Pak. J. Bot., 46(4): 1277-1285, 2014.

BIO-GEOCHEMICAL STUDIES OF INDUS DELTA MANGROVE ECOSYSTEM THROUGH HEAVY METAL ASSESSMENT

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Abstract

In the present study monitoring of heavy metal pollution was done in the mangrove habitats of Indus Delta. Different levels of four heavy metal (Pb, Cu, Cd, and Zn) in abiotic component (sediments and water) and biotic components (mangrove plants parts like, (Pneumatophores, bark, leaves, flowers, and fruits) were determined. The highest average concentration of heavy metals (111 ppm Zn, 60.0 ppm Pb, 52.2 ppm Cu, 1.43 ppm Cd) were measured in sediments and the lowest in the water (0.13 ppm Zn, 0.0014 ppm Cu, 0.0007 ppm Pb , 0.00061ppm Cd). Among the four heavy metals, Zn was the most abundant metal in all components of the ecosystem, followed by Cu, Pb, and Cd (Zn>Cu>Pb>Cd), and hence *A. marina* can be proposed as a hyper-accumulator for Zn, which opens doors for further research.

The pollution load index (PLI) had values higher than 1 and varied between 2.02-1.70 at Indus Delta, whereas at MianiHor the PLI was 0.65, which indicated that Indus Delta mangrove Ecosystem was under threat of pollution under the present scenario.

Introduction

Mangroves are one of the most important and productive ecosystem in the sense of ecology and economic, by providing indefinite food, security and services to human being. They are an integral part of the tropical vegetation and it is a common feature along sheltered coastline where there are constant freshwater discharges (Younus*et al*., 2011). Being the most productive ecosystem of the world, mangroves provide important goods and services to both human society and coastal and marine systems. Their major environmental services include protection and stabilization of shore line and providing significant functions in the coastal zones as buffer against erosion, storm surge and tsunamis. The carbon fixed in mangroves is highly important in the coastal food webs and the litter from mangroves and the subsequent formation of detritus and its tidal export have also profound effect on promoting biodiversity richness (Sthevan, 2011). Despite these facts, mangrove ecosystems world over are under threat due to multi factors among which over harvesting and grazing, urbanization and pollution are the major problems.

The Indus Delta mangroves constitute the largest arid climate mangrove forest of the world. Four species occur in the area but only one, *Avicennia marina* (Forssk.) Vierh, is dominant (Saifullah *et al*., 1994). Along with Indus Delta, mangroves are facing severe degradation though out the world due to urbanization and industrialization, aquaculture, tourism, over exploitation for fuel and fodder, population growth, and pollution. There are some additional threats to the Indus delta mangroves like low fresh water inflow, export of mangrove seedling, over harvesting, sedimentation, coastal and urban development, and sedimentation (Adhikari *et al*., 2010). The westernmost part of the Delta located at Karachi is facing some additional serious problem of industrial and domestic pollution. The mega city of Karachi, with a population of 12 million, consists of more than 6000 different types of industrial units. The most important industries present in these localities involve metal and non-metal manufacturing, textiles, tobacco, food and beverages, chemicals, paints, rubber paper and paper products. They contribute approximately 99% of the total industrial pollution (Khan & Saleem, 1988). Most of this enormous amount of waste discharge is routed to the coastal mangrove habitat without adequate pretreatment (Saifullah, 1997).

Heavy metals are severe in their toxicity, they are persistent and accumulate biologically. Heavy metals are regarded as severe pollutants due to their toxicity and bioaccumualtion problems (Tam & Wong, 2000). They are not transferred from one reservoir to another (Macfarlane & Bruchett, 2000). The occurrence of heavy metals in soil may be beneficial or toxic to the environment. The biota may require some of these elements in trace quantities, rather act as micronutrients causing rapid growth to seedling (Shah *et al*, 2008), but at higher concentration there may be toxicity problems (Kabir *et al*., 2011 and Rout & Das, 2003). An excess of metals may produce some common effects of individual metals on different plants (i.e., both macro- and micro-flora). Shah *et al.*, (2008), reported that concentration of heavy metal when exceeds the critical level, than seedling growth in terms of shoot and root length, number of leaves, and biomass and chlorophyll contents inhibited. Zinc and copper are essential elements and are involved in several metabolic processes, whereas Pb and Cd are not known to have any function in plants (Pahlsson, 1989). Whereas high concentration of Cd reduces significantly plant growth and causes leaf chlorosis, wilting and leaf abscission (Khadijeh *et al*., 2011). Yasari *et al*., 2012 also described that heavy metals concentration alters metabolism of mineral nutrients in plants.It's noteworthy, that metals are transported to estuarine water, accumulated by mangroves and concentrated in leaf detritus and enters estuarine food chain (Sthevan, 2011). Essential or non-essential elements, when present in excess, can be accumulated in plants and other animals. As a result, these contaminants can affect the health and productivity of these organisms and can accumulate in humans if these organisms are consumed (Houshmandfar & Moraghebi, 2011; Page & Feller, 2005).

