Assessment of Chromium in the Water and Sediments of Indus Delta Mangroves

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Summary: Chromium concentration was assessed in water and sediments of different habitats of Indus Delta mangroves. It is observed that highest concentration of chromium was 0.291 ppb in water and in sediments 72.20 ppm at Sandspit, whereas lowest concentration was 0.19 ppb in water and in sediments 18 ppm at Miani Hor, which is considered as comparatively pristine area. The higher level of chromium is considered due to different anthropogenic activities including industrialization and urbanization. Mangrove sediments accumulate greater amounts of heavy metals like chromium than water or any other components of marine ecosystem and therefore, termed as biogeochemical sink. This characteristic of mangrove sediments is due to the high concentration of organic matter and sulphides under permanently reduced conditions.

Introduction

Mangroves grow extensively all along the 240 km southeastern coastline of Pakistan, comprising the Indus Delta [1] which is a typical fan shaped belt. The Indus Delta mangrove forests and ecosystem (67° 9 N; 26° 25E) are located on eastern side of Pakistan including the entire coast of the province Sindh. It is occupied by an area of 260,000 ha [2] of salt tolerant mangroves [3] and therefore, rates as the fifth or sixth largest [4] and in fact the largest arid climate mangrove forest area in the world.

Indus delta mangroves are facing number of threats among which heavy metals pollution is one of them. This has emerges as a serious issue during last two decades, especially in coastal areas close to industrial and agricultural activities [5]. In this study chromium is selected because of its importance, such as it is used in the electroplating and alloy industries and its compounds are used in some of the common textile dyes. Chromium oxides, specifically Cr_2O_6, are used as an effective oxidant, and softener, particularly in tannery. It is also mainly used in paint and plastic industries (Table-1). Besides these usefulness of chromium in different industries, its slightly elevated levels in ecosystem may cause the sublethal effects in living organisms. In case of plants, metals like chromium toxicity generally results in chlorosis and stunting and have a direct bearing on various physiological and biochemical process including reduction of growth photosynthesis, chlorophyll content, inhibition of enzyme activities and degeneration of chloroplasts and mitochondria [6].

Table-1: Concentration (ppm) of Cr in the effluents discharged from different sources

Source	Concentration
Site Nallahs	1.00 ppm
Karachi Tannery	0.20- 8.00 ppm
Pharmaceuticals	546 ppm
Refinery	360 ppm
Tannery	1652 ppm
Textile	593 ppm
Beverage	400 ppm

Results and Discussion

Observations on temperature and salinity of seawater and texture, water holding capacity and organic content of soil are shown in Tables-2 and 3. The temperature values are typical of tropical waters whereas soil/ sediment analysis showed typical characteristic of mangrove soil. The silt and clay fraction is high and the organic matter content is greater than 5 % of the dry wt which categorizes it as organic soil. [7] also found larger fractions of silt and clay and [8] recorded similar organic matter content like the present study. The water holding capacity (W. H. C.) is consequently high. All this speaks for greater accumulation and adsorption of heavy metals in the sediments [9].

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Table-2: Mean values of Water temp. and salinity in mangrove habitat of Karachi

Locality	Water Temp.°C	Salinity ‰
Sandspit	23.08	39.33
Port Qasim	30.75	37.5
Lut Basti	34.34	38.5
Korangi Creek	34.0	40.0
Karachi Horbour	27.78	35
Chara Creek	23.75	38.5

Table-3: Characteristics of sediments of different mangrove habitats

Lacality	Organic Content (%)	*MWHC	Texture	Silt & Clay (%)
Sandspit	8.55	41.5	Clay Loam	57.52
Port-Qasim	7.88	39.41	Clay Loam	50.8
Korangi Creek	6.2	39.82	Clay Loam	18.07
Lut Basti	8.16	39.66	Clay Loam	53.2

* Maximum water holding capacity

Salinity of seawater is generally higher and around 40 % as compared to salinity values of 36 % on the shelf [10]. This may be a result of a drastic cut in the discharge of Indus river water in the recent years to meet the demand of increasing agriculture and industrialization in the country [11]. But, occasional lower values recorded in the area indicate periodic discharge of runoff from the land.

