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Mangrove Sediment Heavy Metals from Southeast Coast of India

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Abstract: Heavy metals such as iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), nickel (Ni), cobalt (Co), lead (Pb) and cadmium (Cd) concentration range were 13330–32500 ppm, 260–780 ppm, 32.7–158 ppm, 27.6–82.6 ppm, 15.6–46.8 ppm, 5.46–42.7 ppm, 3.48–14.7 ppm and 0.15–1.75 ppm reported respectively. At all the sampling sites, the mean concentrations were found to follow the decreasing orders: Fe > Mn > Zn > Cu > Ni > Co > Pb > Cd. ANOVA of variation ratio and level of significance between study areas were 1% significant except manganese (5%) and copper (not significant). Statistical reports also showed 1% significant except cadmium (5%). Iron and zinc can be considered as high level of contamination and a serious threat, copper was a moderate to serious threat, nickel slight contamination and cadmium no hazards.

Key words: Mangroves, sediment, heavy metals, iron, copper, cadmium, lead, nickel.

Introduction

Heavy metals are among the most serious pollutants within the natural environment due to their toxicity, persistence and bioaccumulation problem (MacFarlane and Burchett, 2000). One of the major sources of heavy metal pollution is the mining and smelting of metalliferous ores (Li and Thornton, 2001). Besides the contamination from the weathering and leaching processes of mine tailings, inputs from shipping and agricultural activities, untreated mine drainage and domestic sewage also contribute large amounts of heavy metal to nearby streams and rivers (Guzman and Jimenez, 1992). Heavy metals released into aquatic systems are generally bound to particulate matter, which eventually settle down and become incorporated into sediments. Sediments are the important components of ecosystem in which toxic compounds accumulate through complex physical and chemical adsorption mechanisms depending on the properties of the adsorbed compounds and the nature of the sediment matrix (Leivouri, 1998).

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Previous studies suggested that mangrove environment all over the world are long-term sinks for elevated concentration of heavy metals caused by human activities (Shriadah, 1999; Lacerda et al., 1992; Tam and Wong, 1995; Perdomo et al., 1998; Harris and Santos, 2000; Tam and Wong 2000; Kamaruzzaman et al., 2008; Praveena et al., 2008). High concentration of heavy metals are derived from anthropogenic inputs such as industrial activities, discarded automobiles, batteries and waste water discharge (Marchand et al., 2006; Pekey, 2006; Shriadah, 1999; Bloom and Ayling, 1977). Mangrove ecosystems in the intertidal zone may act as a sink or source of heavy metals in coastal environments because of their variable physical and chemical properties (Pekey, 2006). Marine organisms and vegetation in mangrove environment can uptake metals, increasing for the inclusion of some metals into the food chain. There are some reports on distribution of heavy metals in sediments from Indian regions (Pragatheeswaran et al., 1986; Subramanian and Mohanachandran, 1990; Ananthan et al., 1992;

Senthilnathan and Balasubramanian, 1997; Jonathan et al., 2003; Karthikeyan et al., 2004, 2007; Ananthan et al., 2005; Sankar et al., 2010; Nirmal Kumar et al., 2011).

Since heavy metals cannot be degraded biologically, they are transferred and concentrated into plants and animals tissue from soils and pose long-term damaging effects to the ecosystem. The objective of this work is to study the concentration of heavy metals in sediments of three mangrove environment of Pichavaram, Porto Novo and Mudasal Odai Southeast coast of India for one year. Heavy metals included in this investigation are: iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), nickel (Ni), cobalt (Co), lead (Pb) and cadmium (Cd).

