



RESEARCH PAPER

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Impact of chromium toxicity on water, plankton and bed sediments of River Ravi, Pakistan

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Abstract

The water, plankton and bed sediments collected from three polluted sites (Shahdara Bridge, Baloki Headworks and Sidhnai Barrage) in river Ravi were analyzed quantitatively to assess the impact of chromium toxicity on fish and the aquatic ecosystem. Metallic toxicity of water at all the three sites was generally low but the contamination levels in sediment and plankton were significantly higher indicating the bio-magnification of chromium in higher trophic levels. The uptake and accumulation of chromium by the sediments and plankton was dependent positively and significantly upon metallic toxicity of water. The plankton at Shahdara bridge had significantly higher chromium ($45.47 \pm 10.62 \mu\text{g g}^{-1}$) than that of Balokihead works and Sidhnai barrage with the chromium contamination levels of 35.68 ± 7.32 and $34.94 \pm 6.39 \mu\text{g g}^{-1}$, respectively. The pattern of chromium enrichment through water < plankton < bed sediments demonstrated the bio-accumulation and bio-magnification of chromium through water–plankton–bed sediments interactions. The contamination level of water, bed sediments and plankton of river Ravi by chromium exceeded the recommended permissible limits suggesting regular monitoring of heavy metal enrichment in the water bodies and mitigation measures.

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Introduction

Industrial development in the developing countries has resulted in the heavy metal pollution of the rivers (Allen and Moore, 2004). In aquatic ecosystem, the sediments represent an important sink for trace metals and their metallic ion toxicity would become several times higher than in the overlying water.

Therefore, contaminated sediments pose a significant risk to detritus feeding benthic organisms, phytoplankton and zooplankton and may also act as a long-term source of metallic ion pollution to higher tropic levels (Eimers *et al.*, 2001). Fish and plankton are considered the important indicators of heavy metal enrichment (Gernhofer *et al.*, 2001) and ultimately caused bioaccumulation and biomagnification of heavy metals in the food chain (Nogami *et al.*, 2000).

Chromium is abundantly utilized in the processes of electroplating, steel-making alloys, fertilizers and rubber production. Chromium is biologically significant in both trivalent (Cr^{+3}) and hexavalent (Cr^{+6}) forms. The hexavalent form is more toxic because of its property to readily cross the cell membranes. Therefore, heavy metal concentration is of particular concern due to their toxicity and ability to accumulate in the aquatic ecosystems.

The contamination of freshwaters due to several harmful substances, like metals, through inputs from anthropogenic sources, industrial and agricultural activities, domestic sewage, groundwater leaching and runoffs from agriculture has devastating effects on animals (Donohue *et al.*, 2006).

Rivers are a great source of water supply and serve as a natural habitat for aquatic life harboring biodiversity. Due to heavy metal toxicity, persistence, non-biodegradability and adverse effects on aquatic biota, precise information about their concentration in aquatic ecosystems is required (Janssen *et al.*, 2000). River Ravi is exposed to high input of agricultural drainage water, domestic sewage and untreated industrial effluents that affect living organisms.

Therefore, the objective of this study is to determine the pollution level of chromium and bio-accumulation patterns with particular reference to water, sediments and plankton in the river Ravi.

The data can be used for mitigation measures and regular monitoring of heavy metal enrichment in the water bodies and bio-magnification in the aquatic organisms including fish.

Materials and methods

The river Ravi is a trans-boundary river of Indo-Pak sub-continent and a part of the Indus river Basin. The river Ravi receives heavy loads of industrial, domestic and agricultural pollutants via several tributaries (Jabeen and Javed, 2012).

Water, bed sediments and plankton samples were collected from three different locations (Shahdara Bridge, Baloki headworks and Sidhnai barrage) of the river Ravi (Fig. 1) to monitor year round variations in chromium toxicity, from June, 2009 – May, 2010.

The sampling sites were selected so as to represent varying levels and degrees of pollution due to heavy loads of domestic and industrial effluents discharged into it through 14 major drains.

Hudiaranulla, Degh fall, Farrukhabadnulla, Munshi hospital nulla, Taj company nulla, Bakarmandenulla, Sangla main drain, Manawala main drain, Sarwala drain, Machrala drain and Barianwala drain, Sammudri main drain, Sukhrawa main drain and Khunda drain (Fig. I) (Jabeen and Javed, 2012).