Results shows that highest accumulation of Cr in water was 0.291 ppb ± 0.05 at Sandspit followed by Port Qasim (0.115 ppb ± 0.014) and the lowest value was observed in Miani Hor (0.019 ppb) (Table-4) which is considered as pristine area. The range in concentration of chromium in sea water of different mangrove sites was 0.02-0.48 ppb (Table-2) which is higher than the values recorded in the pristine area of Miani Hor. Lower concentration of Cr is also recorded in offshore clear waters of Pakistan and India [12,13] . Higher values of Cr may be attributed to very high levels of industrial pollution present in the area, specially the effluents from a large number of tanneries and from the wastes originating from different industries (Table-1).

Table 4. Concentration (ppb) of Cr in water of different mangrove sites

Locality	Average conc. ± SE	Range
Sandspit	$0.291+0.05^{a}$	0.136 - 0.48
Port Qasim	0.115 ± 0.014^{b}	0.067 - 0.141
Korangi Creek	0.068 ± 0.006^{c}	0.055 - 0.080
Karachi Harbour	0.062 ± 0.019^{c}	0.030 - 0.157
Lut Basti	0.062 ± 0.010^{c}	0.020 - 0.096
Chara Creek	0.060 ± 0.010^{c}	0.047- 0.080
Miani Hor	0.019^{d}	-

Values given are mean of 5 samples, similar letters are not significantly ($p<0.05$) different from each other $LSD_{(0.05)} = 0.009$

A number of factors are known to affect concentration of heavy metals in seawater i.e. salinity, organic matter and oxides and hydroxides of Fe. In coastal regions these metals can be scavenged by coagulation, adsorption and incorporation into the particulate matter. The production and degradation of organic matter cause changes in water and particulate matter qualities which may affect these processes.

Chemically, Cr is found both as Cr (III) and Cr (IV) in seawater. Cr (IV) occurs as bioavailable form because Cr (III) is scavenged by the Fe oxides and organics [14, 15]. Cr exhibits a nutrient type geochemical behaviour in seawater, i.e. depletion of surface water and regeneration at lower depths. This geochemical distribution is influenced by the quantity and quality of suspended particulates and redox conditions of the seawater profile [16,17].

Mangrove sediments are typically anoxious with grey to black coloration and release a typical smell of hydrogen sulphide when disturbed [8]. They accumulate greater amounts of heavy metals than any other component of a marine ecosystem. Average chromium concentration in sediments was found to be 95.47 ppm with a range in values from 14.00 to 141.00 ppm (Table-5). Similar values were reported from Pakistan India, Kuwait, Maxico and UK estuaries [13, 18-21] whereas much lower values were observed from shelf of Pakistan [12].

Table-5: Concentration (ppm) of Cr in sediments of different mangrove sites

Locality	Average conc. ± SE	Range
Sandspit	72.20 ± 7.11^{a}	28.40 - 141.00
BabaBhit/Shamspir	60.50^{b}	
Chara Creek	57.55 ± 0.25^{c}	–
Korangi Creek	52.00 ± 0.50^{d}	–
Port Qasim	38.97 ± 7.12^{e}	20.10 - 54.20
Lut Basti	25.16 ± 0.58^{f}	14.00 - 34.00
Miani Hor	18.00^{g}	–

Values given are mean of 5 samples, similar letters are not significantly ($p<0.05$) different from each other $LSD_{(0.05)} = 0.83$

As the major sources of chromium in the sea are the industrial effluents [22] its concentrations are, therefore, expected to vary widely in the coastal marine areas as compared with the open sea. It is reported that the values ranging between 1–1317 ppm in world over with about 20 ppm as background concentration in uncontaminated marine sediments [17].

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 [17]. This may be because the sediments accumulate them with time and are not mobile like water. The effluents contaminate the seawater first and then other parts of the ecosystem, therefore, any change in the quantity or quality is reflected in seawater and not in sediments. They are also diluted with distance from the source of the pollution.

