-monsoon		Monsoon				Post-monsoon		
	Component		Component				Component		
	1	2	1	2	3	4	1	2	3
Cd	0.256	0.889	0.242	0.163	0.944	0.133	0.277	0.176	0.935
Co	0.76	0.289	0.4	0.754	0.183	−0.136	0.35	0.912	0.186
Cu	0.832	0.494	0.105	0.179	0.153	0.913	0.762	0.393	0.485
Cr	0.628	0.395	0.444	0.789	0.025	0.24	0.764	0.217	0.342
Fe (%)	0.93	0.212	0.501	0.747	0.268	−0.042	0.464	0.799	0.332
Mg (%)	0.683	0.616	0.723	0.456	0.291	0.305	0.889	0.306	0.293
Mn	0.865	0.089	−0.232	0.533	−0.095	−0.579	0.123	0.981	0.021
Ni	0.868	0.426	0.617	0.664	0.289	0.222	0.847	0.418	0.309
Pb	0.674	0.707	0.46	0.684	0.39	0.22	0.81	0.474	0.299
Zn	0.133	0.946	0.277	0.16	0.93	0.109	0.33	0.138	0.928
Sand (%)	−0.815	−0.522	−0.918	−0.283	−0.166	−0.102	−0.854	−0.407	−0.297
Silt (%)	0.669	0.559	0.81	0.204	0.197	0.103	0.571	0.558	0.445
Clay (%)	0.827	0.376	0.651	0.296	0.013	0.045	0.941	0.201	0.114
OC (%)	0.795	0.558	0.873	0.34	0.293	0.089	0.873	0.303	0.355
TN (%)	0.676	0.551	0.854	0.395	0.204	0.175	0.848	0.142	0.164
TC (%)	0.622	0.562	0.895	0.263	0.258	0.187	0.803	0.5	0.242
TS (%)	0.554	0.766	0.933	0.133	0.282	0.036	0.933	0.136	0.258
% of variance	50.656	32.507	41.235	22.365	15.028	9.206	51.793	23.969	18.13
Cumulative (%)	50.656	83.163	41.235	63.6	78.628	87.834	51.793	75.762	93.892

Assessment of pollution status in sediments of the Cochin estuary

Enrichment factor

Studies elsewhere suggested that, when 0.5≥EF≤1.5, the trace metals are enriched from crustal input or that of natural weathering processes. EF of >1.5, shows a significant portion of trace metals are executed from external by other sources (Zhang et al. 2007). In this study, Cd showed an EF of >1.5 at zones I and II during pre-monsoon and monsoon, respectively, whereas during post-monsoon season, Cd showed negative EF at stations 8 and 9 of zone II (Table 6). Zn also showed an EF of >1.5 at stations 2 of zone I in all the seasons. Metals other than Zn and Cd during pre-monsoon and monsoon, showed an EF of <1.5 indicating their natural weathering processes as source. At all stations (except station 2) of zone I metals like Mg, Cr, Mn, Ni, Cu, Zn and Pb exhibited an EF of <1.5 at post-monsoon, indicating their origin from natural weathering processes. The high EFs for Zn and Cd suggest anthropogenic sources mainly from industries. Other studies also lend credence to these observations. The difference in EF values of various metals may be due to the difference in the magnitude of input for each metal in the sediment and/or the difference in the removal rate of each metal from the sediment.

Contamination factor

CF of the various trace metals in the sediments are presented in Table 7. Mn, Cr and Co showed very low contamination whereas Mg, Fe, Ni, Cu, Zn and Pb gave moderate contamination at all stations of both zones during the pre-monsoon period. Cd reported CF of <3.0 at stations 10 and 11 of zone II whereas all other stations of two zones showed very high contamination factors in the range 7 to 42. At pre-monsoon season, station 2 also exhibits a maximum CF of 42.

