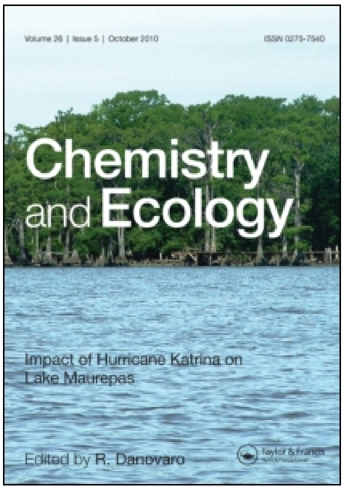

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Geochemistry of heavy metals in the surficial sediments of mangroves of the south west coast of India

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RESEARCH ARTICLE

Geochemistry of heavy metals in the surficial sediments of mangroves of the south west coast of India

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The distribution and speciation of Fe, Mn and Cu in six geographically different mangroves of the south west coast of India have been examined. The metal concentrations in sediments ranged from 0.53–95.44 mg/g for iron, 12.16–325.98 μg/g for manganese and 0.13–243.32 μg/g for copper. The metal levels in sediments were comparable with those from similar aquatic systems. Speciation of metals in sediments and principal component analysis (PCA) of the speciation data indicates that ultimate storage of iron is in the inorganic pyrite form. Manganese and copper exhibit temporary storage by associations with organic matter.

Keywords: mangroves; surface sediment; geochemistry; heavy metals; speciation; India

1. Introduction

Mangroves are highly dynamic ecosystems and their growth and decline often reflect the changing conditions of the coastal environment. The mangals play a special role as a nursery habitat for juvenile fish and prawns. Mangroves act as natural sinks and filtration systems [1]. The geochemistry of mangroves influences the metal distribution and its availability in this environment. These intertidal ecosystems are generally water-logged and anoxic. The redox conditions prevailing in the system determine the fate of metals. The major processes of metal retention in coastal ecosystems are cation exchange, complexation with organics, precipitation as oxides, oxyhydroxides, carbonates and sulphides [2]. Major parameters that influence metal behaviour in natural waters are pH [3,4] and Eh [5–7]. Precipitation of metals at the sediment–water interface is encouraged by high pH values. The adsorption and retention mechanism of metals vary with the soil type and metal species. Other factors controlling the distribution of metals include the levels of organic matter, geochemical composition of sediments, levels of microbial activities and dynamicity of the overlying water column. In mangals tidal deposition is also important in determining metal distribution [8].

With the continuing degradation and destruction of mangroves, there is a critical need to understand them better. Though considerable work has been reported on the mangrove ecosystems of the Kerala Coast, investigations on the geochemical role of metals are rare. The present study

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aims to assess the distribution and speciation of metals in mangrove sediments and to investigate the factors controlling metal biogeochemical behaviour in these ecosystems.

2. Materials and methods

2.1. *Study area*

Six geographically different mangroves of the Kerala Coast were selected for the study (Figure 1). Station 1, Chettuva (10° 31′57″ 76° 02′ 48″E), is a riverine mangrove ecosystem. A lot of mangrove plants have been destroyed here for the construction of a health resort and a hotel. Station 2, Vypin (9° 58′ 54″N 76° 14′ 21″E), is closer to the Arabian Sea than the other stations. High population density is a threat to this system. Mixed agri–silvi-cultural practices are observed in this station. Station 3, Mangalavanam (9° 59′ 18″N 76° 16′ 25″E), a closed mangrove area, is situated in the heart of Cochin City and is connected to Cochin Back waters by a canal. Lack of tidal activity is a characteristic of this system. Oil pollution is a serious threat to this mangrove station. Studies show that the number of migratory birds visiting the area has decreased over the past years [9]. Station 4, Nettor (90° 55′32″N 760° 18′31″E), is an open mangrove area with lots of anthropogenic intervention. Station 5, Ayiramthengu (9° 07′ 45″N 76° 18′ 31″E), is a man made mangrove station. Out of the 17 tree mangroves and 23 semi-mangroves of Kerala, 9 tree mangroves and 11 semi mangroves are available in this area [10]. Station 6, Asramam (8° 52′49″N 76° 35′ 18″E), is on the river mouth of the Kallada river. Waste dumping is observed near the sampling site.

