

AVICENNIA MARINA AND ITS SEDIMENTS: A POTENTIAL INDICATORS OF HEAVY METAL POLLUTION

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ABSTRACT: An ecological survey was carried out to determine the level of heavy metals in the mangrove flora and sediment along the Korangi creek (KC) and Sandspit back waters (SP) of the Karachi coast. The heavy metals included in this study are Fe, Mn, Zn, Pb, Cr, Co and Ni. The metal concentration was found to be higher in mangrove sediment than flora. Fe and Mn concentration were predominant at both the sampling sites whereas Co concentration was least. The study reveals the less contaminated area of Sandpit back water than of Korangi creek.

KEY WORDS: Mangrove, Sediment, Heavy metals, Karachi coast

INTRODUCTION

Marine ecosystem is an essential component of the planet earth. Therefore, the marine environment plays a vital role in nation's economy by the virtue of its resources, productive habitats and rich biodiversity (Harbison, 1986). Over 60% of the global population is estimated to live along the coast. Consequently, the coastal areas of the world are given more importance in recent years owing to increasing human population, urbanization, industrialization, tourism and acceleration in the development activities. Heavy metals exist in surface water as colloidal, particulate and dissolved phases. Mangroves are woody plants that grow at the interface between land and sea in tropical and sub-tropical latitudes where they exist in conditions of high salinity. Its forest is one of the most important resources in the world as it serves as biological filters, help coastal communities by reducing coastal erosion, flooding, storm surge (Ewel *et al.*, 1998). Changes in mangroves have been proposed as a means to monitor change in coastal environment (Duke, 1992).

Sediments metal associations occur primarily through two different phenomena, adsorption processes and complexation by organic matter (McBride, 1994). Grain size distribution is one of the most important characteristics of sediment. It is the fundamental property of sediment particles, affecting their entrainment, transport and deposition. Therefore, grain size is a dominant controlling factor in sediment geochemistry (Axtmann, 1991).

There are more than 6000 small and large scale industrial units in the Karachi coast, all of which discharge untreated effluents directly or indirectly into the Indus Delta (Saleem and Kazi(1998); Ashraf *et al* 1998). Korangi creek receives large-scale discharge of untreated domestic and industrial effluents from Korangi, Landhi and Karachi Export Processing Zone. Approximately 2500 industrial units are working in Korangi Industrial area, including more than 170 tanneries disposing their untreated waste in the creek area. It was estimated that at least 300 million gallons of untreated industrial wastes flow into

the sea everyday through the Malir and Lyari rivers (Kishe and Machiwa 2003).

MATERIALS AND METHODS

Sampling:

The ecological survey was carried out for the sampling of mangrove *Avicennia marina* (Grey mangrove) and its sediment during the period of February to March 2009 from two sampling locations of Korangi creek (KC) 24.7803° N, 67.1030° and Sandspit backwaters (SP) 24.8405° N, 66.9098° E which were further subdivided into four sub-sites as shown in Fig 1.

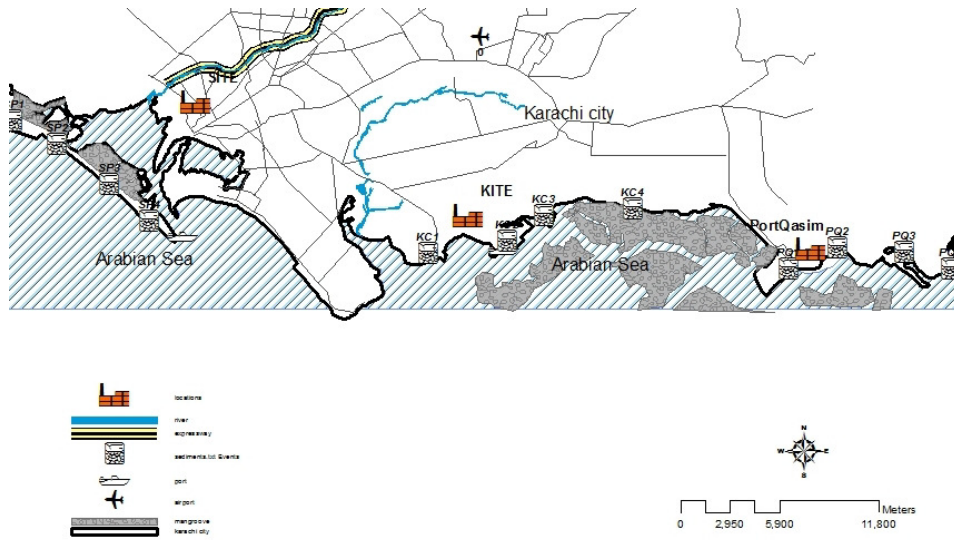


Fig 1. Map showing sampling sites of Karachi coast-Pakistan.