Table 6 Showing the enrichment factor of studied station during three seasons

	St. no.	Cd	Pb	Ni	Co	Zn	Mg	Mn	Cu	Cr
EF in pre-monsoon										
Pre-monsoon	1	10.47	1.18	0.53	0.52	1.67	0.70	0.18	0.54	0.19
	2	31.14	1.29	0.64	0.48	3.74	0.70	0.19	0.76	0.21
	3	10.56	1.01	0.64	0.44	1.13	0.75	0.19	0.62	0.21
	4	5.93	0.66	0.45	0.43	0.51	0.27	0.21	0.54	0.14
	5	10.59	0.70	0.67	0.35	0.83	0.66	0.16	0.58	0.18
	6	9.32	1.02	0.68	0.47	1.31	0.76	0.17	0.69	0.22
	7	10.63	0.75	0.60	0.37	0.94	0.60	0.15	0.56	0.29
	8	7.88	0.73	0.58	0.31	0.76	0.51	0.14	0.56	0.20
	9	5.20	0.60	0.46	0.13	0.55	0.29	0.15	0.54	0.25
	10	3.26	0.59	0.39	0.37	0.10	0.22	0.14	0.62	0.21
	11	5.47	0.86	0.36	0.87	0.25	0.19	0.25	0.51	0.17
	12	6.28	0.73	0.38	0.52	0.33	0.27	0.24	0.41	0.14
	13	7.03	0.81	0.59	0.48	0.71	0.53	0.23	0.57	0.08
	14	10.09	0.82	0.46	0.44	0.98	0.44	0.26	0.45	0.18
EF in monsoon										
Monsoon	1	11.63	0.90	0.67	0.41	1.22	0.74	0.17	0.63	0.13
	2	29.67	0.99	0.62	0.41	3.48	0.58	0.19	0.69	0.15
	3	9.32	0.84	0.59	0.40	0.92	0.63	0.21	0.60	0.17
	4	12.18	1.07	0.59	0.44	0.76	0.61	0.17	3.38	0.20
	5	11.29	1.20	0.71	0.48	1.01	0.64	0.28	0.64	0.23
	6	9.92	0.92	0.62	0.44	1.11	0.72	0.19	0.57	0.14
	7	7.34	0.86	0.60	0.43	0.87	0.56	0.29	0.60	0.19
	8	7.29	0.76	0.67	0.42	0.80	0.57	0.24	0.62	0.27
	9	7.51	0.69	0.41	0.36	0.41	0.25	0.17	0.49	0.09
	10	7.05	0.17	0.39	0.49	0.42	0.26	0.21	0.19	0.11
	11	5.51	0.86	0.39	0.40	0.44	0.18	1.62	0.56	0.18
	12	5.81	0.64	0.36	0.56	0.47	0.22	0.34	0.35	0.10
	13	9.76	0.96	0.64	0.44	0.90	0.59	0.26	0.60	0.18
	14	7.40	0.94	0.52	0.43	0.72	0.43	0.32	0.50	0.17
EF in post-monsoon										
Post-monsoon	1	10.04	1.41	0.85	0.51	1.08	0.93	0.19	0.79	0.48
	2	33.89	1.03	0.62	0.41	3.79	0.60	0.16	0.73	0.28
	3	8.36	1.16	0.64	0.41	1.18	0.67	0.20	0.62	0.19
	4	15.21	0.75	0.53	0.42	1.80	0.67	0.16	0.48	0.18
	5	9.10	1.03	0.68	0.43	1.06	0.70	0.16	0.64	0.23
	6	10.92	1.18	0.68	0.41	1.28	0.65	0.19	0.68	0.16
	7	11.91	1.27	0.80	0.46	1.16	0.79	0.19	0.70	0.46
	8	−0.32	1.16	0.48	0.47	1.08	0.55	0.23	0.53	0.23
	9	−0.60	0.68	0.36	0.34	0.50	0.23	0.12	0.40	0.11
	10	4.57	0.81	0.38	0.40	0.60	0.19	0.16	0.51	0.22
	11	7.12	0.73	0.37	0.37	0.55	0.20	0.20	0.47	0.18
	12	6.47	0.67	0.36	0.56	0.49	0.28	0.33	0.34	0.14
	13	4.76	0.88	0.51	0.45	0.60	0.44	0.25	0.50	0.14
	14	6.86	0.91	0.47	0.49	0.60	0.44	0.25	0.44	0.17