Measurement of heavy metals in soil, plant and animals is considered to be one of the tool to determine the human impact on environment, because these pollutants, adversely affect the density and diversity of living communities including human itself. (Hsu *et al*., 2006). Many studies have been carried out on coastal pollution in Karachi, but those dealing with mangrove habitat are extremely rare, especially related to heavy metals. Most of the studies were conducted on the sediments such as Bryan & Langstan, 1992; Kersten & Fosrstener, 1986; Lacerda *et al.*, 1988; Lacerda & Abrao, 1984; Lacerda & Rezende, 1987; and Cai *et al* 2009. Some of the research work was performed on the seawater like, Bruland *et al*., 1979; Saleem & Kazi, 1998; Seng *et al*., 1987; Sadiq, 1992; Ali & Jilani, 1995. Research work in respect of mangrove plant is also rarely found, but comparative and combined study on different compartment of mangrove ecosystem especially in reference of Indus Delta, is still not available. Therefore, the present study is an attempt to conduct a major baseline study of heavy metals (Ni, Fe, Cr, Pb, Cd, Cu, Zn) in different components of the mangrove ecosystem. The information related to Ni, Fe and Cr is already published (Saifullah *et al*., 2002, 2004; Ismail *et al*., 2006). An attempt has been made in this paper to understand the biogeochemistry of the four heavy metals, Cu Pb, Cd, and Zn, in the Indus Delta Mangrove estuarine ecosystem. This information will provide valuable baseline data by which any further increases of heavy metals in the ecosystem can be properly evaluated.

Materials and Methods

Karachi resides in a subtropical climate with a coastline stretching over 135Km along the N. Arabian Sea. The eastern part of the Karachi coastline is fringed with several creeks and channels, which form the westernmost part of the Indus Delta. It is a city of more than 12 million people and many of the industries of Pakistan are located there (Hogarth, 2001), contributing considerably to marine pollution in the area (Table 1).

The area of study is highly polluted with mostly untreated effluents from more than 6000 industries located in three major industrial sites, namely, the Sindh Industrial and Trading Estate (S.I.T.E.), Landhi, Industrial and Trading Estate (L.I.T.E.) and Korangi Industrial Area (KIA), which discharge their effluents into the Lyari and Malir rivers. Nearly three hundred samples of sediments, water and different parts of mangrove (*A. marina*) plants including leaves, twigs, bark, pneumatophores, flowers, and fruits were collected from various study sites. The different localities selected for sampling in the study were Sandspit (Backwater), Karachi harbor, Korangi creek, Port Qasim, Lut Basti, Baba and Bhit and Chara creek, all separated from each other by few kilometers (Fig. 1). Sampling was also done at Miani Hor, a distant site free from pollution some 100-km away.

All the samples were brought to the laboratory for processing. Plant and soil samples were wet digested in aqua regia and concentrated HNO_3 respectively, whereas heavy metals in seawater were determined by a solvent extraction method (Saifullah *et al.,* 2002). Finally the samples were analyzed using Flame Spectrophotometer AAS (Perkin Elmer Model 3300) and Graphite Furnace AAS (HGAModel 600) with an autosampler (AS Model 60). Statistically the data were subjected to analysis of variance (ANOVA) employing the Duncan Multiple Range Test (Gomez & Gomez, 1984). Methods of sampling, processing and analysis of samples have already been discussed in detail (Saifullah *et al*., 2002).

Table 1. Concentration of Zn, Cd, Pb and Cu (ppm) in the effluents (eff.) discharged from different sources.

Locality	Source	Zn	Cd	Pb	Cu
Mauripur	Various	1.08	0.21	1.48	0.09
GharoPhitti Creek	Steel Mills	0.36	–	–	6.60-11.0
Bakran Creek	Steel Mills	0.03 - 0.97	–	–	0.02-4.50
Eff. of Site Nallahs	Site Nallahs	1.89	–	0.13	3.75
Eff. of Site Tanneries	Tanneries	5.08	0.4	2.3	–
Eff. Sindh Alkalis	Sindh Alkalis	0.22	0.028	0.66	0.138
Eff. of Refineries	Pak. Refinery	0.7	–	–	0.149
Eff. of KIA	Pharmaceuticals	482	73	79	85
Eff. of KIA	Refinery	343	81	75	53
Eff. of KIA	Tannery	1358	986	1166	370
Eff. of KIA	Textile	359	28	94	82
Eff. of KIA	Beverage	4386	20	780	107