Water, sediments and plankton samples were collected by following the proportionate sampling procedure (Steel *et al.*, 1996).

Collection of water samples

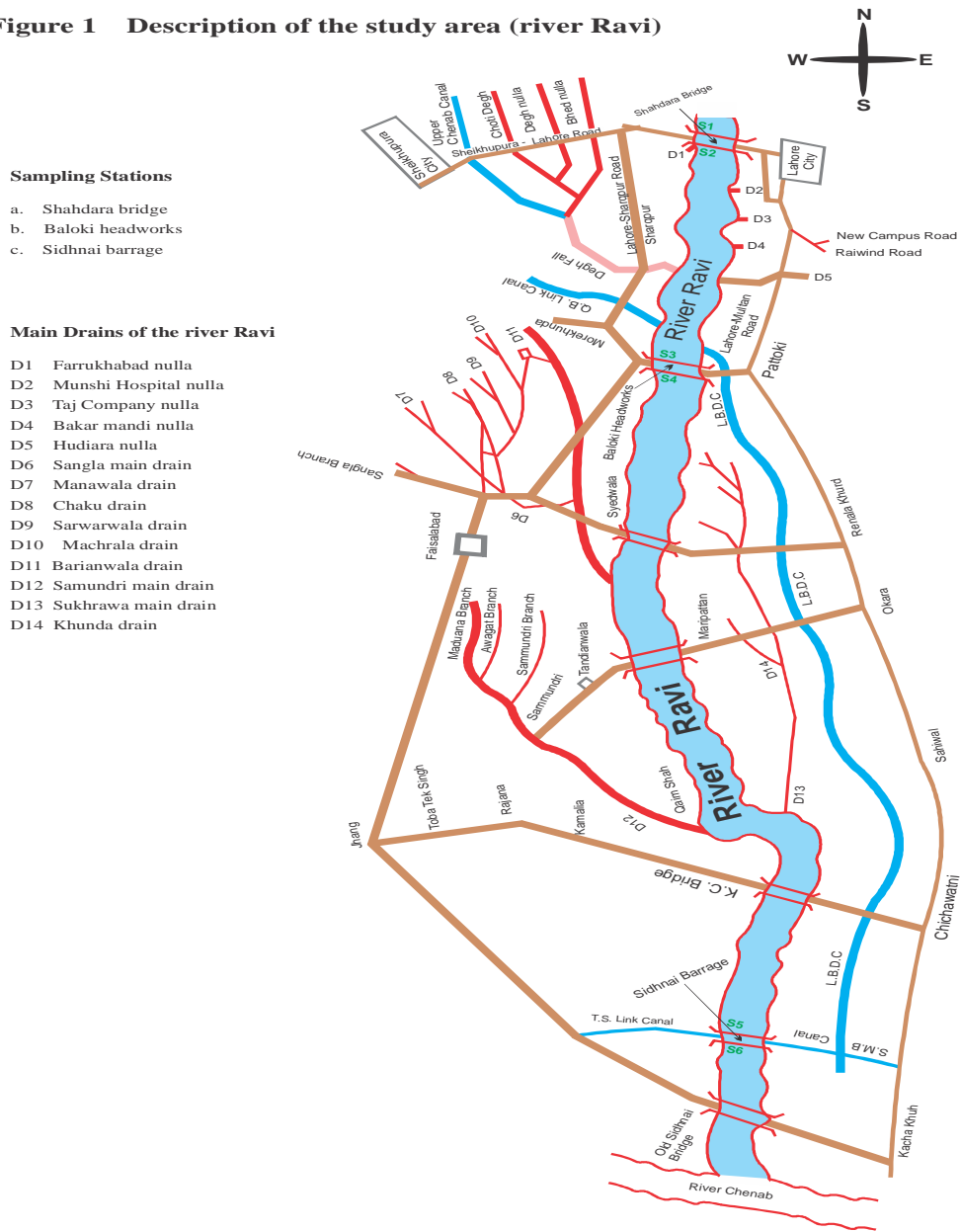
Water samples were collected from the three public fishing sites of the river Ravi, Shahdara bridge, Baloki headworks and Sidhnai barrage, on monthly basis from a depth of one meter just below the surface in Kemmerer bottles and analyzed for the concentrations of chromium.