Table 7 Showing the contamination factor of studied station during three seasons

	St. no.	Cd	Pb	Ni	Co	Zn	Fe	Mg	Mn	Cu	Cr
CF in pre-monsoon											
Pre-monsoon	1	6.88	0.78	0.35	0.34	1.10	0.66	0.46	0.12	0.35	0.12
	2	42.75	1.77	0.88	0.66	5.13	1.37	0.97	0.26	1.05	0.29
	3	14.50	1.39	0.87	0.60	1.56	1.37	1.02	0.26	0.86	0.29
	4	10.50	1.17	0.79	0.76	0.89	1.77	0.48	0.37	0.95	0.24
	5	17.00	1.12	1.07	0.57	1.34	1.61	1.06	0.26	0.93	0.29
	6	10.25	1.12	0.74	0.52	1.44	1.10	0.83	0.19	0.76	0.24
	7	18.63	1.32	1.05	0.64	1.64	1.75	1.06	0.27	0.98	0.52
	8	15.00	1.39	1.11	0.58	1.44	1.90	0.98	0.27	1.06	0.38
	9	7.88	0.91	0.69	0.20	0.84	1.51	0.43	0.22	0.82	0.38
	10	1.63	0.30	0.19	0.18	0.05	0.50	0.11	0.07	0.31	0.10
	11	1.88	0.30	0.12	0.30	0.09	0.34	0.07	0.09	0.18	0.06
	12	6.50	0.76	0.39	0.54	0.34	1.03	0.27	0.25	0.42	0.15
	13	10.63	1.22	0.89	0.73	1.08	1.51	0.80	0.34	0.86	0.12
	14	10.25	0.84	0.47	0.45	1.00	1.02	0.45	0.26	0.45	0.19
CF in monsoon											
Monsoon	1	15.25	1.18	0.88	0.54	1.60	1.31	0.97	0.23	0.83	0.18
	2	51.25	1.71	1.08	0.71	6.01	1.73	1.01	0.32	1.20	0.25
	3	14.13	1.28	0.89	0.60	1.39	1.51	0.96	0.33	0.90	0.26
	4	6.75	0.59	0.32	0.24	0.42	0.55	0.34	0.09	1.88	0.11
	5	17.88	1.89	1.12	0.76	1.60	1.58	1.01	0.44	1.02	0.37
	6	12.13	1.12	0.76	0.53	1.36	1.22	0.89	0.24	0.70	0.17
	7	13.00	1.53	1.07	0.77	1.55	1.77	0.98	0.51	1.06	0.34
	8	14.00	1.45	1.30	0.81	1.53	1.92	1.09	0.46	1.19	0.52
	9	9.00	0.83	0.49	0.43	0.49	1.20	0.30	0.20	0.58	0.11
	10	6.75	0.16	0.37	0.47	0.40	0.96	0.25	0.21	0.18	0.11
	11	3.13	0.49	0.22	0.23	0.25	0.57	0.10	0.92	0.32	0.10
	12	10.38	1.14	0.64	1.00	0.85	1.79	0.40	0.60	0.63	0.18
	13	16.75	1.66	1.09	0.76	1.54	1.72	1.00	0.44	1.03	0.30
	14	9.88	1.26	0.69	0.57	0.96	1.33	0.57	0.42	0.67	0.22
CF in post-monsoon											
Post-monsoon	1	9.88	1.39	0.84	0.51	1.06	0.98	0.91	0.19	0.78	0.47
	2	59.63	1.81	1.09	0.72	6.66	1.76	1.05	0.28	1.28	0.49
	3	12.88	1.79	0.99	0.63	1.82	1.54	1.03	0.31	0.95	0.30
	4	9.75	0.48	0.34	0.27	1.15	0.64	0.43	0.10	0.31	0.12
	5	12.00	1.36	0.90	0.57	1.39	1.32	0.92	0.22	0.84	0.30
	6	18.00	1.94	1.12	0.68	2.12	1.65	1.07	0.31	1.12	0.26
	7	16.25	1.73	1.09	0.62	1.58	1.36	1.07	0.25	0.96	0.63
	8	−0.13	0.46	0.19	0.18	0.42	0.39	0.22	0.09	0.21	0.09
	9	−0.50	0.57	0.30	0.28	0.41	0.83	0.19	0.10	0.33	0.09
	10	3.50	0.62	0.29	0.31	0.46	0.77	0.14	0.12	0.39	0.17
	11	4.63	0.47	0.24	0.24	0.36	0.65	0.13	0.13	0.30	0.12
	12	11.75	1.22	0.66	1.03	0.89	1.82	0.51	0.60	0.62	0.25
	13	5.38	1.00	0.58	0.50	0.68	1.13	0.50	0.28	0.56	0.16
	14	6.88	0.91	0.47	0.49	0.61	1.00	0.44	0.25	0.44	0.17