2.2. *Collection of samples and analysis*

Surface sediment samples were collected on a monthly basis from all six locations from February 2001 to January 2002. Sediment samples were collected using plastic spoons and stored in clean

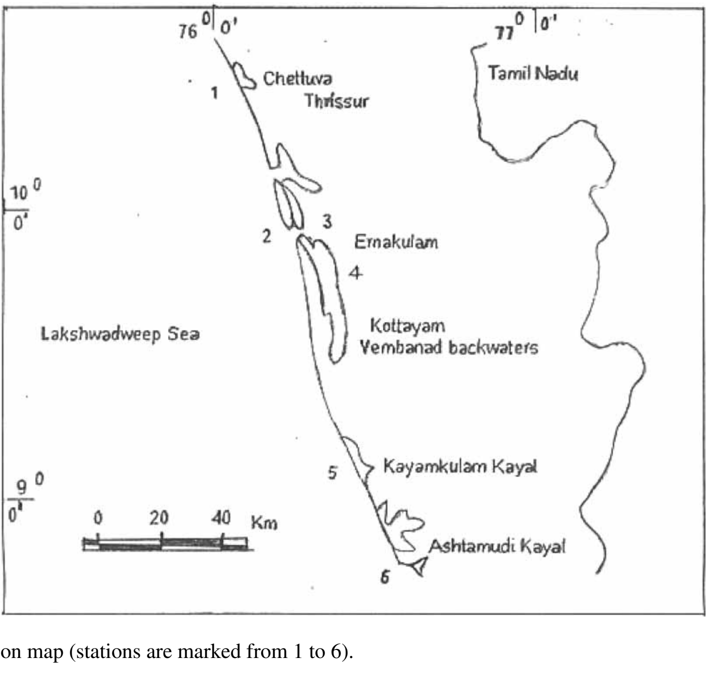

Figure 1. Location map (stations are marked from 1 to 6).

plastic bags. Samples were air-dried, powdered, homogenised and stored in desiccators until analysis. Grain size analysis of the sediment was carried out using standard techniques [11,12]. Sedimentary organic carbon was estimated using wet oxidation method [13,14]. Dried sediment samples were digested with a triacid mixture ($HClO_4$, HNO_3, and HCl in 1:1:3 volume ratio), and analysed for metal content using atomic absorption spectrophotometry (Perkin Elmer, 3110). The accuracy of the analytical procedure was checked using BCSS-1 (standard reference material for marine and estuarine sediments). Triplicate analysis of BCSS-1 showed good accuracy and precision was better than 5% for Fe and Cu, and 17% for Mn.

Speciation analyses of metals were carried out only on a seasonal basis: (February–May) pre monsoon, (June–September) monsoon and (October–January) post monsoon. Speciation studies were performed in duplicate using the scheme of Tessier, Campbell and Bisson [15], modified by Calmano and Forstner [16]. The different steps involved are summarised in a flow chart (Figure 2).