After Rizvi, 1997

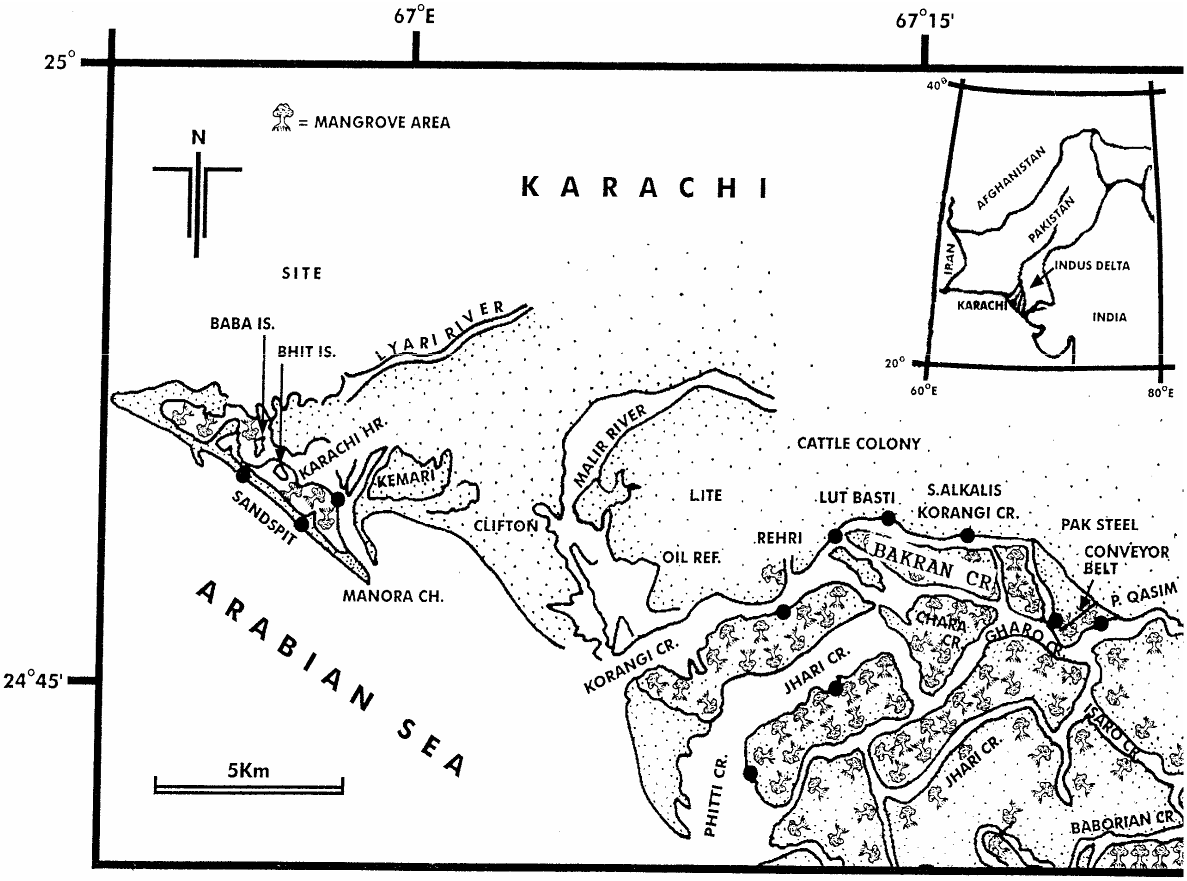

Fig. 1.Map showing study area.

Results and Discussion

Heavy metals in water: Among all the four heavy metals studied, zinc was present in highest concentration (0.13 ppm) in seawater. Ouseph (1992) reported similar concentration of zinc from India. However, a much lower concentration of 0.012 µg/l was recorded in the open sea of Pakistan by Tariq *et al*., (1993). According to Bruland *et al*., (1979), the oceanic concentrations of zinc are less than 1 ug /l. On the contrary, levels in coastal areas and estuaries are often much higher (Morris, 1984). For example, Ali & Jilani (1995) reported much higher concentrations in an area close to the present site, near the Malir river discharge. Saleem & Kazi (1998) and Khan & Saleem (1988) also observed the marked enrichment of zinc. According to them, high concentrations of zinc are associated with the industrial waste from refineries as well as paint, battery, rubber and other industries. These sources are further by Rizvi, (1997) as mentioned in Table. 1. In addition, dissolution of anodes from ships may also aggravate zinc concentrations.