Materials and Methods

The sample sites chosen for sediments cover a variety of estuarine settings and represent a range of natural conditions in terms of channel and bank morphology, tidal energy, vegetation cover, water salinity and land disturbance. The soil samples were collected at monthly intervals from the three sampling sites. The samples were shades dried and homogenized by mortal and pestle and heavy metals analyzed by Guzman and Jimenez (1992). For heavy metal analysis 0.5 g soil samples were mixed with 20 ml of digestive acid such as hydrochloric acid, nitric acid and perchloric acid (HCl, HNO_3 and $HClO_4$) at the ratio of 10:5:1 and incubated for 24 hours in the closed container. It is very dangerous to inhale the smell of digestive acids. Then the samples were digested at optimum temperature using hot plate in the open air (terrace of a building). Care should be taken that the digested samples do not come out from the digestive container during digestion. Normally it takes 4 to 7 hours for better digestion; the colour change from brown to white was the symptom of completed digestion. Few drops of hydrofluoric acid were also added for better digestion. The digests were filtered through 0.44 µm Millipore filter paper and Millipore apparatus. Then the filter was diluted with double distilled water and trace elements like iron, manganese, zinc, copper, nickel, cobalt, lead and cadmium were estimated using an Inductive Coupled spectrophotometer (Japan) and result expressed in parts per million (ppm).

Results

The samples were collected at monthly intervals from three mangrove environments. In southeast India the months such as October, November and December i.e. winter months have got lowest temperature, highest rainfall and fresh water flow. The months like April, May and June i.e. summer months have highest temperature, absence of rainfall and fresh water flow. The heavy metal concentrations were highly changed depends up on the rainfall. Among the different heavy metals analysis the iron and manganese have higher concentrations. The availability of iron decrease from winter to summer months and again increase thereafter. The minimum concentration of iron (13,300 ppm) was recorded in July at Mudasal and maximum was in December at Porto Novo (28,600 ppm). During winter and after summer months highest concentration of iron were recorded in all sampling sites (Figure 1a). Manganese increased gradually from winter to summer months in all sampling sites. During the month of January Mudasal Odai has the lowest concentration of manganese (320 ppm) and maximum (760 ppm) in July at Pichavaram as reported (Figure 1b). There was peak concentration of zinc (158 ppm) in May at Pichavaram and the other two sampling sites have almost similar concentration of zinc from January to June with sudden reduction (42.6 ppm) in February at Porto Novo were obtained (Figure 1c). During January the maximum concentration of copper (82.6 ppm) at Pichavaram and minimum (25.7 ppm) in September at Porto Novo were reported.

After summer months the copper level increased in all sampling sites (Figure 1d). In February there was a sudden reduction of nickel concentration (25.7 ppm) at Porto Novo and in July (26.4 ppm) at Pichavaram were reported. From October to February there was not much change of zinc concentration (15.6–20.5 ppm) at Pichavaram sampling sites and the lowest concentration of nickel were reported during the study period (Figure 1e). There was not much fluctuation of cobalt concentration (5.46–12.7 ppm) at Pichavaram, whereas the other sampling sites (14.6–42.7 ppm) at Porto Novo and (8.57–34.7 ppm) at Mudasal Odai respectively. During summer months particularly in May at Porto Novo (42.7 ppm) and in June at Mudasal Odai (34.7 ppm) the highest concentration of cobalt were reported (Figure 1f). Lead gradually increased from winter to summer months and again reduced thereafter in all sampling sites. The highest peak of lead concentration (14.7 ppm) was recorded in April and May at Pichavaram and Mudasal Odai respectively (Figure 1g). Cadmium concentration changed not much from February to May (1.57 to 1.75 ppm) at Pichavaram and it was the highest concentration of cadmium