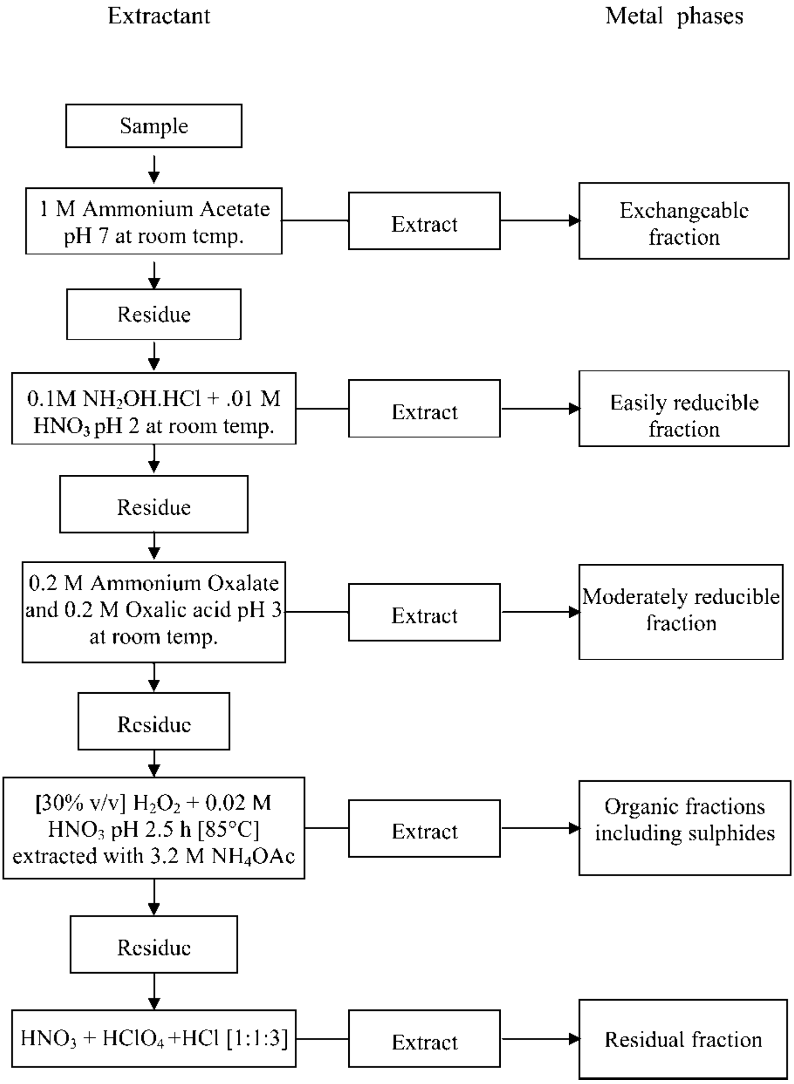

Figure 2. Flow chart of the sequential extraction procedure.

Extracts of different steps were stored in acid – washed plastic containers until analysis. Principal component analysis (PCA) was used as the statistical tool for data compilation and analysis.

3. Results and discussion

3.1. *Hydrographical and sedimentary parameters*

The studies of hydrographical and sedimentary characteristics are prerequisite to describe the ecosystem. Major influences on the hydrography of these systems are land-run off, rainfall, tidal action and temperature [17]. The results of the hydrographical and sedimentary parameters are given in Table 1. In this study, pH values ranged between 6.91 at Station 1 and 8.61 at Station 6. The annual mean station values were between 7.37 (Station 1) and 8.03 (Station 6). The temperature of the surface water showed only moderate variations, between 23.5 °C and 32.5 °C. Salinity values were in the range of 0.32–28.30 psu. Alkalinity ranged from 0.20–4.40 mmol/l. Both the highest and the lowest values were noticed at Station 1, Chettuva.

The composition of the sediment varied from place to place. Organic carbon plays an important role in the dispersal pattern of many major and trace elements. Organic carbon showed wide variations between stations and it was found to be related to the texture of the sediment. The mean organic carbon content varied between 0.59% at Station 4 and 5.97% at Station 6. The increased organic carbon content noticed at Station 6 might be due to the dumping of municipal waste in that area. Textural characteristics of the sediments play a significant role in the distribution of metals and nutrients in the ecosystem. The observed range (%) for sand is 2.67–96.48, for silt is 0.68–60.65 and for clay is 2.42–66.82.

