Spatial Variability and Contamination of Heavy Metals in the Inter-tidal Systems of a Tropical Environment

Ratheesh Kumar, C. S., **Joseph, M. M., Gireesh Kumar, T. R., Renjith, K.R., Manju, M. N. and Chandramohanakumar, N.**

Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, Kochi, Kerala, India

ABSTRACT: Heavy metals in the surface sediments of the two coastal ecosystems of Cochin, southwest India were assessed. The study intends to evaluate the degree of anthropogenic influence on heavy metal concentration in the sediments of the mangrove and adjacent estuarine stations using enrichment factor and geoaccumulation index. The inverse relationship of Cd and Zn with texture in the mangrove sediments suggested the anthropogenic enrichment of these metals in the mangrove systems. In the estuarine sediments, the absence of any significant correlation of the heavy metals with other sedimentary parameters and their strong interdependence revealed the possibility that the input is not through the natural weathering processes. The analysis of enrichment factor indicated a minor enrichment for Pb and Zn in mangrove sediments. While, extremely severe enrichment for Cd, moderate enrichment for Zn and minor enrichment of Pb were observed in estuarine system. The geo accumulation index exhibited very low values for all metals except Zn, indicating the sediments of the mangrove ecosystem are unpolluted to moderately polluted by anthropogenic activities. However, very strongly polluted condition for Cd and a moderately polluted condition for Zn were evident in estuarine sediments.

Key words: Geochemistry, Mangroves, Estuary, Metal pollution, Enrichment factor, Geoaccumulation index

INTRODUCTION

High degree of industrialization and urbanization has led to a strong risk of heavy metal contamination in the coastal ecosystems in tropical and subtropical countries. Mangrove ecosystems may act as a sink or a source of heavy metals in coastal environments, because of their variable physical and chemical properties (Harbison, 1986). Estuaries, which form the part of coastal system are also a major reservoir of trace metals, both of anthropogenic and natural origins (Bryan *et al.*, 1980 and Langston, 1982).Spatial variation of metal concentration in surface sediments of urbanized estuaries is often attributed to mixing of sediments from different origins and to pollution sources (Forstner, 1981). The measurement of trace element concentrations and distribution in marine environment leads to better understanding of their behavior in aquatic environment and is important for detecting the sources of pollution (Unnikrishnan and Nair, 2004). The objective of the study was to determine the total concentrations of some heavy metals in the surface sediments of three mangrove and six adjacent estuarine stations in the Cochin estuary in order to

*Corresponding author E-mail: ratheeshkumar2003@gmail.com

evaluate the degree of anthropogenic influence. Enrichment factor and geoaccumulation index were taken as the tool for the study. An attempt to identify the major factors controlling the distribution of heavy metals in these systems was also made by using the principal component analysis.

MATERIALS & METHODS

Cochin estuary, the largest estuarine system in the southwest coast of India, is a part of the Vembanad-Kol wetlands, a Ramsar Site (No. 1214). This estuary (Lat.09°30'-10°10'N and Long.76°15'-76°25'E) is topographically divisible into two arms; a southern one extending south of bar mouth from Cochin to Thanneermukkam and a northern one extending north from Cochin to Azhikode (Ramamirtham *et al.*, 1986). This tropical aquatic system is under the profound influence of monsoon, which contribute to about 71% of annual rainfall (Jayaprakash, 2002) and accordingly there are three seasonal conditions prevailing-monsoon (June–September), post-monsoon (October–January) and pre-monsoon (February–May). The abundant mangrove vegetation along the

Cochin estuarine system has been shrinking in area due to land reclamation and developmental activities and pollution by industrial effluents as well as domestic sewage. Eloor, the major industrial belt of Kerala is notorious for heavy pollution and is rated as one of the most toxic hotspots of the world by Green Peace International.The major polluting industries in the region include fertilizer plant, oil refinery, rare earth processing plant, minerals and rutiles plant, zinc smelter plant, insecticide factory and organic chemical plant. Three mangroves ecosystems M1, M2 and M3 and six estuarine stations E1 to E6 along is the northern arm of Cochin estuary were selected for the present study (Fig. 1). Among the mangrove locations, Station 1, Puthuvyppu (M1), is a mangrove nursery maintained by the fisheries research unit of Kerala Agricultural University, located about 100 m away from the estuarine front and is free from sewage inputs. Station 2, Murikkumpadam (M2), is a densely populated fishermen-settlement. The discharge of sewage and disposal of garbage and solid waste add to the problem of pollution. Station 3, Manglavanam (M3), is a patchy

