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Assessment of Heavy Metals in Sediments of the River Ravi, Pakistan

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ABSTRACT

The extent of heavy metal contamination viz. cadmium (Cd), chromium (Cr), cobalt (Co) and copper (Cu) in the sediments of the river Ravi has been assessed. Sediment samples were taken from nineteen sampling stations. Metal concentrations in the sediments ranged from 0.99 to 3.17 for Cd, 4.60 to 57.40 for Cr, 2.22 to 18.53 for Co and 3.38 to 159.79 $\mu g\ g^{-1}$ for Cu on dry matter basis. The highest concentration of Cu was found in Taj Company nulla, while minimum concentration of Cd was observed at Lahore Siphon. The results show that the metal concentrations in the sediments decreased in the order: Cu > Cr > Cd > Co. These contaminated sediments, accumulated over the years in the river bed sediments could act as secondary source of pollution to the overlying water column in the river.

Key Words: Heavy metal pollution; Ravi river; Sediments

INTRODUCTION

Unfortunately, overpopulation, local soil erosion, inadequate water use management and intensive deforestation have caused major reductions in the river water quality. The alarming situation has aroused in the urban areas due to careless disposal of industrial waste and faulty drainage system that has badly affected the quality of the river water (Furtado *et al*., 1998; Ugochukwu, 2004; Chindah *et al*., 2004; Emongor *et al*., 2005). Major contributors to heavy metal water pollution are tanneries, brewery, textile, pottery, electroplating, metal finishing, mining, dyeing and printing industries, ceramic, photographic and pharmaceutical industries, scattered in the region (Azzaoui *et al*., 2002; Vutukuru, 2003).

The distribution of heavy metals in sediments can provide researchers with evidence of the anthropogenic impact on aquatic ecosystems and therefore aid in assessing the risks associated with discharged human waste. River bed sediments act as both carriers and source of contamination in an aquatic environment; not only play an important role in river water pollution but can also provide a record of river's pollution history (Tsai *et al*., 2003). By integrating the chemical, toxicological and ecological data, the impact of heavy metal pollution in Le An river in China was assessed by Wang and Tang (1998) and reported that water and sediment pollution has affected the aquatic ecosystem due to effluent discharges into the river. The metals contamination levels in the sediments were wide-ranging significant among river site sampling stations and three main effluent discharging tributaries. The sediments collected from tributaries showed significantly higher tendency towards metallic ion pollution in sediments than that of river system (Ubaidullah *et al*., 2004b). In sediments, mean metal level (Cu, Mn, Zn, Cr, Ni & Pb) were generally higher than the mean levels in water. This could be as a result of adsorption to sediment particles (Obasohan *et al*., 2007). Solubility levels of metals viz. Cu, Cd, Ni, Mn, Zn, Pb, Fe and Cr were higher in the rainy season than that of dry season due to enhanced desorption of metals from the sediments (Fufeyin, 1994).

To overcome the health problem, treatment of contaminated sediments may be as important as the treatment of sewage sluge. To do this, chemical and microbial methods have been reported by Ito *et al*. (2000) and Kitada *et al*. (2000). Heavy metal contamination in sediments of Shing Mun river, Hong Kong was reported by Sin *et al*. (2001). Highest concentrations of Cu, Pb, Zn and Cr were recorded in Fo Tan tributaries, while Al and Cd were found in the Shing Mun river. The present study was aimed to evaluate the pollution level of sediments contaminated with Cd, Cr, Co and Cu in sediment samples of the river Ravi (from Lahore Siphon to Baloki headworks) and its related tributaries.

MATERIALS AND METHODS

The stretch of river Ravi from Lahore Siphon to Baloki headworks (72 km long stretch) was surveyed exhaustively and ten sampling station along both right and left banks of the river *viz* Lahore Siphon Right bank (R B), Lahore Siphon Left bank (L B), Shahdera Bridge (R B),