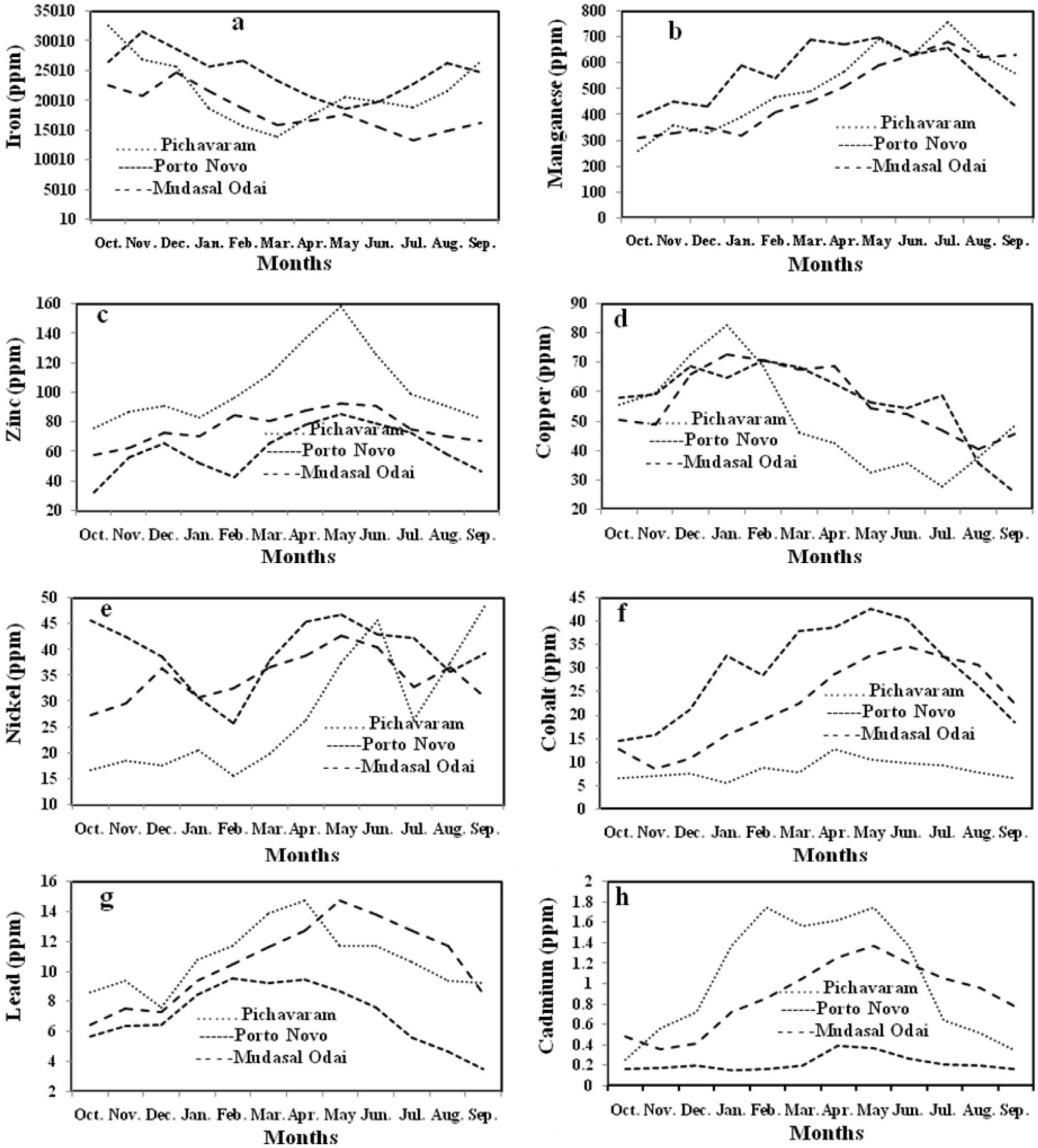

Figure 1: The heavy metals of the soil analyzed in lab: (a) Iron (mg/g), (b) Manganese (mg/g), (c) Zinc (µg/g), (d) Copper (µg/g), (e) Nickel (µg/g), (f) Lead (µg/g), (g) Cobalt (µg/g) and (h) Cadmium (µg/g). Samples collected in three different Mangrove environments (…….. Pichavaram; --------- Porto Novo; - - - - - Mudasal Odai) for one year at monthly intervals.

reported during the study period. In Mudasal Odai the cadmium concentration gradually increased (0.36 to 1.37 ppm) from winter to summer months. There was not much change of cadmium concentration (0.15 to 0.39 ppm) at Porto Novo sampling sites (Figure 1h).