The concentration of copper in sea water in the study area ranged from 0.20 to 5.17 µg/l with an average value of 1.40 ±0.5 µg/l (Table 2). The high concentrations of Cu could be attributed to the release of Cu from the cooling tubes of ships and coastal installations (Saleem & Kazi 1998) and also due to other industries mentioned in table 1. Tariq *et al.,* (1993) recorded very low values in the offshore open waters on the eastern coast of Pakistan. The present values are, however, comparable with those of polluted waters (Subrahmanyan & Kumari, 1990; Seng, *et al*., 1987). Ouseph (1992) and Patel *et al*., (1985) reported even higher values up to 25 µg/l from Cochin estuary and Bombay harbor, respectively, which may be due to the high magnitude of pollution there. Such values have been reported to be toxic to marine phytoplankton but only in experimental cultures (Saifullah, 1978).

Oceanic concentrations of Cd in sea water is reported to vary between 0.02–0.12 µg/l (Bruland *et al*., 1979), but it was higher in the study area, ranging between 0.047 and 1.728 µg/l (Table. 2). Ouseph (1992) observed similar values in Cochin estuary, India, but comparatively lower values were obtained by Seng *et al*., (1987) and Patel *et al*., (1985) from Penang, Malaysia and Bombay harbour, India, respectively.

Sea water concentrations of Pb in the study sites were in the range of 0.10–3.75 µg/l (Table. 2) which were much lower than those observed in Malaysia (Seng *et al*., 1987) and India (Patel *et al*., 1985; Subrahmanyam & Kumari, 1990; Ouseph, 1992). Furthermore, Tariq *et al*., (1993) reported lower values from offshore waters of Pakistan. Lead concentrations in sea and estuarine waters in general have been reported to range between 0.01 and 27mg/l (Sadiq, 1992). Higher values are found in marine areas under human influence such as coastal areas. The order of concentration of heavy metals in seawater is Zn> Cu>Pb>Cd, confirming earlier observations from Pakistan (Ali & Jilani, 1995; Saleem & Kazi, 1998), and other parts of the world (Subrahmanyan & Kumari, 1990).

Table 2. Concentration of Cd, Pb ,Cu& Zn (ppm) in water of different mangrove sites.

Locality	Cd(ppb)	Pb(ppb)	Cu(ppb)	Zn(ppm)
Sandspit	1.017 ± 0.11^{a}	0.51 ± 0.18^{cd}	1.5 + 0.49^{b}	0.146 ±0.028^{abc}
Mean S.E. Range	0.699 - 1.264	0.10 - 1.28	0.06 - 3.29	0.063 - 0.243
Port Qasim	0.936 ± 0.10^{a}	1.29 ± 0.38^{a}	3.06 + 0.63^{a}	0.208 ± 0.065^{a}
Mean S.E. Range	0.584 - 1.333	0.25 - 2.18	1.89 - 5.17	0.081 - 0.435
LutBasti	0.818 ± 0.30^{b}	1.01 ± 0.56^{ab}	1.50 + 0.35^{b}	0.114 ± 0.043^{abc}
Mean S.E. Range	0.047 - 1.728	0.11 - 3.75	0.047 - 1.72	0.030 - 0.361
Chara Creek	0.443 ± 0.20^{c}	0.95 ± 0.36^{b}	0.78 + 0.49^{d}	0.198 ± 0.10^{ab}
Mean S.E. Range	0.190 - 0.853	0.28 - 1.53	0.31 - 1.79	0.081 - 0.410
Korangi Creek	0.323 ± 0.11^{d}	0.26 ± 0.06^{de}	1.17 + 0.87^{c}	0.016 ± 0.001^{d}
Mean S.E. Range	0.092 - 0.450	0.13 - 0.36	0.06 - 1.94	0.013 - 0.019
Karachi Harbour	0.162 ± 0.03^{e}	0.60 ± 0.16^{c}	0.04 + 0.00^{e}	0.100 ± 0.01^{c}
Mean S.E. Range	0.081 - 0.321	0.10 - 1.37		0.081 - 0.194
MianiHor Mean S.E.	0.057^{f}	0.041^{f}	0.08^{f}	0.0112^{e}

Results of a one way ANOVA, letters identical showed non significant difference at $p<0.05$ according to Duncans, Multiple Range Test

Table 3. Concentration of Cd, Pb& Zn (ppm) in sediments of different mangrove sites.