mangrove area in the heart of the city of Cochin. This is an almost closed system with a single narrow canal linking to the estuary, which is the only source for tidal propagation. The pressure of urban development is causing an adverse effect on this sanctuary. The indiscriminate discharge of the untreated effluents containing heavy metals and pesticides from the Eloor industrial belt is a common point source of pollution to the estuary. Samplings of water and sediments were made from these locations during December 2005, April 2006 and July 2006 representing post-monsoon, pre-monsoon and monsoon respectively. Water samples were taken using a Niskin sampler. Van Veen grab (0.042 m^2) and a clean plastic spoon was used for sediment sampling. After being collected, sediments were put into a sealed polyethylene bag, placed in an ice box and were brought back to the laboratory and kept refrigerated at -20°C before analyses. pH in the water column was measured in situ and temperature was measured using a sensitive thermometer. Salinity of the water samples was estimated by Mohr-Knudsen method (Muller, 1999). Modified Winkler method was
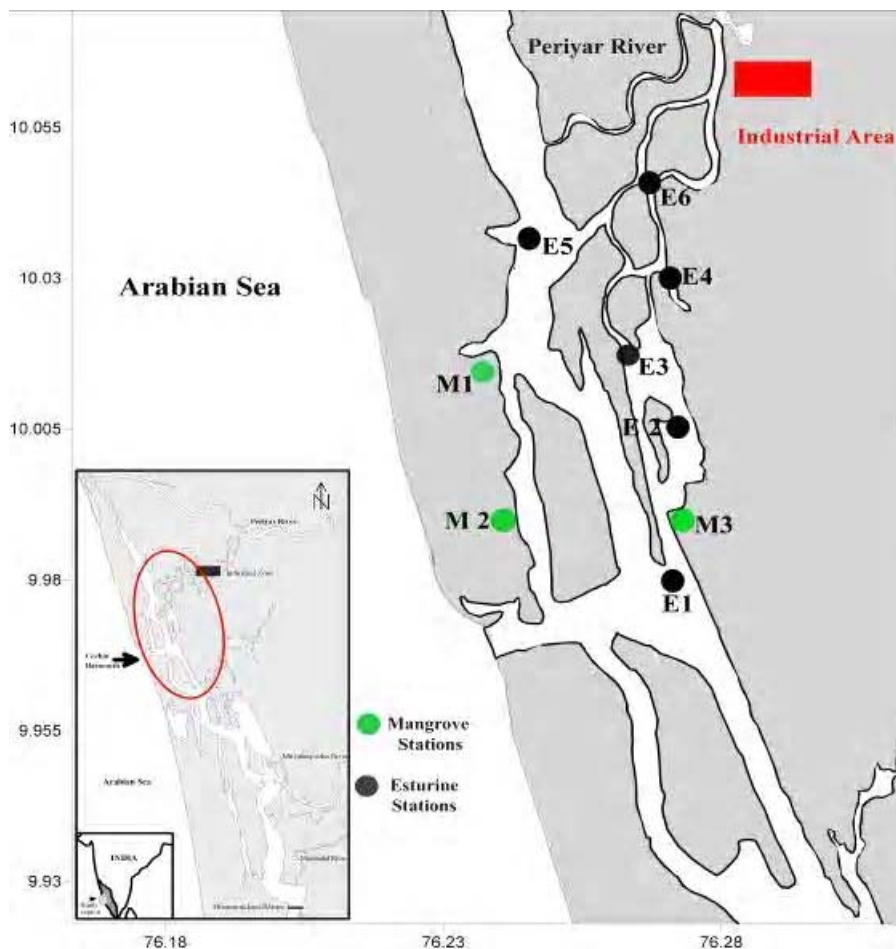

Fig. 1. Location map of the sampling stations

used for the estimation of dissolved oxygen (Hansen, 1999). Alkalinity of the water samples was estimated by the method of Koroleff (Anderson *et al.,* 1999). Phosphate, nitrite, nitrate and silicate were estimated spectophotometrically (Grasshoff *et al.*, 1999). Redox potential (Eh) of the sediment was measured with platinum and standard calomel electrodes standardized against Zobell's solution (Brassard, 1997). Texture analysis of the sediment was done based on Stoke's law using the method of Krumbein and Pettijohn (1938). Finely powdered air dried sediments were used for the further analyses and values are expressed on dry weight basis. Total Carbon, Hydrogen, Nitrogen and Sulphur were determined using a Vario EL III CHNS Analyzer. Sediment organic carbon was estimated by the procedure of El Wakeel and Riley modified by Gaudette *et al.* (1974). Total phosphorous was estimated spectrophotometrically after digestion using a di-acid mixture (1:5 $HClO_4 : HNO_3$).

For the heavy metal analysis (total), about 1 g of the dried and finely powdered sediments was digested in Teflon vessels with a 1:5 mixture of $HClO_4$-HNO_3 (Loring and Rantala, 1992). Complete digestion was ensured by repeating the acidification until a clear solution was obtained and brought into solution in 0.5 M HCl using Milli Q water. Samples were analyzed on a flame AAS (Perkin Elmer 3110) after calibration with suitable elemental standards. The precision and accuracy of the analytical procedure was checked using BCSS-1 (standard reference material for marine and estuarine sediments). Triplicate analysis of BCSS-1 showed a good accuracy and the recovery rate ranged between 90.7 % for Mn and 103.9 % for Zn. The enrichment factor (EF) was calculated for each metal, using iron as normalizing element following the equation EF = (metal/Fe) sediment/ (metal/Fe) crust. EF values were interpreted as suggested by Birth (2003) for metals studied with respect to natural background concentration. The Geoaccumulation Index (Igeo), introduced by Muller (1979) was used to assess metal pollution in sediments according to the equation $Igeo = log_2(Cn/1.5Bn)$, where Cn = measured concentration of heavy metal in the mangrove sediment, Bn = geochemical background value in average shale (Wedepohl, 1995) of element n, 1.5 is the background matrix correction in factor due to lithogenic effects.

RESULTS & DISCUSSION

pH of mangroves ranged between 6.58 and 7.57. Wide fluctuations in salinity were observed and it varied from 1.3 to 34.03 ppt and the highest value was recorded at M2 during pre-monsoon. Dissolved oxygen content in mangroves ranged between 1.44 mg O_2/L (M1, post-monsoon) to 10.24 mg O_2/L (M2, pre-

monsoon). Alkalinity varied from 68 mg $CaCO_3$/L (M3, post-monsoon) to 216 mg $CaCO_3$/L (M2, pre-monsoon). Total nitrogen, Inorganic phosphate, and silicate varied from 6.24, 5.288, 3.55 µmol/L to 48.65, 49.73, 63µmol/L respectively. Total nitrogen content exhibited highest value at M3 during post-monsoon. Highest concentrations of inorganic phosphate and silicate were reported from M2 during post-monsoon and M1 during monsoon respectively.