Sediments of Mangroves are termed as biogeochemical sink for heavy metals beacuse they accumulate very high concentration of heavy metals and that is due to different factors like presence of high concentrations of organic matter and sulphides under permanently reducing conditions [8, 21-25]. At the same time it also indicates that, these sediments could be the probable source of toxic elements for the related biological lives, therefore needs regular check and balance.

Experimental

The area of study is highly polluted with mostly untreated effluents from more than 6000 industrial units located in two major industrial sites S.I.T.E. and L.I.T.E. (Table-1), which drain their effluents through the Lyari and Malir rivers. As much as 2000 tons of BOD of industrial and domestic wastes are dumped mostly untreated into the shores of Karachi. Additional organic effluents are contributed to the area by the Landhi cattle colony, which discharges the wastes of 85,000 buffaloes into Korangi creek. Levels of heavy metals and other contaminants are likewise high [26-28] but very rare data is available regarding the mangrove habitat. Therefore, present study was planed to find out the status of chromium pollution in the sediment and water of mangrove habitat of Indus Delta.

Samples were collected during the period of Dec. 1997-Dec.1998. The different localities selected in the study were Backwater, Sandspit, Baba Bhit/ Shamspir, Karachi harbor, Korangi creek, Port Qasim, Lut Basti and Chara creek seperated from each other by few kilometers [29, 30]. Sampling was also done from Miani Hor a distant site some 100 km away, and is free from pollution. Water temperatures and salinity were in the field by a thermometer and a refrectometer respectively.

Samples were brought to laboratory for further processing. Soil texture was determined both by physical touch method and also through wet sieving of different mesh sizes [31]. Water holding capacity [32] and organic matter content [33] were also determined.

Sediment samples were wet digestion through aqua regia, whereas water samples were processed through solvent extraction method. Sampling, processing and analyzing methods have already been discussed in detail [29]. The samples were analyzed in AAS, Model Perkin Elmer, 3300, using a Graphite Furnace (Model, HGA,600) with an autosampler (Model, AS 60). Statistically the data were subjected to analysis of variance (ANOVA) followed by Duncans Multiple Range Test [34].

References

1. S. M. Saifullah, Mangrove Ecosystem of Pakistan In: The third research on mangroves in Middle East, Japan Cooperation Centre for Middle East, Publication No. 137, Tokyo, Japan (1982)
2. M. I. Mirza, M. Z. Hasan, and S. Akhtar, J. Ali, In: Mangroves of Pakistan: Proceedings of national workshop on mangroves, Karachi. Pakistan Agricultural Research Council Islamabad, Pakistan, pp. 19 (1983),
3. P. J. Harrison, S.C. Snedaker, S. I. Ahmed, and F. Azam, *An overview Tropical Ecology*, **35**, 155 (1995)
4. S. C. Snedaker, In: (eds: B.U. Hag and J.D. Millman) Marine Geology and Oceanography of Arabian Sea and Coastal Pakistan. Van Nastrand Reinhold Co., New York, USA pp. 255 (1984).
5. R. Raza, S. A. Sayed, R. Siddiqui and S. Naz, *Jour. Chem. Soc. Pak.*, **25** (4), (2003).
6. G. N. Reddy and M. N. V. Prasad, *A. Review. Environ. Exp. Bot.*, **30**, 251 (1990).
7. N. F.Y. Tam and Y. S. Wong,. *Hydrobiologia*, **352**, 67 (1997).
8. L. D. Lacerda, J. J. Abrao, *Rev. Brasil. Bot.*, **7**, 49 (1984).
9. L. D. Lacerda, In: (eds: B. Kjerfive, L. D. Lacerda and E. S. Drop,) Mangrove Ecosystem studies in Latin America and Africa 17, UNESCO, Paris. (1997).
10. S. M. Saifullah, , In: (Ed: Taylor/Scliger). Toxic dinoflagellates blooms., Elsevier North Holland Inc. 203 (1979)
11. S. M. Saifullah,. In: (eds :B. U. Haq, S. M. Haq, J. M. Stel), Coastal Zone Management Imperative for Maritime Developing Nations,