Locality	Cd	Pb	Cu	Zn
LutBasti	1.59 ± 0.44^{a}	51.86 ± 4.387^{c}	69.02 + 8.09^{a}	100.15 ± 6.09^{b}
Mean S.E. Range	1.10 - 1.95	44.20 - 59.40	56.90 - 85.60	84.10 - 110.60
Sandspit	1.47 ± 0.06^{b}	66.40 ± 2.901^{b}	48.09 + 2.43^{c}	119.40 ± 6^{a}
Mean S.E. Range	1.03 - 1.95	23.70 - 93.00	28.90 - 65.70	82.70 - 156.20
Baba &Bhit	1.48^{b}	75.01^{a}	57.60 + 1.35^{b}	125.10^{a}
Mean S.E. Range	–	–	–	–
Chara Creek	1.34 ± 0.17^{c}	53.85 ± 9.44^{c}	46.55 + 1.35^{c}	115.70 ± 3^{a}
Mean S.E. Range	1.16 - 1.51	44.40 - 63.30	–	112.70 - 118.70
Korangi Creek	1.34 ± 0.17^{c}	65.10^{b}	48.10^{c}	105.00 ± 2^{b}
Mean S.E. Range	1.16 - 1.51	–	–	103.00 - 107.00
Port Qasim	1.36 ± 0.07^{c}	47.73 ± 2.97^{d}	44.02 + 0.07^{d}	101.30 ± 4.23^{b}
Mean S.E. Range	1.12 - 1.49	40.92 - 54.80	36.7 - 51.20	95.30 - 110.60
MianiHor	0.86^{d}	19.99^{e}	9.80^{e}	38.60^{c}
Mean S.E. Range	–	–	–	–

Results of a one way ANOVA, letters identical showed non significant difference at $p<0.05$ according to Duncans, Multiple Range Test.

A number of factors are known to affect concentration of heavy metals in seawater like, metal chloro-complex formation, pH, temperature, alkalinity, concentration of organic matter and suspended particulate. Metals behave as nutrient in seawater due to biological and geochemical processes (Sadiq, 1992). In coastal regions, coagulation, adsorption and incorporation into particulate matter can scavenge them from the water. The production and degradation of organic matter cause changes in water and particulate matter qualities, which may affect these processes.

Accumulation of heavy metals in sediments: As compared to seawater, the concentrations of heavy metals were higher in sediments by several orders of magnitude, which also supported by Stethan *et al*., (2011) and Yunus *et al*., (2011). Thus the average concentration of Zn was 112 ± 50 mg/kg (82.7-156.00 mg/kg) as shown in Tables 3 and 5. Prudente *et al*., (1994) and Lacerda & Abrao (1984) observed similar levels of Zn from Manila Bay and Brazil, respectively.

Concentration of Pb in sediments was as high as 75.0 mg/kg (Table 3). Sadiq (1992) found very wide variation in Pb concentrations in sediments from different parts of the world. Lead forms practically insoluble compounds at a rapid rate, so that its dispersion in marine environments is generally limited to areas near the source (Scoullos, 1986). Lead in marine sediments is strongly associated with oxides and hydroxides of Fe (Balistrieri & Murray, 1982, 1984; Scoullos, 1986) and with the carbonate fraction (Dominiki & Ropin, 1983; Abaychi & Doubal, 1986).

Table 4. Concentration of Cd, Pb, Cu& Zn (ppm) in leaves of different mangrove sites.

Locality	Pb	Cd	Cu	Zn
Sandspit	0.75 ± 0.06[a]	0.63 ± 0.07[a]	4.78 + 1.22[b]	40.22 ± 3.23[d]
Mean S.E. Range	0.10 - 1.52	0.13 - 0.90	0.40 - 19.70	10.30 - 99.20
Chara creek	0.71 ± 0.17[a]	0.56 ± 1.17[a]	7.45 + 1.29[a]	52.81 ± 6.85[b]
Mean S.E. Range	0.11 - 1.35	0.10 - 040	2.70 - 13.20	30.01 - 72.20
LutBasti	0.70 ± 0.14[a]	0.38 ± 0.58[b]	4.97 + 1.23[b]	32.97 ± 3.69[e]
Mean S.E. Range	0.50 - 1.12	0.11 - 0.30	0.60 - 7.50	29.90 - 38.20
Port Qasim	0.66 ± 0.19[a]	0.31 ± 0.03[b]	3.39 + 0.96[c]	46.20 ± 2.04[c]
Mean S.E. Range	0.29 - 0.97	0.21 - 0.54	0.60 - 7.50	42.20 - 48.70
Korangi Creek	0.65 ± 0.28[a]	0.11 ± 0.002[c]	6.76 + 0.38[b]	29.21 ± 5.59[f]
Mean S.E. Range	0.27 - 1.18	0.01 - 0.07	6.00 - 7.30	23.10 - 47.20
Baba &Bhit	0.58[a]	0.66[a]	6.30[b]	166.30[a]
Mean Range	–	0.11 - 0.93	–	–
MianiHor	0.21 ± 0.08[b]	0.04 ± 0.02[d]	1.21 + 0.23[d]	17.85 ± 1.65[g]
Mean S.E. Range	0.13 - 0.30	–	0.96 - 1.45	16.20 - 19.50

Results of a one way ANOVA, letters identical showed non significant difference at $p<0.05$ according to Duncans, Multiple Range Test

Table 5. Overall average conc. of Cd, Pb, Cu and Zn (ppm) in sediments, seawater and different parts of mangroves.