Discussion

The concentration of all heavy metals analyzed in the sediment of three mangrove sampling sites are comparable with concentrations of metals found in other tropical areas (Table 1). Iron and manganese at the highest values and cadmium was the lowest value of heavy metals in all sampling sites (Figures 1a-1h). This trend was distinctly similar in mangrove sediments from Hong Kong (Ong Che, 1999). Defew et al., (2005) recorded iron (9827 ppm), zinc (105 ppm), lead (78.2 ppm), copper (56.3 ppm), nickel (27.3 ppm) and cadmium (<10 ppm) in the mangrove sediment from Punta Mala Bay, Pacific Panama. According to the background values from the Hong Kong Environment Protection Department (Tam and Wong, 2000), concentration of Fe, Zn and Pb measured in Punta Mala Bay can be considered to present a high level of contamination and a serious threat to the mangrove ecosystem. Cu currently presents a moderate to serious threat, whilst Ni can be considered to be causing slight contamination in the bay. At this time Cd appears to present no hazard to mangrove system. Compared to the present study the iron and zinc trend was almost similar, the lead concentration was very low while the copper and nickel concentrations were high (Figures 1a-1h). The statistical analysis showed most of the heavy metals 1% significant between the study areas except manganese (5%) and copper (not significant). The result also showed, except cadmium (5%), all other heavy metals from the monthly interval samples, 1% significant (Table 1).

Average concentration of iron in the study areas with mean (21,500, 24,580, 18,180 ppm) at Pichavaram, Porto Novo and Mudasal Odai respectively was higher than others (Figure 2). The highest average iron concentration (15,593, 9827, 6118 ppm) were reported at Cienaga Grande, Punta Mala Bay, and Punta Piuta by Perdomo et al., (1998), Defew et al., (2005) and Guzman and Jimenez (1992) respectively (Table 2). Clay minerals and Fe oxides are well-known inorganic scavengers that control metal mobility and distribution within sediments and soils (Forstner et al., 1976; Thornton, 1983; Alloway, 1990). Highest concentration of iron was recorded during monsoon in the present study at all sampling sites, which is attributed to the increased land runoffs (Figure 1a). The similar trend was reported by Ganesan and Kannan (1995) at Tuticorin coast. Average manganese concentration was (500, 560, 480 ppm) recorded at Pichavaram, Porto Novo and Mudasal Odai sampling sites (Figure 2) which was similar (623, 525 ppm) at Cienaga Grande, Colombia and Punta Piuta, Costa Rica reported by Perdomo et al., (1998) and Guzman and Jimenez (1992).

The average range of manganese is 96–295 ppm as reported from different parts of the world (Table 2). Karthikeyan et al. (2007) recorded the average concentration of manganese in 600 ppm (range from 200 to 3000 ppm). Zinc was the third largest concentration of heavy metals with mean (103.1, 161.3, 76.12 ppm) at Pichavaram, Porto Novo and Mudasal Odai sampling sites respectively (Figure 2) which was lower than Port

Table 1: ANOVA of variance ratio and level of significance between study areas and between month interval samples

No.	*Source of variation*	*Variance ratio ('F') and level of significance between stations*		*Variance ratio ('F') and level of significance between months*	
1.	Iron (ppm)	13.03[a]	**	3.92[a]	**
2	Manganese (ppm)	4.30[b]	*	9.82[a]	**
3.	Zinc (ppm)	54.47[a]	**	8.31[a]	**
4.	Copper (ppm)	1.60[n]	NS	4.46[a]	**
5.	Nickel (ppm)	30.01[a]	**	3.54[a]	**
6.	Lead (ppm)	23.28[a]	**	5.32[a]	**
7.	Cobalt (ppm)	43.85[a]	**	3.98[a]	**
8.	Cadmium (ppm)	24.36[a]	**	2.81[b]	*

** Significant at 1% ; * Significant at 5% ; NS – Not significant

Table 2: Comparison of sediment metals levels (ppm dry wt) between present study of South Indian coast and other documented sediment levels (ppm dry wt) from around the world