3.2. *Total metal content in the sediments*

Metal concentrations change from place to place because their concentrations are influenced by sediment characteristics. Origin and composition of the sediment, particle size, distribution and post depositional reactions play an important role in determining the metal concentrations in

Table 1. Hydrographical and sedimentary parameters.

	pH		Temperature (°C)		Salinity (psu)		Alkalinity	
Stations	Average	Range	Average	Range	Average	Range	Average	Range
1	7.37 ± 0.23	6.91–7.64	28.77 ± 2.06	24.0–31.0	12.04 ± 8.52	0.32–24.65	0.71 ± 22.72	1.88–3.96
2	7.64 ± 0.29	7.01–7.90	29.05 ± 2.08	23.8–30.8	12.50 ± 8.30	2.10–22.70	0.88 ± 48.37	0.20–3.64
3	7.66 ± 0.23	7.39–7.95	28.61 ± 2.04	24.3–30.5	11.68 ± 8.42	2.30–25.67	0.96 ± 44.32	0.88–3.74
4	7.65 ± 0.19	7.43–8.07	28.43 ± 2.95	23.5–32.5	11.77 ± 9.34	1.29–28.30	0.84±24.65	1.48–4.40
5	7.68 ± 0.35	7.07–8.12	29.24 ± 2.51	23.5–32.0	15.12 ± 6.95	4.99–22.70	0.69 ±25.73	1.16–3.36
6	8.03 ± 0.45	7.46–8.61	30.03 ± 1.76	26.0–32.1	14.61 ± 10.28	3.30–27.80	0.65 ± 36.61	0.48–2.76
	OC %		Sand %		Silt %		Clay %	
1	0.89 ± 0.41	0.23–1.61	50.67 ± 5.78	14.31–89.73	19.48 ± 13.71	2.00–42.19	24.56 ± 16.22	3.08–48.26
2	2.27 ± 0.54	1.51–2.88	29.36 ± 21.16	2.67–65.33	30.31 ± 15.50	0.68–48.28	35.77 ± 19.22	8.58–66.82
3	2.38 ± 0.93	1.52–4.80	62.16 ± 19.01	35.48–88.61	25.88 ± 21.53	3.68–52.69	13.04 ± 8.92	4.87–33.67
4	0.59 ± 0.24	0.29–1.02	79.38 ± 14.76	49.31–90.52	12.43 ± 12.99	1.72–37.15	12.59 ± 14.13	2.76–48.96
5	1.50 ± 0.79	0.61–2.85	88.02 ± 9.12	72.73–96.48	5.51 ± 5.27	0.85–13.93	5.47 ± 3.00	2.42–11.29
6	5.97 ± 1.41	3.64–8.62	51.73 ± 23.45	22.63–88.66	25.16 ± 16.38	3.28–60.65	23.11 ± 16.62	6.60–56.51

Table 2. Total metal concentrations in mangrove sediment samples.

	Fe mg/g		Mn μg/g		Cu μg/g	
Stations	Average	Range	Average	Range	Average	Range
1	25.17 ± 25.31	0.59–92.54	88.90 ± 42.92	12.16–153.91	14.17 ± 10.47	6.03–34.94
2	51.48 ± 19.57	21.13–86.26	203.51 ± 79.93	110.29–325.98	31.30 ± 3.75	27.9–39.95
3	14.43 ± 7.73	6.50–30.97	79.15 ± 56.62	28.00–220.81	11.77 ± 9.86	0.13–34.49
4	14.32 ± 7.47	3.75–27.39	28.43 ± 2.95	12.44–43.62	5.11 ± 1.68	2.79–8.25
5	13.63 ± 28.88	1.20–95.44	27.2 ± 9.71	12.22–43.55	3.40 ± 1.53	1.16–6.69
6	22.07 ± 24.64	0.53–79.38	165.87 ± 45.44	46.57–216.18	144.88 ± 65.89	34.77–243.32

Table 3. Concentrations of metals reported in mangroves and coastal sediments.