Mangrove whole twig samples were collected from each site and washed with distilled water to remove any adhering dust particles. The samples were oven dried at 90° C till constant weight, then grinding and finally stored in plastic bottles. Sediments samples were also collected from each site by digging 15 cm using PVC corer and collected in plastic bottles and then oven dried at 110° C, then grinded by using pistol mortar and finally preserved in tightly stored plastic bottles. Sediments from backwaters and sea fronts were also collected in the same manner as discussed earlier.

Digestion:

About 2 g mangrove and sediment samples were taken and add 10 mL HNO₃ (60%) and 10 mL HClO₄ (65%) were added into the samples and heated on hotplate at 90° C until the frothing ceases. Digested samples were filtered using Whatmann 42 filter paper and finally the solution was made upto 100 mL using deionized water for further chemical analysis using AA 700 Perkin Elmer Atomic absorption spectrometry.

RESULTS AND DISCUSSION

The present study represents some salient contributors that influence the ecology of coastal areas. The nature of these contributions depends upon the type and concentration of the metals involved. Present results demonstrate appreciable variability in the concentration of metals within the same locality of Korangi creek (KC) and Sandspit (SP).

The overall pattern shows that the concentration of metals is lower in mangrove flora in comparison to its sediments as shown in Tables 1-2. The low availability of metals for mangrove may be due to the oxygen exuded by underground roots forming iron oxide with the iron and thus adheres to the root surfaces and prevent trace metals from entering the root cells (Harbison, 1986). In addition to that high content of oil in sediment also adheres to the root surface and may become the cause of lower metal uptake. The other reason is that the mangrove swamp contains high concentration of sulfur that has tendency to form insoluble heavy metal compounds and get fixed in the sediment (Waldichuk, 1985).

The highest concentration of iron was observed among all the metals under study at the sampling sites. Higher concentration of iron is due to several reasons as it is the part of mineral fraction of soil which is usually found in the form of hematite (Fe_2O_3) and magnetite (Fe_3O_4). Secondly the precipitation of iron as iron sulfide is very common in mangrove sediments (Berner, 1984). The concentration of iron is higher in Korangi creek as compared to Sandspit may be due to the pollution from Pakistan Steel mill where iron ores are used in appreciable amount and other major industrial units are present in the vicinity of the area. The mean concentration of Cr was found to be in mangrove of Korangi creek as 13.352 mg/Kg and in sediment as 34.857 mg/Kg. All the sewage sludge and effluents produced especially from the tanneries and other industries directly enter to the Korangi creek. Tanneries use extensive chromium compounds such as chromic acid, chromium sulfate and potassium dichromate during the process of corrosion and chrome tanning. The effluents of these tanneries and industries are directly discarded into Malir River, which ultimately falls into the Korangi creek. Cr^{+3} is readily substituted in Fe^{+3} mineral structure and sometime may be co-precipitated with it (McBride, 1994). Therefore, the higher concentration of iron represents the higher amount of chromium. The results revealed that mangrove and sediments of Korangi creek have more lead concentration as compared to Sandspit mangrove 8.928 and sediment 28.804 mg/Kg. Pb concentration is mainly because of Pakistan Steel mill and dyes/paint industries in Korangi creek (Tables 1 and 2). Their drainage effluent is the contributors to the lead pollution. The other source of the metals is the discharge of domestic wastes which contribute much more concentration. The mean Ni concentration in mangrove was found to be 18.331 mg/Kg in Korangi creek and 12.087 mg/Kg in Sandpit and in sediment it was found to be 44.682 mg/Kg in mangrove and 59.058 mg/Kg in Korangi creek, as Ni is used in large amounts in ghee industries as a catalyst during the process of hydrogenation. In Korangi creek due to sludge's generated by sewage treatment plants and stainless steel, an alloy of iron and chromium may contain up to 35% Ni (Doull *et al.*; 1986).