Location	*Fe*	*Mn*	*Zn*	*Cu*	*Ni*	*Co*	*Pb*	*Cd*
India								
Pichavaram[a]	21500	500	103.1	50.85	23.45	8.260	10.78	1.06
Porto Novo[a]	24580	560	161.3	56.95	39.45	29.20	07.10	0.22
Mudasal Odai[a]	18180	480	76.12	57.07	34.59	22.62	10.56	0.88
Panama								
Punta Mala Bay[b]	09827	295	105.00	56.30	27.30	-	78.20	<10.00
Toro Point[c]	01885	295	019.90	04.90	82.40	-	38.00	06.60
Galeta[c]	01748	143	010.90	04.00	74.00	-	32.50	07.20
Payardi[c]	02094	228	016.10	04.00	91.80	-	33.30	07.50
Costa Rica								
Punta Portete[c]	03225	268	014.70	08.40	102.00	-	34.50	07.30
Punta Piuta[c]	06118	525	011.40	09.80	099.00	-	25.60	06.00
Colombia								
Cienaga Grande[d]	15593	623	091.10	23.30	032.50	-	12.60	01.92
Australia								
Port Jackson[e]	-	-	145.00	62.00	-	-	180.00	-
Port Jackson[e]	-	-	351.00	102.00	-	-	443.00	-
Hawksbury[e]	-	-	094.00	018.90	-	-	026.40	-
Port Hacking[e]	-	-	010.30	001.10	-	-	002.50	-
Queensland[f] 01050	103	023-56	1-12	09.00	-	036.00	00.60	
Brazil								
Clean Mangrove[g]	*02464*	-	*024.20*	*03.82*	-	-	-	*00.60*
Hong Kong								
Clean Mangrove[h]	*01080*	*096*	*043.00*	*02.60*	*02.90*	-	*031.20*	*00.32*

Documented 'clean' mangrove sites are noted in italics.
Australian mangroves in Port Hacking was deemed a clean and unpolluted mangroves, situated within a National Park. Hawksbury and Port Jackson, Australia were reported to be polluted mangroves with regard to metal pollution.
[a]Present study; [b]Defew et al., 2005; [c]Guzman and Jimenez, 1992; [d]Perdomo et al., 1998; [e]MacFarlane, 2002; [f]Preda and Cox, 2002; [g]Harris and Santos, 2000; and [h]Tam and Wong, 2000.

Jackson, Australia (351 ppm) and almost equal (105 and 91 ppm) at Punta Mala Bay and Cienaga Grande, Colombia (MacFarlane, 2002; Defew et al., 2005; Perdomo et al., 1998). Zinc has a complex chemical behaviour and can co-precipitate with either Fe or Mn oxides, and with clays such as smectite-illite. Zinc can also be very mobile under oxidising and acid conditions, but it can be immobilised in sulphides or in soils as a variety of inorganic complexes (Kiekens, 1990). Copper was the fourth largest concentration of heavy metal with mean (50.85, 56.95, 57.07 ppm) at Pichavaram, Porto Novo and Mudasal Odai sampling sites (Figure 2). The average mean value of copper (1-56 ppm) has been reported by others (Table 2). Copper can be rapidly desorbed from sediments under saline conditions (Moore, 1991). The affinity of copper for metal-organic complex makes this metal more easily extractable from sediments than other heavy metals (Baker, 1990).

Zinc and copper are generally good indicators of anthropogenic inputs (Forstuer and Wittman, 1979). Copper and zinc are essential micro nutrients required in chloroplast reaction, enzyme systems, protein synthesis, growth hormone and carbohydrate metabolism (Shaw, 1990). Lead is a non-essential heavy metal and tends to be toxic to some species (Wozny and Krzeslowska, 1993). In the present study the average mean of lead (10.78, 7.1, 10.56 ppm) at Pichavaram, Porto Novo, and Mudasal Odai sampling sites was seventh rank heavy metal (Figure 2). The average mean value of lead (2.5–443 ppm) is reported in other parts of the world (Table 2). The mean values of cadmium concentration (1.06, 0.22, 0.88 ppm) at Pichavaram, Porto Novo and Mudasal Odai sampling sites (Figure 2) were greater than those measured in Vamleshwar mangrove area, Gujarat, India by Nirmal Kumar et al., (2011), Buloh River and Khatib Bongsu River at Singapore by Cuong