	Cd	Pb	Cu	Zn
Sediments	1.43 + 0.04[a]	59.99 + 4.27[a]	52.23 + 3.86a	111.87 +50[a]
Pnuematophores	1.04 + 0.47b	14.75 + 3.2[b]	11.78 + 2.84b	90.40 + 28[b]
Bark	0.70 + 0.10[c]	9.956 + 2.52[c]	15.37 + 2.84b	80.08 + 12.38[c]
Leaves	0.46 + 0.07[d]	0.681 + 0.025[d]	5.36 + 0.60d	61.28 + 21.37[d]
Flowers	0.40 + 0.07[d]	0.178 + 0.141[d]	1.87 + 0.35d	18.08 + 10[g]
Fruits	0.38 + 0.08[de]	0.433 + 0.05[d]	1.80 + 0.87e	37.76 + 60[f]
Twigs	0.24 + 0.09[e]	0.59 + 0.06[d]	4.89 + 1.65d	39.54 + 6.62[e]
Water	0.00061 + 0.00014[f]	0.0007 + 0.0001[d]	0.0014 + 0.0005f	0.130 + 0.012[h]

Values given are mean of 5 samples, similar letters are not significantly ($p<0.05$) different from each other

Copper concentrations in sediments ranged between 28.9 and 85.6 mg/kg, with an average value of 52.2 ± 3.9 mg/kg (Table 3). Great variation, from 0.3 to 12000 mg/kg, has been noted in sediment concentrations of Cu from different parts of the world (Sadiq, 1992). Copper concentrations in pristine marine sediments have been reported to be generally below 10 ppm. The adsorption and precipitation of Cu on oxides and hydroxides of Fe are considered the primary scavenging mechanisms operating in oxic and suboxic seawaters. In anoxic seawater, the precipitation of Cu sulfides may become a major removal mechanism.

The average concentration of Cd in the sediment was 1.43 mg/kg (Table 4). This is similar to concentrations reported by Sadiq & Zaidi (1985) from Saudi Arabia. Comparatively higher values were recorded for the Bermuda coast, Hamburg harbour, Chile, and UK estuaries by Lyons *et al*., (1983), Kersten & Forstner (1986), Salamanca *et al*., (1988) and Bryan & Langston (1992), respectively.

The overall sequence of heavy metal accumulation in sediments was Zn>Pb>Cu>Cd which was also observed by researchers in other parts of the world, (Lacerda & Abrao, 1984; Kurokawa & Tatsukawa, 1990; Chiu & Chou, 1991; Mackey & Hodgkinson, 1995; Paez-Osuna*et al*., 1993; Tam & Wong, 1995; Saleem & Kazi, 1995; Thomas & Fernendez, 1997).

Significant variation in water and sediment concentrations for different localities were noted, which are evident from the values of ANOVA (Tables 2, 3, 5) and also established by Duncan's multiple range test. Concentrations of heavy metals were found to be very low in the pristine mangrove habitat of Miani Hor. This emphasizes again the anthropogenic influence in the observed high levels of heavy metals in the study area (Cia *et al.*, 2009).

When compared with values in water, the concentration of heavy metals in sediments are far less variable with time and space on a global scale (Sadiq, 1992). This may be because the sediments accumulate metals over time, and metals in sediments are not mobile like metals in water. The effluents contaminate the seawater first and then other parts of the ecosystem. Therefore, any change in the quantity or quality of pollutant is reflected in seawater first and only later in sediment and other parts of the ecosystem.