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Shahdera Bridge (L B), Purani Bheni, Mohnalwal, Chakighera, Sunder, Baloki headworks (Up stream), Baloki headworks (Down stream) and nine effluent discharging tributaries *viz*. Mehmood Booti nulla, Shad Bagh nulla, Farrukhabad nulla, Munshi Hospital nulla, Taj Company nulla, Bakar Mandi nulla, Hudiara nulla, Degh Fall and Q B. Link Canal were selected. Sediment samples were taken from each site on fortnightly basis. Each sampling station was divided into three sub-sampling stations with in diameter of 100 m. Samples were collected with the help of steel pipe (2 inch diameter) pressed with pressure through the water column to obtain a sediment layer of about one foot. Sediment samples collected from three sub-sampling stations at each station were homogenized to obtain a composite sample. The sediment samples (4-5 g) were dried at 100°C for 48 h in the oven. The dried samples were passed through standard screen to remove large particles and 1 g sediment sample was transferred to 100 mL quartz tube and digested in concentrated HNO_3 and HCl (1:3 v/v) on a hot plate. The tubes were cooled and volumes prepared with double distilled water in volumetric flask. The digested samples were analyzed for Cd, Cr, Co and Cu according to APHA (1998) on Atomic Absorption Spectrophotometer (Perkin Elmer, AAnalyst-400).

Statistical analysis. Analysis of variance and DMR tests were applied to find-out statistical differences among various parameters (Steel *et al*., 1996).

RESULTS

There were highly significant variations among fortnights and sampling stations for the contaminations of Cd, Cr and Co although the mean Cu concentration did not vary significantly among the fortnights. The sampling stations showed highly significant ($p<0.001$) differences for the mean Cu toxicity levels of bed sediments collected during the study period over one year (Table I). The mean Cd concentrations in the river bed sediments fluctuated between a maximum value of 3.17 µg g^{-1} (Shahdera Bridge, L.B.) and a minimum mean value of 0.99µg g^{-1} at Lahore Siphon (L B). The sediments collected from Mohnalwal had the mean annual Cd concentration of 2.98 µg g^{-1} showing significant differences with the contamination levels of Chakighera and Sunder (Fig. 1). Among the tributaries, Shad Bagh nulla exhibited the mean annual Cd contamination of 2.48 µg g^{-1} followed by that of 2.24, 2.24 and 2.16 µg g^{-1} recorded at Hudiara, Munshi Hospital and Mehmood Booti nullas, respectively. Degh Fall had the mean lowest Cd contamination (1.53 µg g^{-1}) in its sediments. Other tributaries showed variable sediment toxicities (Fig. 2).

River bed sediments collected from Chakighera were the most contaminated with Cr having the mean annual contamination of 40.34 µg g^{-1}, while it was minimum (4.60 µg g^{-1}) at Lahore siphon (L B). Among the tributaries, Hudiara nulla appeared the site with the highest Cr contaminated sediments (57.40 µg g^{-1}), followed by the contamination levels recorded at Farrukhabad nulla and Mehmood Booti nulla. The lowest mean annual Cr concentration in the sediments was recorded at Q B. Link Canal (16.04 µg g^{-1}). The sediments collected from Shahdera Bridge (L B) were highly contaminated with Co (18.53 µg g^{-1}), followed by the contamination level recorded at Mohnalwal (16.82 µg g^{-1}) with non-significant difference. Lahore Siphon contained the least toxic sediments. The sediments collected from this sampling station had the mean lowest Co concentrations of 2.22and 3.05 µg g^{-1} at right and left banks, respectively. Among the tributaries, Farrukhabad nulla had the mean highest Co contamination level of 17.23 µg g^{-1} in their sediments while Q B. Link Canal showed the mean lowest contamination level of 6.05 µg g^{-1} (Table I).

Among the river sites, Shahdera Bridge (L B) had the highly Cu contaminated sediments, while it was the lowest at Lahore Siphon (R B) with the mean annual values of 46.28 and 3.38 µ gg^{-1}, respectively. The highest Cu contamination in sediments was recorded at Shahdera Bridge, followed by the contamination levels of 41.35 and 35.83 µg g^{-1} recorded at Sunder and Mohnalwal, respectively. Among the tributaries, Taj Company nulla exhibited the mean annual copper contamination level of 159.79 µg g^{-1} in their sediments, while it was the lowest at Q B. Link Canal with the concentration of 21.90 µg g^{-1}. The difference between Taj Company nulla and Q B. Link Canal, for the toxicity levels of their sediments, appeared statistically significant.