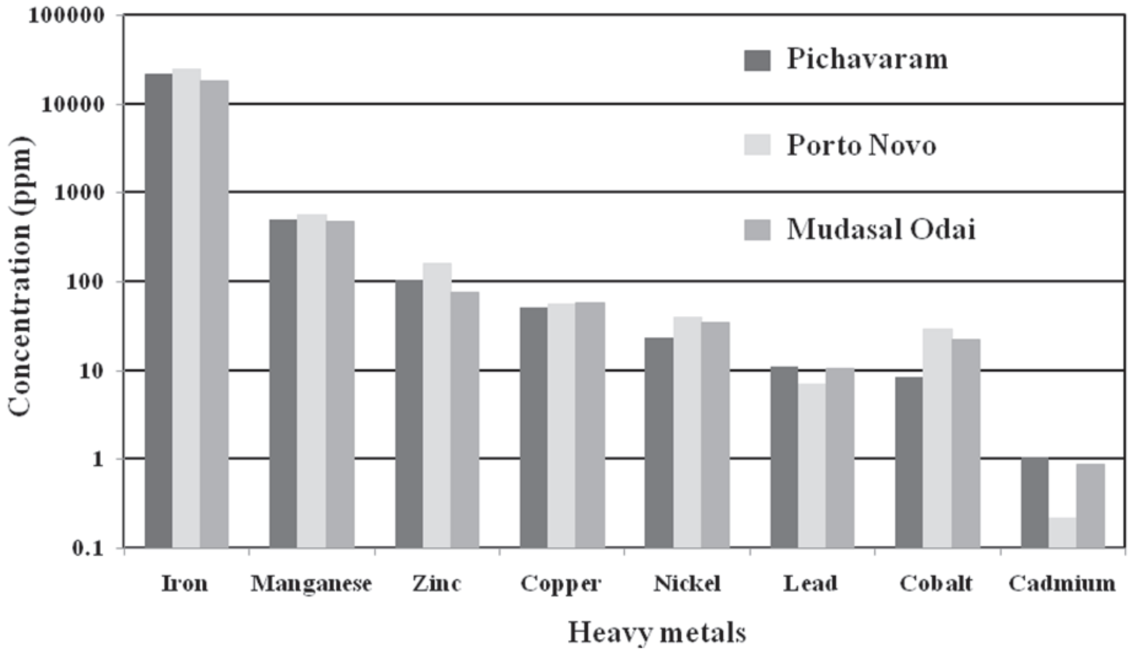

Figure 2: Average concentration of iron, manganese, zinc, copper, nickel, cobalt, lead and cadmium in sediment from three mangrove environments such as Pichavaram, Porto Nov and Mudasal Odai using Inductive Coupled spectrophotometer (Japan) and result expressed in parts per million (ppm).

et al. (2005), Brisbane River, Australia by Mackey et al. (1992) and Mai Po river, Hong Kong by Ong Che (1999).

Malin et al. (2003) and Alloway (1995) discussing the sources of heavy metals contaminations in soils, stated although heavy metals are ubiquitous in soil parents, the anthropogenic sources of heavy metals in study area are agricultural wastes, sewages sludge, fossil fuel combustion, etc. The other sources are large aquaculture development and domestic sources (Environmental Impact Assessment, 1992). The higher concentration of heavy metals were observed in monsoon during the present study (Figures 1a-1h). The heavy rainfall and subsequent river runoff, bring much industrial and land-derived materials along with domestic, municipal and agricultural wastes, which include residues of heavy metal containing pesticides (Pragatheeswaran et al., 1986; Senthilnathan and Balasubramanian, 1997; Ananthan et al., 1992, 2005, 2006; Karthikeyan et al., 2004, 2007). Mechanical and chemical weathering of rocks, wind-blown dust, forest fire and volcanic particles are other sources of heavy metals (Bryan, 1984). Toxic heavy metals accumulate in mangrove ecosystems due to urban development and sources of metal contamination range from domestic garbage dumps to agricultural runoff (Stark, 1998). High level of copper, iron, manganese and lead concentration indicates more polluted mangrove ecosystem of Tamil Nadu, South India (MacFarlane et al., 2003; Defew et al., 2005).

Conclusion

The mean values of eight heavy metal concentrations from this study were found to follow decreasing order: Fe > Mn > Zi > Cu > Ni > Co > Pd > Cd. Results obtained in the study generally revealed the presence of these metal sources from motor vehicles and industrial emissions via atmosphere depositions, wastes from petroleum products, agriculture and aquaculture through fresh water inflow along these sites. This finding will be a foundation in the consideration of using mangrove wetlands as a sewage treatment facility.

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