Table 1. Concentration of heavy metals in mangrove Flora (mg/Kg \pm st.dev).

Site	Fe	Co	Zn	Mn	Ni	Cr	Pb
SP1	533.090 \pm 9.391	0.501 \pm 0.012	22.952 \pm 1.542	49.815 \pm 2.345	14.312 \pm 1.714	9.245 \pm 2.114	16.478 \pm 1.378
SP2	431.291 \pm 11.712	0.642 \pm 0.011	23.714 \pm 1.458	47.458 \pm 4.125	9.254 \pm 0.987	8.965 \pm 1.254	15.988 \pm 1.548
SP3	655.943 \pm 3.291	0.824 \pm 0.021	24.315 \pm 3.487	46.687 \pm 3.547	13.547 \pm 2.547	7.845 \pm 3.245	14.569 \pm 2.147
SP4	519.444 \pm 4.255	0.875 \pm 0.071	24.897 \pm 4.587	44.025 \pm 0.987	11.235 \pm 1.354	9.658 \pm 2.547	16.987 \pm 1.154
MEAN	534.942	0.71	23.969	46.996	12.087	8.928	16.005
KC1	836.086 \pm 3.05	1.368 \pm 0.098	38.105 \pm 4.715	97.487 \pm 2.475	19.547 \pm 0.987	11.387 \pm 1.547	24.365 \pm 2.547
KC2	780.745 \pm 4.12	1.456 \pm 0.024	29.874 \pm 2.175	82.457 \pm 2.587	18.245 \pm 1.548	13.965 \pm 2.417	22.458 \pm 1.564
KC3	705.028 \pm 3.41	1.354 \pm 0.098	27.935 \pm 4.874	87.569 \pm 4.569	17.548 \pm 1.254	15.487 \pm 1.879	25.789 \pm 1.254
KC4	711.313 \pm 4.514	1.445 \pm 0.054	36.215 \pm 5.214	97.145 \pm 3.257	17.987 \pm 1.554	12.569 \pm 2.998	29.875 \pm 3.254
MEAN	758.293	1.405	33.032	91.164	18.331	13.352	25.621

Table 2. Concentration of heavy metals in mangrove sediment (mg/Kg \pm st.dev).

Site	Fe	Co	Zn	Mn	Ni	Cr	Pb
SP1	833.090 \pm 9.391	5.501 \pm 1.012	80.295 \pm 1.542	449.815 \pm 6.345	44.312 \pm 1.714	29.245 \pm 2.114	46.478 \pm 1.378
SP2	851.191 \pm 7.712	5.642 \pm 1.721	83.714 \pm 2.468	457.338 \pm 5.215	49.541 \pm 1.997	28.969 \pm 2.244	45.989 \pm 1.145
SP3	795.933 \pm 7.291	6.841 \pm 1.322	84.315 \pm 4.467	466.677 \pm 3.574	43.547 \pm 2.743	27.385 \pm 3.215	44.569 \pm 2.348
SP4	729.344 \pm 4.555	5.858 \pm 2.071	81.827 \pm 3.881	444.120 \pm 2.772	41.331 \pm 2.334	29.618 \pm 1.542	46.787 \pm 1.154
MEAN	802.389	5.96	82.537	454.487	44.682	28.804	45.955
KC1	1236.08i \pm 6.005	9.338 \pm 1.098	98.105 \pm 3.735	697.482 \pm 2.172	59.527 \pm 0.992	31.321 \pm 1.432	64.125 \pm 2.546
KC2	1061.432 \pm 8.141	11.556 \pm 1.064	99.743 \pm 2.171	782.457 \pm 5.282	68.223 \pm 1.221	33.324 \pm 2.423	62.543 \pm 2.064
KC3	1105.017 \pm 6.547	11.854 \pm 2.098	87.350 \pm 2.821	727.663 \pm 4.562	57.251 \pm 2.234	35.327 \pm 3.675	55.789 \pm 3.432
KC4	1117.119 \pm 5.544	10.445 \pm 1.454	96.225 \pm 5.342	797.141 \pm 3.251	51.231 \pm 1.439	39.459 \pm 2.432	69.175 \pm 3.254
MEAN	1129.912	10.798	95.355	751.185	59.058	34.857	62.908