DISCUSSION

The main sources of pollution in the river Ravi stretching from Lahore Siphon to Baloki headworks are urban, agricultural and industrial wastewaters discharged from various industries like electroplating workshops, steel factories, paper and pulp industries, medicine and scientific laboratories, as well as surface runoff and municipal sewage. The present study revealed that Mehmood Booti, Shad Bagh, Farrukhabad, Munshi Hospital, Taj Company, Bakkar Mendi and Hudiar nullas, added substantially towards deterioration of river water and bed sediments. However, maximum metal contaminated water was discharged by upstream tributaries like Farrukhabad, Munshi Hospital, Taj Company, Bakkar Mandi and Hudiara nullas and Degh Fall. Wang and Tang (1998) concluded that water and sediment pollution has affected the aquatic ecosystem due to toxicity of effluent discharged into the Le An river in China.

Sediment pollution associated with the moderate biological and ecological deterioration prevailed downstream of the river. Since water flow rate in the main river stretch was quite slow and most of the metals coming from effluent discharging tributaries deposited immediately after entering the main river channel. Nonetheless, lowest levels of metal in the sediments were recorded in Lahore

Table I. Analysis of variance on metal concentrations in the river and tributary sediments during the study period

S.O.V.	D.F.	Mean squares			
		Cd	Cr	Co	Cu
Fortnights	23	1.611**	841.390**	38.654**	683.861^{NS}
Sampling Stations	18	6.960**	5142.728**	452.717**	45195.676**
Error	414	0.515	143.220	16.593	490.616

S.E. for:

Fortnights =	0.1646	2.7455	0.9345	5.0815
Sampling Stations=	0.1465	2.4428	0.8315	4.5213

COMPARISON OF MEANS (±SD)

Sampling Stations	Cd (µg g^{-1})	Cr (µg g^{-1})	Co (µg g^{-1})	Cu (µg g^{-1})
River sites				
Lahore Siphon (R B.)	1.05±0.66g	6.47± 2.42k	2.22±1.12i	3.38± 1.37j
Lahore Siphon (L B.)	0.99±0.53g	4.60± 1.56k	3.05±1.87i	3.54± 1.41j
Shahdera Bridge (R B.)	2.16±0.78 bcde	30.43± 6.01i	9.34±2.72g	20.22± 8.61i
Shahdera Bridge (L B.)	3.17±0.97a	39.36±11.65efgh	18.53±9.70a	46.28±20.83f
Purani Bheni	2.14±0.58bcde	34.88± 7.57ghi	14.14±5.28cd	23.83± 6.01hi
Mohlanwal	2.98±0.93a	35.56±13.57ghi	16.82±5.91ab	35.83±20.09fgh
Chakighera	2.29±0.71bc	40.34±10.54defg	10.53±2.95fg	29.65±11.40ghi
Sunder	2.46±0.57b	32.68± 9.43hi	11.19±3.04efg	41.35±24.80fg
Baloki headworks (Up stream)	1.84±0.72def	37.12±11.11fghi	10.01±3.88fg	31.48±11.02ghi
Baloki headworks (Down stream)	1.79±0.59ef	37.58±13.06fgh	10.38±3.36fg	31.06±12.24ghi
Tributaries				
Mehmood Booti nulla	2.16±0.91bcde	53.93±20.13ab	15.61±4.09bc	64.09±17.76e
Shad Bagh nulla	2.48±0.87b	45.31±14.12cde	13.48±3.56cde	87.67±24.92d
Farrukhabad nulla	1.84±0.73def	55.42±17.53a	17.23±3.32ab	106.26±45.06c
Munshi Hospital nulla	2.24±0.70bcd	46.65±21.23cd	11.54±3.19efg	129.79±33.53b
Taj Company nulla	1.90±0.71cdef	47.56±13.20bc	12.86±4.88de	159.79±51.36a
Bakar Mandi nulla	2.03±1.05cde	42.66±10.87cdef	11.77±3.42ef	86.31±18.93d
Hudiara nulla	2.24±0.92bcd	57.40±21.18a	13.20±4.65de	83.53±17.81d
Degh Fall	1.53±0.46f	38.56±19.73efgh	11.75±3.48ef	27.27± 9.78hi
Q B. Link Canal	1.94±0.67cdef	16.04± 3.31j	6.05±1.99h	21.90± 6.78i
Annual mean				
River sites	2.09±0.71a	29.90±13.18b	10.62±5.20 b	26.66±14.38b
Tributaries	2.04±0.28b	44.84±12.43a	12.61±3.10 a	85.18±44.46a