	Metal concentrations (μg/g)		
Location	Fe	Mn	Cu
Mangroves			
New Zealand [18]			26.8–196.5
Gunabara Bay, Brazil [19]		71.7–273	53.3–610
UAE [20]	4230000		46
Saudi [21]	2.0–69.0		
Singapore [22]			7.44–11.65
Punta Mala Bay, Pacific Panama [23]	9827	295	56.3
Pichavaram [24]	16200–46900		3.0–81.0
Bhitarkanika Orissa [25]	25200–4690000	6.8–10.9	2.6–6.7
Godavari [26]	4575	1059	47.8
Coastal ecosystems of Kerala			
Ashtamudi [27]	18000		60
Kayamkulam estuary [28]	10000–63000	58–400	11.0–81.0
Cochin estuary(N) [29]	14000–62000	151–337	5.0–53.0
Cochin estuary(S) [30]	2056–82658	7.26–361.65	0.08–44.14
Mangroves of Kerala Coast–Present Study	530–92540	12.16–325.98	0.13–243.32

sediments [18]. Distributions of Fe, Mn and Cu in mangrove sediments are reported in Table 2. The values of iron fluctuated between 0.53 and 95.44 μg/g. Manganese levels in sediments were between 12.16 and 325.98 μg/g. In the present study, the concentrations of copper varied from 0.13 μg/g at Station 3 to 243.32 μg/g at Station 6. The highest annual mean concentrations of Fe and Mn was noticed at Station 2. The annual average concentration of Cu was highest at Station 6, most of the values were greater than 100 μg/g. Station 5 recorded the lowest mean concentrations for all the three metals studied. The sediments of Stations 4 and 5 were sandy in nature and the metal concentrations were comparatively lower at these stations. The metal concentrations in the present study were well within the range reported from other mangroves of the world with some exceptions. The levels of metals were also comparable with those from neighbouring estuarine ecosystems (Table 3).

3.3. *Chemical fractionation of metals in sediments*

Even though the metal content in the sediment is a valuable index of pollution; it is not an indicator of the available metal content. The tendency and the rate by which a metal participates in geochemical and biological processes depends on the physiochemical forms in which the metal exists. Speciation is not only useful to determine the degree of associations of trace metals in sediment and the extent of remobilisation into the environment, but also helps to distinguish metals with a lithogenic origin. Metals with anthropogenic origin are mainly obtained in the first steps of extraction and the residual component represents the fraction mainly bonded to lithogenic minerals of sediments [31,32]. The metals bound to the residual phase are unlikely to be reactive during sedimentation and diagenesis and pose little environmental nuisance [33]. Non-residual fractions are susceptible to remobilisation and hence contribute to bio availability. Fractionation studies also provide an insight into the diagenetic processes occuring after deposition in the sediment.

The iron content (%) in different fractions of the sediment can be summarised as follows: 0–0.13 for exchangeable, 0.01–0.33 for easily reducible, 0.05–8.57 for moderately reducible, 0.39–14.77 for organic fraction including sulphides and 76.22–99.00 for reducible fraction (Figure 3). The contributions of exchangeable and easily reducible fractions were less than 1% of the total. The