Accumulation of heavy metals in mangrove: Although soil conditions and other environmental factors play a decisive role in metal uptake and toxicity in plants, leaf tissue concentration (CLT) is considered a more direct measurement tool for toxicity prediction. The CLT observed to cause toxicity in different plants for Zn, Cd, and Cu are 200-300 ug/g, 3-10 ug/g and 15-25 ug/g, respectively (Pahlsson, 1989), which are much higher than the concentration of heavy metals found in leaves of *A. marina* in the present study(Table 4). This indicated that the mangrove plants accumulate considerably lower concentration of heavy metals than the other components of the ecosystem. Among different parts of the mangrove, pneumatophores and bark accumulate higher concentrations of heavy metals (Table 5). On the other hand, leaves, twigs and flowers contained less than one third the concentrations in pneumatophores and bark. Similarly Lacerda (1997), Tam *et al*., (1995) and Tam & Wong (1996) also reported significantly higher heavy metals content in roots than in the aerial parts of mangroves, indicating that the roots act as a barrier for metal contamination. Chiu and Chou (1991) also discovered a sequential decline from roots to branches and leaves. Chen *et al*., (1995) and Tam & Wong (1997) described roots as a good absorptive sponge to heavy metals in soil and water. They further explained that growth of mangroves is not inhibited by the high concentration of heavy metals because metals absorbed or adsorbed by roots are often bound with the cell wall material or other macromolecules to prevent them from translocation to the sensitive plant parts. The most efficient mechanism is the neutralization of heavy metals by establishment of oxidant geochemical micro-environments that lead to the formation of iron plaques around the root surface. The observed discrepancy in values in the different parts of the mangrove tree may be accounted for by the nature of tissues. Pneumatophores and bark are perennial organs and also possess higher concentration of tannins than any other parts which are known to bind heavy metals (Zheng *et al*., 1997, Jaysekera, 1988, Silva *et al.,* 1990, Lacerda *et al*., 1988). According to Tam & Wong (1997) the roots mostly retain the heavy metals, but the excess amount passes on to the trunk and later to flowers and fruits. At each stage, there is retention of heavy metals so that by the time they reach the flowers they are at minimal concentrations.

The accumulation of Zn was higher in different parts of mangrove than Cu, Pb and Cd, and the sequence is similar to that of seawater, i.e., Zn>Cu>Pb>Cd, suggesting that uptake by the mangroves is proportional to the amount present in the non living environment (Table 5). Macfarlane, (2002), Macfarlane & Burchett, (2001) and Baker and Walker, (1990) classified *Avicennia marina* as an indicator species for Zn accumulation. The greater accumulation of Zn suggests that the plant actively takes up the element, as Zn is required for metabolic (including photosynthetic) processes (Baker & Walker, 1990). When the uptake exceeds metabolic requirements, however, a toxic impact may be expected (Macfarlane & Burchett, 2001). *Avicennia marina* can actively sequester much of the accumulated metal in root tissue with limited translocation to leaf tissue (Macfarlane *et al*., 1999; Kumar, 2011). Zn is mobile but its translocation is restricted to the shoot due to the endodermal caspian strip, while Pb is actively excluded at the root epidermis (Macfarlane & Burchett, 2000; Macfarlane, 2002)

Silva *et al*., (1990) consider mangroves to be poor concentrators of heavy metals and Lacerda (1997) labeled them as ‘inefficient accumulators’ as compared to terrestrial plants. However, the present study shows that efficiency of accumulation differs by element, as *A. marina* efficiently accumulates Zn as indicated by the high concentration factor (Table 6). Although it was observed that Cd is least accumulated among the metals studied, its higher value of CF and high accumulation in pneumatophores clearly indicates that Cd behaves like Zn and is easily taken up by plants, in agreement with earlier studies (Pahlsson, 1989). However, Cd is less mobile than Zn, and moves slowly from roots to leaves; subsequent redistribution to the youngest leaves occurs only at trace levels (Page & Feller, 2005). Unlike Cd and Zn, the availability of Pb and Cu from the soil is limited. Initially Cu and Pb appears to be accumulated in the roots, and the concentrations in the leaves remain normal until the roots are saturated.

Although, the mangrove sediments are enriched in heavy metals due to contamination, yet the metals are not fully bioavailable to the plants for a number of reasons. According to Lacerda & Rezende, (1987), Di Toro, (1990) and Chiu & Chou, (1991) metals in mangrove sediments precipitate as sulfides which are stable under the anoxic conditions of these sediments and, therefore, unavailable to plants. Apart from sulfide precipitation, organic matter complexation may also decrease the availability of some trace elements to mangroves (Sthevan, 2011). Formation of redox barriers such as iron plaques on root surfaces may be particularly efficient in preventing trace metal uptake (Lacerda, 1997; Macchado & Lacerda, 2000). Moreover, bioavailability of metals depends not only on their own concentrations but on those of sediment components (e.g. oxides of iron or organic matter) to which they are adsorbed (Bryan & Langstan, 1992). Plants also remove heavy metals by surface adsorption or absorption plus incorporation into their own systems or store the metals in a bound form (Tam & Wong, 1997). Macfarlane & Burchett (2001) suggested it could be the result of an exclusion mechanism. Besides a number of factors like sediment pH, redox potential, and species of plants, changes in seasonal growth rates and age of plants also affect metal uptake (Bryan & Langstan 1992; Silva *et al*., 1990; Wigham *et al*., 1989). The present study explains the following order of sequence of accumulation of heavy metals in the mangrove ecosystem; sediments > pneumatophores > bark > leaves > flowers > twigs > water. This once again confirms that mangrove sediments act as sink for toxic pollutants and traps and filter them before they can enter sea water or accumulate in any other biological system (Tam & Wong, 2005, Yunus *et al*., 2011, Harbison, 1986, Silva *et al*, 1999, Tam & Wong, 2003, Sthevan *et al*., 2011).