In the estuary, pH values varied from 6.08 to 8.15 and 5.95 to 8.77 for the surface and bottom waters respectively. As the distance from the bar mouth increases the decreasing trend in pH was observed. The salinity of the samples varied from 0.01 to 34.92 ppt and 0.03 to 36.02 ppt for surface and bottom samples respectively with the highest values observed at E1. Dissolved oxygen concentrations were higher during monsoon period ranging between 4.57 and 7.68 mg O_2/L for surface and 3.04 and 8 mg O_2/L for bottom waters respectively. Alkalinity varied from 12 to 317 mg/l and 16 to 208 mg/L for surface and bottom samples respectively. Bottom waters of E4 exhibited the highest total nitrogen content during monsoon and it ranged between 6.24 and 48.65 µmol/L. Inorganic phosphate varied from 5.29 to 49.73 µmol/L and the highest concentration was recorded at bottom waters of E1during post-monsoon. Silicate content displayed its highest content at surface waters of E6 during monsoon and ranged between 3.55 and 63 µmol/L.

In the case of mangrove sediments, pH varied from 5.85 to 7.10 (Table 1). Marked variation in Eh values was recorded in sediments (-398 to +12 mV) and highly negative redox condition was observed at M3. Texture analysis showed that sand content ranged between 0.94 and 36.60%. M1 exhibited the highest silt content during pre-monsoon period and it varied from 28.51 to 71.79%. Clay content ranged between 19.07 and 39.68% with the highest value at M2 during post-monsoon. Total carbon and organic carbon content varied from 2.91 to 7.64% and 2.2 to 6.66 %, respectively. Total nitrogen content ranged between 0.27 and 0.66 % and the total sulphur varied from 0.22 to 1.96 % of the sediment. The variation in total P content was from 0.22 to 2.80% of the sediment. The highest values for the contents of total C, organic C, total P and total N was observed at M3 during post-monsoon but total S concentration exhibited its highest value at the same station during pre-monsoon.

In the estuarine sediments (Table 2), pH ranged between 5.60 and 7.80 and was maximum at E2 during post- monsoon. The highest redox condition was noticed at E3 during pre-monsoon. The predominance of the silty nature was observed up to E3 and higher

Table 1. Chemical parameters estimated for mangrove sediments

Parameters	M 1			M 2			M 3		
	Pre	**Mon**	**Post**	**Pre**	**Mon**	**Post**	**Pre**	**Mon**	**Post**
pH	6.2	5.85	7	6.46	6.48	7.1	6.65	-	6.6
Eh	-98	-16	-10	12	-41	-53	-337	-	-398
Sand %	6.73	36.6	8.87	4.34	2.32	0.94	23.59	-	10.46
Silt %	71.79	28.51	58.92	59.97	63.78	59.38	45.56	-	70.47
Clay %	21.45	34.89	32.2	35.69	33.9	39.68	21.97	-	19.07
Total C %	3.73	6.75	4.72	2.91	3.31	6.25	5.52	-	7.64
Organic C %	2.80	6.30	3.90	2.20	2.50	4.90	5.00	-	6.70
Total N %	0.34	0.5	0.32	0.27	0.29	0.46	0.47	-	0.66
Total P %	2308	2226	2249	2987	2387	2933	28000	-	28665
Total S %	0.32	0.25	0.62	0.35	0.22	0.63	1.96	-	1.14
Cd (µg/g)	0.07	0.064	0.089	0.098	0.059	0.062	0.223	-	0.223
Co (µg/g)	22.30	17.73	21.42	22.20	22.80	23.08	12.82	-	15.70
Cr (µg/g)	90.22	73.18	76.08	85.28	89.77	89.05	53.30	-	63.27
Cu (µg/g)	30.75	24.98	23.97	27.75	31.38	31.58	29.17	-	39.12
Fe %	5.83	4.26	4.56	5.76	5.74	5.71	5.62	-	5.74
Mg%	1.78	1.24	1.53	1.72	1.69	1.68	1.23	-	1.27
Mn (µg/g)	315.32	227.82	257.83	227.20	210.50	299.08	260.95	-	225.95
Ni (µg/g)	55.5	55.425	54.75	68.75	69.35	65.57	30.60	-	40.25
Pb (µg/g)	35.25	21.25	37.50	39.50	33.25	32.5	25.25	-	19.5
Zn (µg/g)	128.80	101.30	111.30	116.30	112.55	132.55	315.05	-	455.675

-The sample from M3 during monsoon was not able to collect due to technical reasons.

sand content was seen from E4 onwards. The silt and clay content was observed to be higher in E1 during pre and post-monsoon seasons respectively. A decreasing trend was observed for the concentrations of the chemical parameters such as total N (0.02-0.3%), total S (0.01-1.7%) and total P (0.01-0.8%) from E1 to E6. Total nitrogen content was higher at E1 during monsoon. The higher contents of organic carbon, total P and total S was also recorded at E1 during pre-monsoon.