Collection of sediments

River bed sediment samples were collected on monthly basis with the help of a PVC pipe (5cm) pressed with pressure through the water column to obtain the sediment layer of about 0.25m and shifted to polyethylene bags.

The sampling site was further divided into three sub-sampling sites within 100m of sampling site so that a systemic composite sediment sample of approximately 500g can be obtained. The samples were put in ice cooler during transportation to the laboratory and stored in a deep freeze.

Figure 1 Description of the study area (river Ravi)



Collection of plankton

Plankton samples were collected both from the surface and column by filtering 70-80 liters of water with the aid of plankton net (pore size, 10µm). The dry weights of the planktonic biomass, in the river Ravi, were determined by using an evaporation method (Javed, 1988).

Analyses of water, bed sediments and plankton

Samples of water, bed sediments and filtered plankton were acid digested by using nitric acid and perchloric acid (3,1) on a hotplate until the solution became clear. Chromium contamination levels in the water and dry plankton samples were determined through the methods of A.P.H.A (2005).

The acid digested samples of water, bed sediments and plankton were analyzed for chromium toxicity on Atomic Absorption Spectrophotometer (Perkin Elmer, AAnalyst-400). Two-way ANOVA and Tukey's/Student Newman-keul tests were employed using SPSS 10.1 computer program to find the significant differences of chromium contaminations in water, plankton and sediment samples. The level of significance was set at $p < 0.05$.

Results

Chromium in water

There existed statistically highly significant differences among three fishing sites for chromium toxicity in water during 12 months study period. At Shahdara bridge, the mean maximum and minimum chromium concentrations of 36.11 ± 0.66 and $17.58 \pm 0.38 \text{ mg L}^{-1}$ were recorded during November

and June, respectively with statistically significant difference. At Balokiheadworks, the chromium toxicity fluctuated significantly within the mean values of 32.70 ± 0.08 and $12.71 \pm 0.56 \text{ mg L}^{-1}$ during November and May, respectively.

The water at Sidhnai barrage exhibited significantly variable chromium toxicity that fluctuated between a minimum mean concentration of $17.56 \pm 0.08 \text{ mg L}^{-1}$ (July) and a maximum mean value of $34.25 \pm 0.42 \text{ mg L}^{-1}$ (October). The water at Shahdara bridge was significantly more contaminated with chromium than the other two sampling stations. The mean annual concentrations of chromium at Shahdara bridge, Baloki headworks and Sidhnai barrage were computed as 25.77 ± 6.31 , 23.80 ± 5.77 and $25.47 \pm 5.50 \text{ mg L}^{-1}$, respectively with statistically significant differences (Table I).

Table 1. Chromium concentrations (mg L^{-1}) in the water of river Ravi.

Source of Variation	Degree of Freedom	Mean Square	Standard Error	Probability
Replications	5	0.393	0.0933	N.S.
Sampling Stations	2	161.257	0.0660	$p < 0.01$
Months	11	579.778	0.1320	$p < 0.001$
Sampling Stations x Months	22	49.851	0.2286	$p < 0.001$
Error	175	0.314		
Total	215			