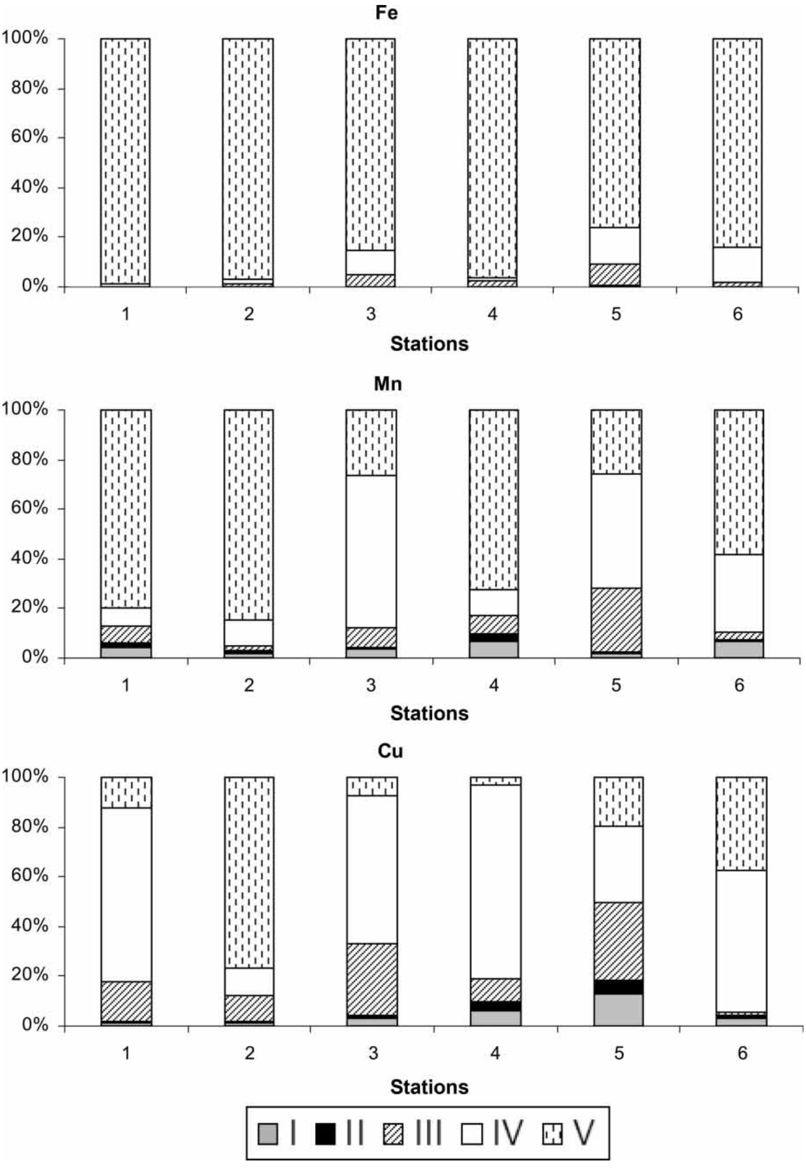

Figure 3. Speciation of metals in mangrove sediments (I, II, III, IV, and V represent the respective concentrations (%) in exchangeable, easily reducible, moderately reducible, organic including suphides, and residual fractions of the sediment).

major contributing component in the speciation of iron was the residual fraction. In most of the samples residual iron content in sediments was greater than 85% of the total. A similar trend was noticed by many previous researchers [34,35]. The lithogenous origin of iron is evident from its high percentage in the residual fraction. The oxyhydroxide and sulphide minerals of iron are also stable in a reducing environment and are estimated along with the residual component. In sulphidic sediments the storage of iron is through mineralisation as pyrite. Iron can also form oxyhydroxide minerals. Pyrite is the most thermodynamically stable form of iron. Amorphous iron sulphides and gregite are meta stable with respect to pyrite [36].

Exchangeable manganese content in sediment samples ranged between 0.47 and 20.74%. Both iron and manganese are redox sensitive metals. Higher manganese content in the exchangeable fraction was also reported earlier [37]. High values for exchangeable Mn content compared to exchangeable Fe content may be related to the differences in the stability of iron and manganese sulphides. Acid volatile sulphide generated by oxidation of organic matter is an important ligand for metals. Metal sulphides have low solubilities in natural waters and their formation plays an important role in fixing these metals in sediments [38]. The differences in the distribution pattern of metals can be accounted for by the solubilities of metal sulphides. The metal content in other fractions of the sediment were Mn_2: 0–9.29%, Mn_3: 0–25.93%, Mn_4: 7.16–61.26% and Mn_5: 25.52–84.51%. In the speciation of manganese, the contributions of the first three fractions were negligible. In most of the samples, exchangeable manganese values were less than 1 μg/g. The contribution of an easily reducing fraction was even lower than that of the exchangeable fraction. Here also the major contributor is the residual fraction. The second highest contributor to the speciation of manganese are organic fractions including sulphides. Manganese being an essential plant nutrient, the export occurs through plant detritus. During diagenesis, the organically bound manganese is released as soluble Mn [II].