The range of heavy metal concentrations in surface sediments of mangrove ecosystems (Table 1) were 4.26-5.83% for Fe, 1.23-1.78% for Mg, 210.5-315.35 µg/g for Mn, 101.3-455.68 µg/g for Zn, 53.30- 90.22 µg/g for Cr, 30.60–69.35 µg/g for Ni, 19.5-39.50 µg/g for Pb, 23.97-39.12 µg/g for Cu, 12.82-23.08 µg/g for Co and 0.062-0.223 µg/g for Cd. The variation in the metal content in estuarine sediments (Table 2) was Fe (0.33-5.21%), Mg (0.01-1.76%), Zn (51.93-741.93 µg/g), Mn (14.73-252.93 µg/g), Cr (0.15-89.38 µg/g), Ni (2.08-58.20 µg/g), Cu (0.28-41.80 µg/g), Pb (0-34.5 µg/g), Co (3.90-21.58 µg/g), Cd (0-11 µg/g). Mn exceeded Zn and Cu exceeded Pb in mangrove sediments, but reverse trend observed in the estuarine system. In mangrove sediments, ANOVA revealed that cadmium was significantly higher (p=0.004) at M3. But significant seasonal variations were absent. Co and Cr also did not show any seasonal trend, but were significantly lower (p=0.005 and p=0.016 respectively) at M3. Copper, iron, magnesium and manganese did not show any significant spatial and

seasonal variations. But nickel was significantly lower (p=0.001) at M3. Lead showed no significant seasonal and spatial variations. Zinc was significantly higher (p=0.002) at M3. In the case of estuarine sediments, ANOVA established significantly (p=0.047) high values for Cd during pre-monsoon, with no spatial variations. Co and Cr also showed similar distributional trends (p=0.026 and p=0.013 respectively). No spatial and temporal variations were exhibited by Cu, whereas Fe was significantly high (p=0.019) during pre-monsoon. Mn showed significant spatial (p=0.036) variations and was lower at sandy stations E5 and E6. Concentrations of manganese and magnesium were higher during pre-monsoon season (p=0.01 and p=0.007 respectively). Ni showed no spatial variations, but was high during pre-monsoon (p=0.015). Zn content was significantly lower at sandy stations E5 and E6 (p=0.036) and was high (p=0.01) during pre-monsoon. Pearson correlation matrix of the sedimentary parameters of mangrove and estuarine systems revealed differences in interrelationships existing among the geochemical parameters in these systems. In mangrove systems, sand exhibited highly significant negative correlation with Mg and silt was positively correlated with Fe. Clay fraction exhibited highly significant negative correlations with the metals such as Cd and Zn, but showed significant positive correlation with Ni. In estuarine sediments, no significant correlations were noticed between the textural parameters and the heavy metals. Highly significant negative correlations of total C, organic C and total N with Mg and Pb were recorded

Table 2. Chemical parameters estimated for the estuarine sediments

Parameters	E 1			E 2			E 3			E 4			E 5			E 6		
	Pre	Mon	Post	Pre	Mon	Post	Pre	Mon	Post	Pre	Mon	Post	Pre	Mon	Post	Pre	Mon	Post
pH	6.60	7.61	7.57	7.24	6.53	7.80	7.17	7.60	7.60	7.31	6.65	7.65	7.26	5.60	7.19	7.05	6.96	6.86
Eh(mV)	-209	-205	-208	-233	34	-165	-200	-213	-248	-237	-150	-260	-219	130	-235	-193	146	-125
sand %	10.64	9.65	13.50	73.68	75.93	87.69	61.44	70.30	17.18	57.12	70.32	78.55	94.52	95.48	86.75	96.57	97.21	85.39
Silt %	61.47	57.75	48.63	9.90	16.56	4.07	27.23	21.40	45.55	30.41	22.00	14.89	3.06	3.32	9.32	1.69	1.56	8.29
Clay %	27.90	32.59	37.87	16.42	7.51	8.24	11.34	8.32	37.27	12.47	7.68	6.56	2.42	1.20	3.93	1.74	1.23	6.32
Total C %	2.90	3.00	3.04	0.47	1.32	0.83	0.98	0.54	2.85	0.82	0.58	2.10	0.67	0.38	0.64	0.38	0.48	0.42
Org.C %	2.76	1.90	2.75	0.22	0.96	0.54	0.45	0.24	2.30	0.38	0.29	1.80	0.28	0.18	0.56	0.23	0.52	0.38
Total N %	0.26	0.30	0.27	0.02	0.13	0.04	0.05	0.05	0.27	0.02	0.04	0.18	0.03	0.02	0.09	0.02	0.03	0.08
Total S %	1.70	1.48	1.50	0.18	0.57	0.25	0.76	0.29	1.41	0.14	0.32	0.78	0.18	0.28	0.54	0.09	0.16	0.18
Total P %	0.80	0.10	0.30	0.36	0.04	0.16	0.10	0.03	0.18	0.12	0.04	0.16	0.10	0.02	0.12	0.06	0.01	0.08
Cd (µg/g)	9.38	0.05	5.10	11.00	3.70	3.25	7.88	3.40	10.50	9.03	2.45	1.83	1.35	1.20	ND	ND	0.53	0.30
Co (µg/g)	19.43	4.80	8.68	19.00	8.05	7.13	20.75	5.35	17.28	21.58	12.45	7.65	5.33	5.73	4.63	3.90	4.95	4.58
Cr (µg/g)	84.18	4.38	23.30	86.35	25.35	16.73	70.48	7.90	52.55	89.38	27.58	17.95	4.85	6.00	0.15	5.93	11.38	0.58
Cu (µg/g)	41.80	0.95	13.03	38.08	11.28	7.73	13.03	3.53	28.43	38.85	19.70	10.88	1.60	2.50	0.28	1.20	2.73	0.58
Fe %	4.76	1.34	1.54	4.19	1.29	5.01	4.03	5.11	3.34	5.21	1.62	1.24	0.38	0.37	0.33	0.49	0.82	0.38
Mg %	1.16	0.06	0.29	1.76	0.34	0.20	1.58	0.09	0.79	1.48	0.26	0.16	0.07	0.04	0.01	0.02	0.01	0.01
Mn (µg/g)	236.05	22.03	58.80	249.18	56.95	112.30	241.68	31.60	252.93	190.00	167.30	142.93	21.88	19.10	20.75	23.60	19.10	14.73
Ni (µg/g)	54.23	5.38	16.40	58.20	18.60	11.38	56.45	4.40	38.03	54.65	22.05	15.60	4.15	5.08	2.80	2.08	5.05	2.33
Pb (µg/g)	13.50	ND	12.00	34.50	7.50	6.50	28.00	5.75	22.25	22.50	21.00	11.25	4.50	9.75	ND	0.25	5.50	1.75
Zn (µg/g)	741.93	110.68	331.93	716.93	246.30	231.93	645.05	211.93	630.68	658.18	227.55	156.30	146.93	85.68	52.55	82.55	58.18	51.93