Table 6. Concentration factors for different parts of the mangrove plant.

	Pb	Cd	Cu	Zn
Pneumatophores	0.24	0.73	0.22	0.809
Bark	0.16	0.493	0.29	0.715
Leaves	0.11	0.325	0.10	0.547
Flowers	0.002	0.28	0.03	0.161
Fruits	0.007	0.265	0.03	0.337
Twigs	0.008	0.173	0.09	0.35

Concentration factors = Concentration of plant parts/Concentration of sediments

Table 7. Contamination factor (CF) and pollution load index at different location of study area.

Location	Cd		Pb		Cu		Zn		PLI
	C_{metal}	CF	C_{metal}	CF	C_{metal}	CF	C_{metal}	CF	
World	0.3	–	25	–	45	–	100	–	–
LutBasti	1.59	5.3	51.86	2.07	69.02	1.53	100.15	1	2.02
Sanspit	1.47	4.9	66.40	2.65	48.02	1.06	119.40	1.19	2.01
Baba &Bhit	1.48	4.93	75.01	3.00	57.60	1.28	125.10	1.25	2.81
Chara Creek	1.34	4.46	53.85	2.15	46.55	1.03	115.70	1.15	1.83
Korangi Creek	1.34	4.46	65.10	2.60	48.10	1.06	105.00	1.05	1.87
Port Qasim	1.36	4.53	47.73	1.90	44.02	0.97	101.30	1.01	1.70
MianiHor	0.86	2.86	19.99	0.799	9.80	0.21	38.6	0.38	0.65

In order to understand the level of trace metal contamination, the contamination factor (CF) was calculated. While computing the CF of sediments of the study region, world average concentrations of these elements reported by different sources were taken as the background values. However, the pollution level of trace metals was calculated by a simple method based on the Pollution Load Index (PLI) (Tomlinson *et al.,* 1980; Ray *et al.,* 2006). The equations for CF and PLI are:

$$CF = C_{metal}/C_{background}$$
$$PLI = \sqrt[n]{CF_1 x CF_2 x CF_3 x \ldots . CF_n}$$

where CF= Contamination Factor, n= number of metals, C_{metal}= metal concentration in polluted sediments, $C_{background}$= background value of that metal

The study results show that the contamination factor (CF) and pollution load index (PLI) values of Pb, Cd, Cu, Zn (Table 7) in the study area are greater than unity due to industrial and other anthropogenic inputs. Conversely, the CF and PLI values are lower (<1) at Miani Hor, indicates that the mangrove area of Miani Hor is much less polluted. Despite low PLI, the CF values for Cd and Pb are much higher than expected for uncontaminated sites, indicating anthropogenic inputs that are still less severe than observed in the Indus Delta.

It may be concluded that both at abiotic (sediments) and biotic levels (mangrove plant) heavy metals are efficiently immobilized in mangrove habitats which, therefore serve as a biogeochemical sink or a biofilter precluding their entrance into the adjacent coastal waters. However it is a concern that the pollution level increasing day by day, and attention should be given to the fast development of industries and habitation in the area, which may lead to a situation beyond control. Mangrove plants, especially *A. marina*, are less vulnerable to pollution in a general sense. Yet many of the organisms which live in or depend on a mangrove system are highly vulnerable to increasing pollutant levels. Crustaceans, an important member of the mangrove food chain, accumulate heavy metals which affect both their long term reproductive capacity and their quality for human consumption. Hence, mangrove and related ecosystem of Indus Delta, along with the local population are in great danger due to continuous increase of harmful toxic pollutants.Therefore, there is a dire need that government and non- government organizations and researchers, become alert and start some appropriate environmental monitoring and assessment programs to understand and to keep constant check on heavy metals and other toxic pollutants in the aquatic environment as a whole and specially in the vulnerable mangrove and related ecosystems.

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(Received for publication 8 January 2013)