Table 8 Showing the geoaccumulation index of studied station during three seasons

	St. no.	Cd	Pb	Ni	Co	Zn	Fe	Mg	Mn	Cu	Cr
GAI in pre-monsoon											
Pre-monsoon	1	2.20	−0.95	−2.12	−2.13	−0.45	−1.19	−1.71	−3.65	−2.09	−3.59
	2	4.83	0.23	−0.77	−1.18	1.78	−0.13	−0.64	−2.51	−0.52	−2.37
	3	3.27	−0.11	−0.78	−1.32	0.05	−0.13	−0.55	−2.54	−0.81	−2.38
	4	2.81	−0.36	−0.92	−0.99	−0.75	0.24	−1.64	−2.03	−0.65	−2.64
	5	3.50	−0.42	−0.49	−1.40	−0.17	0.10	−0.50	−2.55	−0.69	−2.37
	6	2.77	−0.42	−1.01	−1.53	−0.06	−0.45	−0.85	−2.97	−0.99	−2.66
	7	3.63	−0.19	−0.51	−1.23	0.13	0.22	−0.50	−2.49	−0.62	−1.54
	8	3.32	−0.11	−0.44	−1.36	−0.06	0.34	−0.62	−2.45	−0.50	−1.97
	9	2.39	−0.72	−1.12	−2.88	−0.84	0.01	−1.79	−2.76	−0.87	−1.99
	10	0.12	−2.34	−2.95	−3.04	−4.96	−1.59	−3.74	−4.46	−2.29	−3.85
	11	0.32	−2.34	−3.62	−2.33	−4.12	−2.13	−4.50	−4.13	−3.09	−4.65
	12	2.12	−0.98	−1.94	−1.47	−2.16	−0.54	−2.45	−2.61	−1.84	−3.32
	13	2.82	−0.29	−0.75	−1.05	−0.48	0.01	−0.91	−2.14	−0.80	−3.63
	14	2.77	−0.84	−1.68	−1.75	−0.58	−0.56	−1.75	−2.52	−1.73	−3.01
GAI in monsoon											
Monsoon	1	3.35	−0.34	−0.77	−1.47	0.09	−0.19	−0.63	−2.71	−0.85	−3.10
	2	5.09	0.19	−0.48	−1.08	2.00	0.20	−0.58	−2.21	−0.32	−2.57
	3	3.24	−0.23	−0.75	−1.32	−0.11	0.01	−0.65	−2.20	−0.73	−2.52
	4	2.17	−1.34	−2.21	−2.62	−1.83	−1.44	−2.15	−3.99	0.32	−3.76
	5	3.57	0.33	−0.43	−0.99	0.09	0.08	−0.57	−1.76	−0.56	−2.03
	6	3.01	−0.42	−0.98	−1.49	−0.15	−0.30	−0.76	−2.66	−1.11	−3.17
	7	3.12	0.03	−0.49	−0.97	0.05	0.24	−0.61	−1.56	−0.50	−2.16
	8	3.22	−0.05	−0.21	−0.88	0.03	0.36	−0.46	−1.69	−0.34	−1.52
	9	2.58	−0.86	−1.62	−1.80	−1.61	−0.32	−2.31	−2.91	−1.36	−3.80
	10	2.17	−3.22	−2.02	−1.69	−1.89	−0.65	−2.61	−2.87	−3.08	−3.83
	11	1.06	−1.61	−2.76	−2.73	−2.58	−1.40	−3.92	−0.71	−2.23	−3.85
	12	2.79	−0.40	−1.23	−0.58	−0.83	0.25	−1.91	−1.31	−1.25	−3.08
	13	3.48	0.14	−0.46	−0.98	0.04	0.19	−0.58	−1.77	−0.55	−2.31
	14	2.72	−0.25	−1.12	−1.39	−0.64	−0.17	−1.39	−1.83	−1.16	−2.74
GAI in Post-Monsoon											
Post-monsoon	1	2.72	−0.11	−0.84	−1.57	−0.50	−0.61	−0.72	−3.00	−0.95	−1.68
	2	5.31	0.27	−0.47	−1.06	2.15	0.23	−0.51	−2.42	−0.23	−1.62
	3	3.10	0.26	−0.60	−1.25	0.28	0.04	−0.54	−2.26	−0.66	−2.32
	4	2.70	−1.64	−2.16	−2.48	−0.38	−1.23	−1.81	−3.88	−2.28	−3.69
	5	3.00	−0.14	−0.74	−1.41	−0.11	−0.19	−0.70	−2.79	−0.83	−2.33
	6	3.58	0.37	−0.43	−1.15	0.50	0.14	−0.48	−2.26	−0.42	−2.52
	7	3.44	0.21	−0.46	−1.27	0.07	−0.14	−0.48	−2.56	−0.65	−1.26
	8	0.00	−1.72	−3.00	−3.02	−1.83	−1.93	−2.80	−4.05	−2.84	−4.07
	9	0.00	−1.41	−2.34	−2.42	−1.86	−0.85	−2.99	−3.89	−2.19	−4.04
	10	1.22	−1.28	−2.37	−2.28	−1.70	−0.97	−3.39	−3.60	−1.94	−3.18
	11	1.62	−1.67	−2.62	−2.65	−2.08	−1.21	−3.53	−3.50	−2.31	−3.70
	12	2.97	−0.30	−1.19	−0.55	−0.75	0.28	−1.57	−1.33	−1.27	−2.61
	13	1.84	−0.59	−1.38	−1.57	−1.14	−0.41	−1.58	−2.41	−1.41	−3.25
	14	2.20	−0.72	−1.67	−1.61	−1.31	−0.58	−1.77	−2.56	−1.78	−3.17