in mangrove sediments. The absence of significant relationships of the heavy metals with total C, organic C and total N was noticed in estuarine system. In estuarine sediments total P exhibited significant positive correlations with the heavy metals such as Cd, Ni, Cu, Cr, Zn and Fe whereas in mangrove systems total P exhibited highly significant positive correlations with Cd and Zn and highly significant negative correlations with Co, Cr and Ni. Clays have high specific surface area and can directly trap heavy metals, but they also may act as a substrate for organic matter flocculation (Kiel *et al.*, 1994) that in turn adsorbs metals. Several investigations repeatedly advocate that the metal scavenging ability of sediments increases as the particle size decreases (Unnikrishnan and Nair, 2004 and Casey *et al.* 2007).

The inverse relationship of the metals Cd and Zn with texture in the mangrove sediments pointed toward the anthropogenic enrichment of these metals in the mangrove systems. The absence of any significant correlation of the heavy metals with texture, organic C, total N and total N in the estuarine sediments also reflects that the input is not through the natural weathering processes. The significant increases in the concentration of most of the heavy metals in the estuarine sediments during pre-monsoon also testify the point source contamination. Normalization was attempted to differentiate between the metals originating from human activity and those from natural weathering processes. It is a powerful tool for the regional comparison of trace metals content in sediments and can be applied to determine enrichment factors for the studied metals with respect to crustal average (Nolting *et al.*, 1999). Since Al, Fe, and grain size all tend to co-vary, the use of a single normalizer can often represent several underlying geochemical relationships. In this work, EFs were computed by normalizing with Fe (Blomqvist *et al.*, 1992). Iron is conservative during diagenesis (Berner, 1980) and its geochemistry is similar to that of many trace metals both in oxic and anoxic environments. Natural concentrations of Fe in sediments are more uniform than Al and beyond the influence of humans, justify its use as a normalizer (Daskalakis and O'Connor, 1995). An EF value less than 1.5 suggests that the trace metals may be entirely from crustal materials or natural weathering processes (Zhang and Liu, 2002 and Feng *et al.*, 2004).However, an EF value greater than 1.5 suggests that a significant portion of the trace metal is delivered from non-crustal materials, or non-natural weathering processes and that the trace metals are provided by other sources (Feng *et al.*, 2004). In order to determine the extent of pollution in sediment and better estimate anthropogenic

inputs using the heavy metals load in sediment, the geoaccumulation index can also be employed (Ridgway and Shimmield, 2002). The values of enrichment factor for mangrove sediments indicated a minor enrichment for Pb and Zn and no enrichment for other metals. The EF values for Pb in mangrove systems ranged between 0.78 and 1.88 with its highest value being recorded at M1 during post-monsoon. The highest EF value for Zn was reported from M3 and the values for enrichment factor varied from 0.94 to 3.82 respectively. The analysis of the EF values of the estuary revealed that Pb exhibited only a minor enrichment in the surface sediments with a variation of 0 to 2.95 and the highest value was observed in E4 during pre-monsoon. Cadmium exhibited extremely severe enrichment (up to 505.57) in all estuarine stations. Moderately severe enrichment at the first five stations and a moderate enrichment at E6 were observed for Zn (EF range: 1.90-10.39) with highest value at E1 during monsoon period. A minor enrichment of Cr at E2 and Cu at E4 was also noticed in estuary, but no enrichment was noticed for any other heavy metals. The geo accumulation index revealed similar trends as that of EF and exhibited very low values (Igeo <0) for the mangrove sediments in the case of all metals except Zn (>1.0 at M3), indicating the sediments of ecosystem are unpolluted to moderately polluted as a result of anthropogenic activities. The Igeo values of estuarine sediments revealed that Cd exhibited very strongly polluted condition in all the stations. Zn exhibited moderately polluted condition upto E4 and the highest value for Igeo was reported at E1 during post monsoon season and all other metals were in the unpolluted condition.

Zinc is a very mobile element under oxidizing and acidic conditions, while the mobility substantially decreases in alkaline and reducing environments, due to its affinity for S and the tendency to form sulphide phases (Thornton, 1983 and Alloway, 1990a). Highly significant positive correlations of Zn with total S and highly significant negative correlation with Eh in mangroves support this argument. Lead is the only chalcophile element that is immobile under any pH- Eh conditions, although acidic conditions can trigger Pb desorption to a greater degree than alkaline environments. The adverse effects of environmental lead pollution are well recognized (Landrigan and Todd, 1994). Strong negative correlation of cadmium with clay and Eh and its positive correlation with total S in mangrove sediments suggested the anthropogenic origin and its accumulation under anoxic condition. Adsorption and desorption of Cd is highly variable depending on the type of colloid and local pH-Eh conditions. It