Mn is one of the more abundant elements in the earth's crust and is distributed naturally in soils, sediments, rocks, water and biological materials. The present study reveals higher concentration of Mn in Korangi creek mangrove and sediment than Sandspit (Tables 1-2). This is due to the industries related to dry cell batteries, matches, porcelain and glass binding materials situated in Korangi creek and Landhi industrial areas. However, the major source of Mn in Sandspit is due to the human activities and industrial effluents through Lyari River during low tides. The concentration of Zn was found to be lower in mangroves and higher in sediment.

Zinc occurs as sulphide material in rocks and it has high tendency to adsorb and co-precipitate as oxide of iron and manganese (McBride, 1994). The higher concentration of Zn in Korangi creek may be due to higher concentration of iron and manganese as (Tables 1-2). The waste streams from zinc manufacturing chemical industries such as pharmaceuticals, pesticides and from urban discharge causes the significant amount in Korangi creek. Zinc coating is also used as protective agent of iron in Steel mill. The results show that besides all metals cobalt concentration is much lower as at higher pH, its solubility decreases due to formation of cobalt hydroxide as (Tables 1-2).

Pais and Jones (2000) reported that Cr concentrations higher than 10mg kg^{-1} had a phytotoxic effect on plants. In the present study mean Cr concentrations were 60mg kg^{-1} in the sediment, 44mg kg^{-1} in the root, and 21mg kg^{-1} in the leaf (Tables 1 and 2).

CONCLUSION

A strong, positive relationship between metals in sediments and mangroves suggests potential use of these tissues as a bio-indicator of estuarine contamination and these metals are entering into the biotic environment. Thus the above factors, chemical pollution, particularly accumulation and bio-transformation of toxic metals could be a significant factor for reduction of mangrove forest at the two study sites. The study further highlights a positive role of mangroves in sequestering metals from sediments and the water column and thus protect the estuarine environments from pollution. Therefore, the government and concerned organizations should give priority towards protection and conservation of mangrove ecosystem for best utilization of this natural resource for the future generations.

REFERENCES

- Axtmann, E.V. and S.N. Luoma. 1991. Large-scale distribution of metal contamination in the fine-grained sediments of the Clark Fork River. *Appl. Geochemist.* 6: 75-88.
- Ashraf, M., M. Jaffar and K. Masud. 1998. Selected trace metal concentration in seven fish species from the Arabian Sea. Pakistan. *J. Chem. Soc. Pak.* 15: 1-6.
- Berner, R.A. 1984. Sedimentary pyrite formation: An update. *Geochim. Cosmochim. Acta.* 48: 605-615.
- Duke, N.C. 1992.. Mangrove floristics and biography In: Robertson, A.I. and Alongi, D.M. (Eds) Tropical mangrove ecosystems. Coastal and estuaries studies No.41. American Geophysical Union.
- Doull, J., C.D. Klassen and M.D. Amdur (Eds).. 1986. Casarett and Doull's Toxicology

3rd Edition NY, Macmillan Co., Inc., p 610.

Ewel, K.C., R.R. Twilley and J.E. Ong. 1998. Different kinds of mangrove forests provide different goods and services. *Global Ecology and Biogeography Letters*. 7: 83-94.

Harbison. 1986. Mangrove mud- A sink and source for trace metals. *Mar. Poll. Bull.* 17: 246-250.

Kishe, M.A and J.F. Machiwa. 2003. Distribution of heavy metals in sediment of Mwanza Gulf of Lake Victoria, Tanzania. *Environmental International* 28: 619-625.

McBride, M.M., 1994. Environmental chemistry of soil. Oxford University Press. NewYork. NY, USA.

Pais, I. and J.B.. Jones. 2000. The Handbook of Trace Elements. St. Luice Press, Florida.

Saleem, M. and G.H. Kazi. 1998. Concentration and distribution of heavy metals in Karachi shore and offshore sediment. *Pak. J. Mar. Sci.* 7: 67-71.

Waldichuk, M. 1985. Biological availability of metals to marine organisms. *Mar. Poll. Bull.* 16: 7-11.