(Mean values with similar letters in a single column are statistically similar at $p<0.05$); ** = $p<0.001$

Fig. 1. Pattern of metals fluctuations in the river sediments

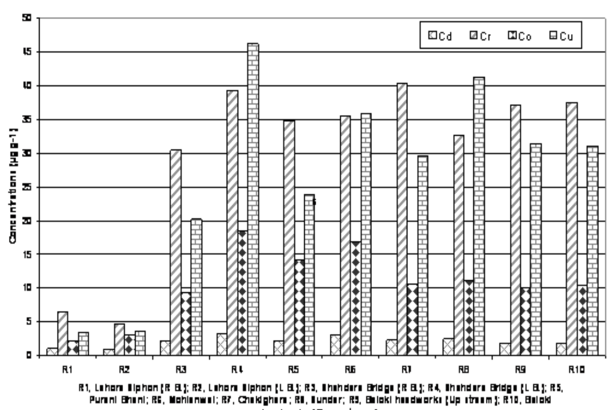
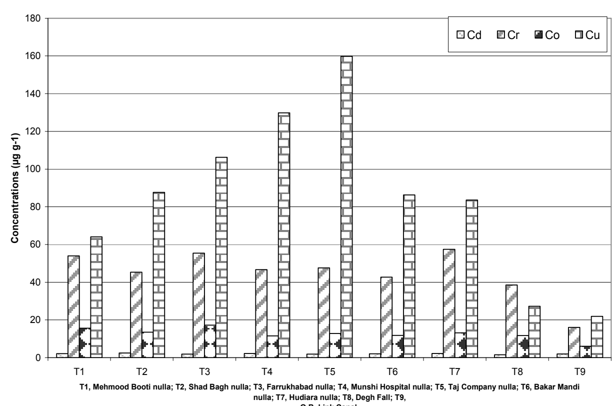


Fig. 2. Pattern of metals fluctuations in the tributaries sediments



Siphon. The magnitude of heavy metals in both river stretch and tributary sediments were Cu > Cr > Cd > Co. Altindag and Yigit (2005), while studying the heavy metal concentrations in the food web of lake Beysehir, reported heavy metal accumulation in the order: Cd > Pb > Cr > Hg in water; Pb > Cd > Cr > Hg in sediments and Pb > Cd > Cr > Hg in plankton.

There are numerous sources of domestic and industrial effluents that lead to heavy metal enrichment of water, sediments, vegetation and fish in rivers. The population of plankton and fish can be taken as indicators of the distribution of heavy metals in water and sediments. Significantly higher concentration of metals in the water of effluent discharging tributaries increased the heavy metals toxicity of the river bed sediments significantly (Javed & Hayat, 1995). Therefore, enrichment of metals in the bed sediments proved an important factor for detecting the sources of heavy metal in an aquatic ecosystem (Ubaidullah *et al*., 2004) because suspended particles carried by industrial effluents and domestic sewage are ultimately deposited as the sediments containing measurable quantities of Cd, Cr, Co and Cu. Sediments are important sinks for various pollutants like pesticides and heavy metals that play a significant role in the remobilization of contaminants in aquatic systems under favorable conditions. Direct transfer of chemicals from sediments to organisms is regarded as a major route of exposure to many species (Zoumis *et al*., 2001). The release of trace metals from sediments into the water and consequently to the fish in the aquatic habitats depends on the rate of precipitation, complexation, absorption and solubilization of metals and physico-chemical characteristics of the aquatic system (Morgan & Stumm, 1991; Javed, 2003). The present study indicates that the sediments of the river Ravi and effluent discharging tributaries have been heavily contaminated with Cd, Cr, Co and Cu. Though most of the illegal discharges in the area have been reduced for some time, the highly contaminated sediments of the river Ravi could continue to act as secondary sources of pollution to the overlying water column.

In conclusion, heavy metal levels in the river sediments were remarkably high, but varied among sampling stations. Our results suggest that special attention must be given to the issue of metal re-mobilization, because a large portion of metals in sediments are likely to release back into the water column.

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