can also form complexes with Cl or can be adsorbed in larger quantities by organic matter or Fe oxyhydroxides than by smectitic clays, despite the latter's high cation exchange capacity (Alloway, 1990b). Cadmium is released to pore waters during organic matter diagenesis and authigenically enriched in sediments where Mn has been depleted (Gobeil *et al.*, 1997). The mangrove mud can be considered as a massive, sub-oxic bed reactor (Aller, 1998), the repetitive redox cycling may induce dissolution of some forms of heavy metals and explain their lower concentrations in mangrove sediments as compared to the estuarine system. The redox state of the sediment controls the solubility, or bioavailability of heavy metals (Kehew, 2001). The lack of a clear enrichment of other metals in the mangrove sediments may be caused by their strong soluble complexes with reduced sulphur (Emerson *et al.*, 1983), which will increase the migration of these elements from sediments to the water column (Huerta-Diaz and Morse, 1992). In estuarine system, total S showed no significant correlations with the

heavy metals. Fe displayed highly significant positive correlations with all other metals in estuary, except Mn. The poor association of Mn with other metals suggests that Mn-oxide may be only a minor host phase for these elements in both environments. Pollution of the natural environment by heavy metals is a worldwide problem as these metals are indestructible and have toxic effects on living organisms when they exceed a certain concentration limit (MacFarlane and Burchett, 2000). Sediment-associated metals pose a direct risk to detrital and deposit-feeding benthic organisms and may also represent long-term sources of contamination to higher trophic level (Mendil and Uluözlü, 2007). Therefore, ecotoxicological sense of heavy metal contamination in sediments was determined using sediment quality guidelines developed for marine and estuarine ecosystem (Bakan and Ozkoc, 2007). The ecological effects identified were the effect range low (ERL) and the effect range median (ERM). Zn content was found to be close to ERL value at M1 and M2 and exceeded ERM at M3, while Pb was
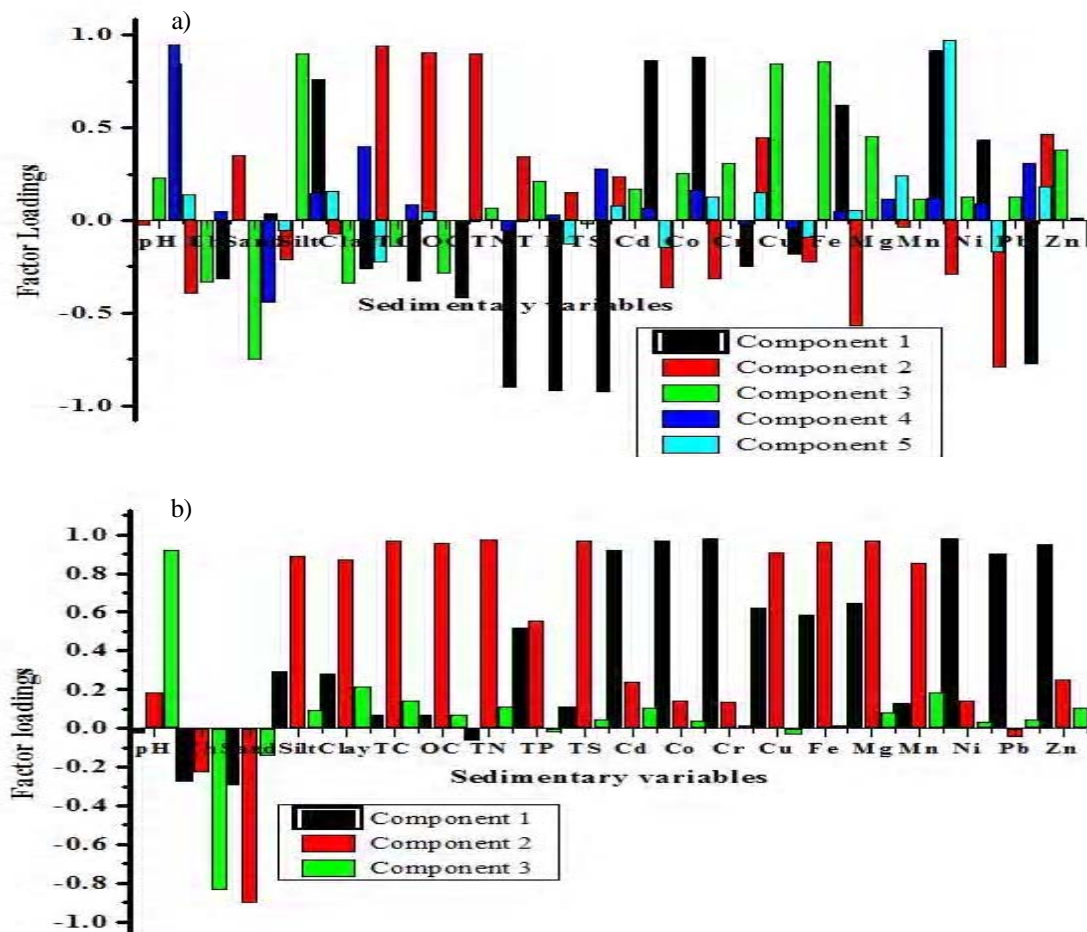

Fig. 2. Factor loadings for the geochemical parameters in (a) mangrove and (b) estuarine sediments

lower than ERL value at all the mangrove systems. In estuary, Cd concentrations exceeding ERM level at E2 and E3 during pre and post-monsoon seasons respectively. Cadmium content in the estuarine sediments exhibited values close to ERL at the first four stations and exceeded ERM value occasionally. The concentration of Zn exceeded the ERM level at first four stations during pre-monsoon period. It was observed that Cr content in the sediments of estuary exceeded ERL value at first four stations during pre-monsoon period. Stations E1, E2 and E4 showed Cu concentration exceeding ERL value during pre-monsoon. Principal Component Analysis was employed to deduce the geochemical processes in these ecosystems. Varimax orthogonal rotation was applied in order to identify the variables that are more significant for each factor based on the significance of their correlations that are expressed as factor loadings (Buckley *et al*., 1995 and Davis, 2002).