During the monsoon period Mg, Cr, Mn, Fe, Co, Cu, Zn and Pb revealed minimum to moderate levels of contamination at all the stations, whereas Cd showed very high contamination levels at all the stations of zones I and II.

Moderate levels of contamination were found at all the stations for Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn and Pb during post-monsoon. Cd showed negative CF values for at stations 8 and 9 of zone II during the post-monsoon period. Cd showed very high CF during post-monsoon for all stations of zone I and stations 10, 11, 12, 13 and 14 of zone II. The contamination factor for Zn and Cd at station 2 of zone I indicated very high values for all three seasons for all the stations.

Index of geoaccumulation

I_{geo} classifies polluted environments along a scale of 0 to 5 representing increasing levels of pollution as explained earlier. The negative I_{geo} values reported for Mg, Cr, Mn, Ni and Cu (Table 8). However, for Zn and Cd, the I_{geo} values are much higher than the average continental crustal values which indicate that these metals cause pollution to the respective environment.

Conclusions

The spatial and temporal distribution of trace metals in the Cochin estuarine system was investigated. Although all metals showed varied concentrations, the approaches of factor analysis, correlation matrix and cluster analysis were effectively used to differentiate the natural and anthropogenic sources of metals and also the complex dynamics of trace metal pollutants. The results indicate that Fe–Mn hydroxide coating and adsorption into organic phases are the major removal pathways of metals in Cochin estuary. Metal pollution in sediment using EF, contamination factor and geoaccumulation index, revealed that Zn and Cd mainly from industrial effluent outfall were the primary pollutants. The results from geoaccumulation index reveal that sediments of Cochin estuary are free from pollution loads of Mn, Fe and Cu but moderately with Zn and very strongly with Cd. The results reported herein would be helpful in developing effective management strategies/protocol to control metal discharges in water bodies, thereby lessening the loading of contaminants in the estuarine sediment.

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