The average copper content in different fractions of the sediment were 2.95% for Cu_1, 2.05% for Cu_2, 19.65 % for Cu_3, 47.96 % Cu_4 and 27.39 % for Cu_5. Exchangeable and easily reducing fractions made only a small contribution to the total copper content. Of the six stations, Station 6 recorded the highest copper values for all the five different fractions. Organic fractions including sulphides made a significant role in the speciation of copper. The predominance of copper in the organic phase has also been observed in fresh water and marine sediments [39–42]. Copper was mainly associated with organic matter for which it has a high affinity [43]. Copper is an important trace element for nutrition to the plants and animals, including human beings [44]. Copper can easily form complexes with organic compounds which make it rather stable in the environment [38]. In aqueous systems, natural organic matter markedly affects the distribution of copper as humic materials and amino acids. Increased Cu_4 values at Station 6, Asramam, may be attributed to a higher organic load which is the result of the waste dumping at Station 6. Here the sediment is reducing with anoxic overlying waters. The presence of large amounts of H_2S at this station is evident from its intense smell in the sediment samples.

An exchangeable fraction indicates the form of the metals that are most available for plant uptake [45]. Generally the contribution of the exchangeable fraction to the total metal content was less than 10% of the total. The percentage contribution of the exchangeable fraction to the total metal content can be summarised as follows – Fe: 0–0.13%, Mn: 0.47–20.74% and Cu: 0.22–12.6%. Non-residual fractions are important when considering the bioavailability of metals. The range of metals in non- residual fractions were in the order Cu: 23.24–96.71% >Mn: 15.49–74.48% >Fe: 1.01–23.77 %. The relative abundance of metals in different fractions of the sediment follows the order:

Iron : $Fe_5 > Fe_4 > Fe_3 > Fe_1 > Fe_2$
Manganese : $Mn_5 > Mn_4 > Mn_3 > Mn_1 > Mn_2$.
Copper : $Cu_4 > Cu_5 > Cu_3 > Cu_1 > Cu_2$.

The higher values of iron and manganese in the residual fraction indicate the locked nature of these elements. For all the metals studied, the moderately reducing fraction made the lowest contribution to the total metal content. The contributions of exchangeable cations and easily reducing fractions (individually) to the total metal content were always less than 10%.

3.4. *Principal component analysis*

Principal component analysis was carried out using the statistical programme SPSS 10.0 for Windows to find out the major biogeochemical processes controlling the distribution and partitioning of metals. The results of the PCA analysis are given in Table 4. Since we consider only the sediment, additions and removals from the sediment are our major concern. The metal distribution and partitioning in sediments are controlled by a number of biogeochemical processes. A number of sub processes govern these major processes. Processes such as inorganic/organic complexations, adsorption/desorption, precipitaton/dissolution, ion exchange and oxidation-reduction (redox) reactions contribute to the storage of metals in sediments. Transformations during early diagenesis and changing redox state characterise the chemical forms of metals in aquatic sediments. Since

Table 4. Varimax Rotated Component Matrix for the speciation of metals in mangrove sediments (M_1, M_2, M_3, M_4 and M_5 represents the respective concentrations (%) in exchangeable, easily reducible, moderately reducible, organic including suphides, and residual fractions of the sediment).