PCA analysis of mangrove sediments (Fig.2a) showed that five components account for a total of 97.41% variance. First factor, which accounted for 39.86 % of the total variance, is characterized by very high positive loadings on clay, Eh, Co, Cr and Ni and strong negative loadings on total P, total S, Cd and Zn. This component reflects the redox process controlling the heavy metals distribution in mangrove sediments. Factor 2 accounted for 24.13% of total variance, has high loadings on carbon and nitrogen and negative loadings on Pb. This could be attributed to the flocculation and sedimentation of the organic matter. 19.18% of the total variance is explained by Factor 3, which exhibited high positive loadings on silt and Fe and negative loadings on sand. This component likely to be the granulometric factor. Fourth factor is the pH effect, which seems to be negligible in the geochemical distribution as there is very less pH variation in the study region. In estuarine sediments, PCA revealed that three factors ascribed almost 88.46 % of the total variance of the system (Fig. 2b). Factor 1 accounted for 45.60 % of the total variance and had significant positive loadings on all heavy metals analyzed and totals P. It showed no loadings on the other sedimentary parameters and this could be attributed to anthropogenic factor. The factor 2 has significant positive loadings on silt, clay, total C, Org C, total N Total S, Fe, Mn and Mg and accounts for 34.12 % of the total variance. This seems to be the granulometric factor and sorption/desorption on the fine-grained minerals and organic matter. The influence of redox potential and pH changes on these metals in sediment could be deduced from factor 3 which scores 8.74 % of the total variance.

CONCLUSION

The combined use of different approaches for evaluating sediment metal contamination facilitates a comprehensive interpretation of the sedimentary characteristics in terms of the background influences. The observations suggest that the mangrove ecosystems are relatively unpolluted but the estuarine stations are under the threat of severe accumulation of the toxic trace metals. Among the studied heavy metals only Pb, Cd and Zn are of major concern, which occasionally may be associated with adverse biological effects based on the comparison with sediment quality guidelines. The sediments are almost not polluted by other heavy metals and they seem to reflect background concentrations in the study area.

REFERENCES

Aller, R. C. (1998). Mobile deltaic and continental shelf muds as suboxic, fluidized bed reactors. Mar. Chem., **61**, 143-155.

Alloway, B. J. (1990 a). Soil processes and the behaviour of metals. (*In*: Alloway, B.J. (Ed.) Heavy Metals in Soils, New York, Blackie, J Wiley and Sons, Inc., pp.7-28.

Alloway, B. J. (1990 b). Cadmium. (*In*: Alloway, B. J. (Ed.) Heavy Metals in Soils, New York, Blackie, J Wiley and Sons, Inc., pp. 100-124.

Anderson, L. G., Turner, D. R., Wedborg, M. and Dyrssen, D. (1999). Determination of alkalinity. (*In:* Grasshoff, K., Ehrhardt, M., Kremling, K. (Eds.), Methods of Sea Water Analyses, Chemie, Weinheim, Verlag, pp. 127-147.

Bakan, G. and Ozkoc, H. B. (2007). An ecological risk assessment of the impact of heavy metals in surface sediments on biota from the mid-Black Sea coast of Turkey. Int. J. Environ. Stud., **64**, 45-57.

Berner, R. A. (1980). Early Diagenesis: a Theoretical Approach. Princeton, Princeton University Press.

Birth, G. (2003). A scheme for assessing human impacts on coastal aquatic environments using sediments. (*In*: Woodcofie, C. D., Furness, R. A. (Eds.) Coastal GIS 2003. Wollongong University Papers in Center for Maritime Policy, **14**, Australia.

Blomqvist, S., Larsson, U.and Borg, H. (1992). Heavy metal decrease in the sediments of a Baltic Bay following tertiary sewage treatment. Marine Pollution Bulletin, **24**, 258–266.

Brassard, P. (1997). Measurement of Eh and pH in aquatic sediments. (*In*: Mudroch, A., Azcue, J. M., Mudroch, P.

(Eds.) Mannual of Physico-chemical Analysis of Aquatic sediment, CRC Press, Inc.Lewis Publishers, pp 47-69.

Bryan, G. W., Langston, W. J.and Humberstone, L. G. (1980). The use of biological indicators of heavy metal contamination in estuaries, with special reference to an assessment of the biological availability of metals in estuarine sediments from South-West Britain. Marine Biological Association of the United Kingdom, Occasional Publication No. 1, 73 pp.

Buckley, D., Smith, J. and Winters, G. (1995). Accumulation of contaminant metals in marine sediments of Halifax Harbour, Nova Scotia: environmental factors and historical trends. Applied Geochemistry, **10,** 175-195.

Casey, R. E., Simon, J. A., Atueyi. A., Snodgrass, J .W., Karouna-Renier, N.and Sparling, D. W. (2007). Temporal trends of trace metals in sediment and invertebrates from stormwater management ponds. Water Air Soil Pollut., **178,** 69-77.

Daskalakis, D. K. and O'Connor, T. P. (1995). Normalization and elemental sediment contamination in the coastal United States. Environmental Science and Technology, **29**, 470-477.

Davis, J. C. (2002). Statistics and Data Analysis in Geology pp. 638. New York: Wiley.