Kullenberg pp. 336, Kluwer Acad. publ., The Netherlands. (1997)

12. J. Tariq, M. Jaffer, and M. Moazzam, *Mar. Pollut. Bull.*, **26**, 644 (1993).
13. B. Patel, V. S. Bangera and M. C. Balani, *Mar. Pollut. Bull.*, **16**, 22 (1985).
14. R. Rosental, G. A. Eagle and M. J. Orren, *Estu. Coast Shelf Sci.*, **22**, 303 (1986).
15. M. Amedurur, D. Elder, and P. H. Santschi, In: (eds: C. S. Wong, E. Boyle and K. Bruland,) Trace Metals in Seawater. Plenum Press New York, pp. 537 (1983).
16. J. W. Murray, B. Spell and B. Paul, In (eds: Wong, C.S. *et. al.*), Trace Metals in Seawater. Plenum Press, New York, pp. 643 (1983).
17. M. Sadiq, Toxic Metal Chemistry in Marine Environments, Mercel Dekker, Inc. New York, USA; p 390 (1992).
18. M. S. Saleem and G. H. Kazi In: (edt. M.F. Thompson, N.M. Tirmizi) The Arabian Sea - Living Marine Resources and the Environment, American Institute of Biological Science, Lahore, p 659 (1998).
19. V. C. Anderlini, O. S. Muhammad, M. A. Zerba, S. W. Fowler and P. Miramand, *Bull. Environ. Contam. Toxicol.;* **28**: 75 (1982).
20. F. Paez-Osuna, A. V. Botello and S. Villanueva, *Mar. Pollut.*, **17**, 516 (1986).
21. G.W. Bryan, W. J. Langston, *Environ. Pollut.*, **76**, 89 (1992).
22. J. O. Nriagu and E. Niebour, Wiley Series in Advances in Environmental Science & Technology, **20**, John Wiley & Sons, New York (1980).
23. L. D. Lacerda, C. E. V. Carvallo, K. F. Tainzaki, A. R. C. Ovallil and C. E. Rezende, *Biotropica*, **25**, 252 (1993)
24. A. P. Mackey, M. Hodgkinson, *Environmental Pollution,* **90**, 181 (1995).
25. N. F. Y. Tam and Y. S. Wong, *Environ. Pollut.*, **911**, 283 (1996)
26. IUCN, Socio- Economic and Public Health Survey. Korangi/Phitti Creek, Karachi, Paksitan. Preliminary Report, International Union for the Conservation of Nature, Switzerland (1987).
27. I. Ali and S. Jilani In: (eds: M. F. Thampson and N. M. Tirmizi, The Arabian Sea: living Marine Research and the Environment. Oxford/Indian Book House, pp. 653 (1995).
28. P. J. Meynell, In: (eds: M. F. Thompson and N. M. Tirmizi). The Arabian Sea living marine resources of the environment. Oxford Indian Book House, New Delhi, Bombay and Calcutta, India. Pp. 371 (1995).
29. S. M. Saifullah, S. H. Khan and S. Ismail, *Marine Pollution Bulletin*, **44** (6), 483(2002a)
30. S. M. Saifullah, S. Ismail and S. H. Khan. In: (eds: R. Ahmed, K. Malik) Prospects for Saline Agriculture. Kluwer Acad. Press, The Netherlands, (2002b).
31. S. M. Saifullah, S. S. Shaukat, and S. Shams, *Aquatic Botany*, **47**, 329 (1994).
32. G.W. Cox, Laboratory manual of General Ecology, 3rd ed. W.C. Brown, Dubuque, I. A., p 232 (1976)
33. K.G. Boto, In: (eds: J. C. Snedekar, J. G. Snedekar) The mangrove Ecosystem Research Methods, UNESCO, Paris 114 (1984).
34. K. A. Gomez and A. A. Gomez, Statistical Procedures for Agriculture Research. 2nd ed. Wiley, New York, U.S.A., 680 p (1984)