	Component		
Variables	1	2	3
(a) Iron			
Fe_1	0.650	−0.151	
Fe_2	0.669	−0.379	
Fe_3	0.772	−0.255	
Fe_4	0.928	0.151	
Fe_5	−0.966	−9.962E-03	
OC	0.465	0.581	
Sand	0.178	−0.932	
Silt	−5.774E-02	0.884	
Clay	−0.303	0.818	
Rotation converged in 3 iterations.			
(b) Manganese			
Mn_1	0.166	0.894	−3.618E-02
Mn_2	−2.757E-02	0.906	−0.130
Mn_3	−0.685	3.408E-02	0.451
Mn_4	7.795E-02	−0.423	0.877
Mn_5	0.152	−5.719E-02	−0.980
OC	0.644	−9.756E-02	0.324
Sand	−0.871	−0.265	0.137
Silt	0.880	−2.798E-02	5.540E-03
Clay	0.745	0.487	−0.187
Rotation converged in 4 iterations.			
(c) Copper			
Cu_1	0.818	8.193E-02	3.420E-03
Cu_2	0.886	0.215	−9.919E-02
Cu_3	0.490	−7.670E-02	0.754
Cu_4	−0.151	−0.966	−0.132
Cu_5	−0.345	0.852	−0.342
OC	−0.484	−1.281E-02	0.657
Sand	0.916	−0.303	0.118
Silt	−0.845	7.242E-02	−8.425E-02
Clay	−0.815	0.308	−8.660E-02
Rotation converged in 5 iterations.			

diagenesis is associated with the destruction of organic matter, loading of organic carbon is taken as an index of diagenesis. Associations with organic matter are taken as an index of vegetative origin and the residual fraction is an index of lithogenic character. Grain size is important in determining the transport of sediment and it can be taken as an indicator for sorption/desorption processes.

Principal component analysis of iron content in different geochemical fractions of the sediments resulted in two major components with % variances of 40.04 and 32.34 respectively. Positive loadings for Fe_1, Fe_2, Fe_3, Fe_4 and organic carbon and negative loadings for Fe_5 in the first factor suggested diagenesis as the major process controlling the speciation of iron. The loading pattern in the principal factor also supported the opposite behaviour of residual and non-residual fractions of iron in sediments. Non-residual fractions of (Fe_1, Fe_2, Fe_3 and Fe_4) are retained in the sediment as the active component and residual iron (Fe_5) represented the fraction of iron stored in sediments as stable sulphides. This represented the fraction of iron unavailable for further biogeochemical processes operating in the system. The second factor with 32.34 % of variance has positive loadings for organic carbon, silt and clay and negative loading for sand. Deposition is the process indicated by this factor. PCA results showed that the speciation of Mn and Cu were also governed by diagenesis. For manganese, the first factor (33.66 % of variance) exhibited positive loadings for silt, clay and organic carbon and negative loading for Mn_3. The principal component for copper (47.62 % of the total variance) showed positive loadings for Cu_1, Cu_2, Cu_3 and sand, and negative loadings for organic carbon, silt and clay. The second factor for manganese (23.56 % of variance) has positive loadings for Mn_1, Mn_2 and negative loadings for Mn_4. Positive loading for Cu_5 and negative loading for Cu_4 are obtained in the second factor for copper. Negative loading for organic fraction including sulphides, common in both the cases, points to the contributions from plant litter. For manganese and copper, the third factor accounts for sorption/desorption processes occurring at the sediment water interface. This factor has positive loadings for Mn_3 and Mn_4 and negative loading for Mn_5. In the PCA of copper speciation data, the third factor has positive loadings for organic carbon and Cu_3. Metals associated with organic matter can undergo remineralisation. The iron showed a strong storage tendency in the inorganic pyrite form and copper in a non-residual fraction. A comparison of the geochemical behaviours of the three metals Fe, Mn and Cu presented the independent geochemical possibility in residual and non-residual fractionation. An ultimate storage character can be observed only with iron in the pyrite form, whereas manganese and copper have only a temporary or intermediate storage by associations with organic matter. The copper and manganese will thus retain their labile character even during the burial. The source character of the copper and manganese, mainly of plant origin, along with the nature of diagenesis in the anoxic condition, may be the contributing factor for this.

4. Conclusions

The data revealed significant differences in the speciation pattern of metals. Residual fraction was the major host for iron and manganese. For copper, the organic fraction including sulphides made the largest contribution to the total metal content. Plant litter additions, diagenesis, and sorption/desorption processes determine the geochemical character of the mangrove ecosystem. The distribution of the metal species in different fractions of the sediment was observed to be the result of the simultaneous operations of these processes which will be manifested differently among the metals.

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