Emerson, S., Jacobs, L. and Tebo, B. (1983). The behavior of trace metals in marine anoxic waters: Solubilities at the oxygen-hydrogen sulfide interface. *(In* : Wong, C. S., Boyle, E., Bruland, K. W., Burton, J. D., Goldberg, E. D. (Eds.) Trace Metals in Sea Water Plenum, New York, pp. 579-608.

Feng, H., Han, X., Zhang, W. and Yu, L. (2004). A preliminary study of heavy metal contamination in Yangtze River intertidal zone due to urbanization. Mar Pollut Bull., **49**, 910-915.

Filgueiras, A. V., Lavilla, I., and Bendicho, C. (2004). Evaluation of distribution, mobility and binding behaviour of heavy metals in surficial sediments of Louro River (Galicia, Spain) using chemometric analysis: A case study. The Science of the Total Environment, **330**, 115 129.

Forstner, U. (1981). Metal Transfer between Solid and Aqueous Phases, *In*: Metal Pollution in the Aquatic Environment, Springer, Berlin, pp. 197-269.

Gaudette, H. E., Flight ,W. R., Toner, L. and Folger, D. W. (1974). An inexpensive titration method for the determination of organic carbon in recent sediments. J Sediment Petrol., **44**, 249-253.

Gobeil, C., MacDonald, R. W. and Sundby. B. (1997). Diagenetic separation of cadmium and manganese in suboxic continental margin sediments. Geochim. et Cosmochim Acta, **61**, 4647-4654.

Grasshoff, K., Kremling, M. and Ehrhardt, M. (1999). Methods of Seawater Analysis, 3rd Ed., pp. 263-271, Wiley-VCH.

Hansen, H. P. (1999). Determination of oxygen, (*In*: Grasshoff, K., Ehrhardt M., Kremling K. (Eds.) Methods of Sea Water Analyses. Verlag Chemie,Weinheim, pp. 75-90.

Harbison, P., (1986). Mangrove muds: a sink and a source for trace metals. Mar. Pollut. Bull., **17**, 246-250.

Huerta-Diaz, M. A. and Morse, J. W. (1992). Pyritization of trace metals in anoxic marine sediments. Geochimica et Cosmochimica Acta, **56,** 2681-2702.

Jayaprakash, A. A. (2002). Long term trends in rainfall, sea level and solar periodicity: A case study for forecast of Malabar sole and Oil sardine fishery. J Mar Biol Ass India, **44**, 163-175.

Kehew, A. E. (2001). Applied Chemical Hydrogeology, Prentice Hall, New Jersey.

Keil, R. G., Montlucon, D. B., Prahl, F. R. and Hedges, J. I. (1994). Sorptive preservation of labile organic matter in marine sediments. Nature, **370**, 549-552.

Krumbein, W. C. and Pettijohn, F. J. (1938). (Eds.) Sedimentary petrography, Appleton Century Crofts, Inc., New York, pp. 349.

Landrigan, P. J. and Todd, A. C. (1994). Lead poisoning. West J. Med., **161**, 53-159.

Langston, W. J. (1982). The distribution of mercury in British estuarine sediments and its availability to deposit-feeding bivalves. Journal of the Marine Biological Association of the United Kingdom, **62,** 667-684.

Loring, D. H. and Rantala, R. T. T. (1992). Manual for the geochemical analyses of marine sediments and suspended matter. Earth-Science Reviews, **32**, 235-283.

Macfarlane, G. R. and Burchett, M. D. (2000). Cellular distribution of Cu, Pb and Zn in the grey mangrove Avicennia marina (Frorsk.) Vierh. Aquatic Botany, **68**, 45-59.

Mendil, D. and Uluözlü, O. D. (2007). Determination of trace metal levels in sediment and five fish species from lakes in Tokat, Turkey. Food Chemistry, **101**, 739-745.

Muller, G. (1979). Schwermetallen in den Redimen des rheins. Veranderrugen Seit. Umschau **79**, 778-783.

Muller, T. J. (1999). Determination of salinity (*In*: Grasshoff, K., Ehrhardt, M., Kremling K. (Eds.) Methods of SeaWater Analyses . Chemie,Weinheim, Verlag, pp. 41-74.

Nolting, R. F., Ramkema, A. and Everaats, J. M. (1999). The geochemistry of Cu, Cd, Zn, Ni and Pb in sediment cores from the continental slope of the Banc d'Arguin (Mauritania). Continental Shelf Research, **19**, 665-691.

Ramamirtham, C. P., Muthusamy, S. and Khambadkar, L. R. (1986). Estuarine oceanography of the vembanad lake, part-I the region between Pallipuram (vaikom) and Thevara (Cochin). Ind. J. Fish., **33**, 85-94.

Ridgway, J. and Shimmield, G. (2002). Estuaries as respositories of historical contamination and their impact on shelf seas. Estuarine, Coastal and Shelf Science, **55**, 903-928.

Thornton, I. (1983). Applied Environmental Geochemistry. Academic Press, London.

Unnikrishnan, P. and Nair, S. M. (2004). Partitioning of trace metals in dissolved and particulate faces in a tropical backwater system of Kerala, India. Int. J Environ Stud., **61**, 659–676.

Walkley, A. and Black, I. A. (1934). An examination of the Degtjareff method for determining soil organic matter and proposed modification of the chromic acid titration method. Soil Sci., **37**, 29–38.

Wedepohl, K. H. (1995). The composition of the continental crust. Geochimica et Cosmochimica Acta **59**, 217-239.

Zhang, J. and Liu , C. L. (2002). Riverine composition and estuarine geochemistry of particulate metals in China – Weathering features, anthropogenic impact and chemical fluxes. Estuarine, Coastal and Shelf Science, **54**, 1051–1070.