Months	MEANS (\pm SD)			Overall mean concentrations for three Sampling Stations
	Shahdera Bridge	Balokiheadworks	Sidhnai barrage	
June, 2009	17.58 ± 0.38 j	15.36 ± 0.33 k	20.65 ± 0.04 g	17.86 ± 2.66 i
July	19.40 ± 0.08 i	18.64 ± 0.10 j	17.56 ± 0.08 i	18.53 ± 0.92 h
August	25.46 ± 0.36 e	20.70 ± 0.08 g	23.39 ± 0.13 ef	23.18 ± 2.39 f
September	21.46 ± 0.43 f	30.38 ± 0.07 c	26.73 ± 0.28 c	26.19 ± 4.48 e
October	33.00 ± 0.22 c	28.77 ± 0.70 d	34.25 ± 0.42 a	32.01 ± 2.87 b
November	36.11 ± 0.66 a	32.70 ± 0.08 a	34.22 ± 0.54 a	34.34 ± 1.71 a
December	30.19 ± 0.49 d	31.87 ± 1.40 b	28.68 ± 0.38 b	30.25 ± 1.60 c
January	33.78 ± 0.81 b	24.37 ± 0.55 e	29.03 ± 0.59 b	29.06 ± 4.71 d
February	24.24 ± 0.46 f	22.39 ± 0.50 f	22.90 ± 0.60 f	23.18 ± 0.96 f
March	27.68 ± 0.97 d	19.01 ± 0.51 ij	23.94 ± 0.67 de	23.54 ± 4.35 f
April	20.02 ± 0.67 h	19.72 ± 1.02 h	26.24 ± 0.98 c	21.99 ± 3.68 g
May, 2010	20.36 ± 0.28 gh	12.71 ± 0.56 i	18.04 ± 0.49 hi	20.04 ± 1.86 j

(Single column means are nonsignificant at $p < 0.05$)

Sampling Stations	Shahdera Bridge	Balokiheadworks	Sidhnai barrage
	25.77 ± 6.31 a	23.80 ± 5.77 c	25.47 ± 5.50 b

Chromium in Bed Sediments

The data regarding year-round variations in toxicity of chromium in the river bed sediments, at three sampling stations, are presented in Table 2. The chromium toxicity levels of bed sediments fluctuated significantly among three sampling stations and during 12 months of the study period. Chromium toxicity was maximum during December at all the

three sampling stations, Shahdara bridge, Baloki headworks and Sidhnai barrage with the mean contamination levels of 100.60 ± 2.83 , 97.80 ± 2.74 and $100.70 \pm 1.86 \mu\text{g g}^{-1}$, respectively. At both Shahdara bridge and Baloki headworks, the contamination of chromium in sediments appeared significantly minimum during July while that at Shahdara bridge was significantly maximum as $71.36 \pm 21.20 \mu\text{g g}^{-1}$.

Table 2. Chromium concentrations ($\mu\text{g g}^{-1}$) in the bed sediments of the river Ravi.

Source of Variation	Degree of Freedom	Mean Square	Standard Error	Probability
Replications	5	7.081	0.4771	N.S.
Sampling Stations	2	4590.401	0.3374	$p < 0.001$
Months	11	8599.429	0.6748	$p < 0.001$
Sampling Stations x Months	22	477.675	1.1687	$p < 0.001$
Error	175	8.195		
Total	215			

MEANS (\pm SD)								
Months	Sampling Stations						Overall mean concentrations for three Sampling Stations	
	Shahdera bridge		Balokiheadworks		Sidhnai barrage			
June, 2009	52.77 \pm 5.13	i	28.34 \pm 2.84	j	44.85 \pm 2.01	h	41.99 \pm 12.46	h
July	41.78 \pm 8.72	j	19.40 \pm 2.48	k	38.67 \pm 1.61	i	33.28 \pm 12.12	j
August	44.61 \pm 4.40	j	31.04 \pm 1.82	i	32.56 \pm 1.21	j	36.07 \pm 7.43	i
September	43.40 \pm 2.79	j	40.64 \pm 3.36	h	58.08 \pm 1.79	g	47.37 \pm 9.37	g
October	70.22 \pm 2.81	h	52.06 \pm 1.62	f	76.00 \pm 1.66	e	66.09 \pm 12.49	f
November	81.76 \pm 2.85	e	58.20 \pm 2.73	e	86.54 \pm 1.44	cd	75.50 \pm 15.17	e
December	100.60 \pm 2.83	a	97.80 \pm 2.74	a	100.70 \pm 1.86	a	99.70 \pm 1.65	a
January	84.08 \pm 2.68	d	74.61 \pm 2.34	d	84.16 \pm 2.26	d	80.95 \pm 5.49	c
February	91.90 \pm 2.70	c	92.79 \pm 1.64	b	87.34 \pm 1.88	c	90.68 \pm 2.92	b
March	75.94 \pm 0.92	f	54.70 \pm 2.59	f	69.45 \pm 1.57	f	66.70 \pm 10.88	f
April	72.31 \pm 2.42	gh	84.47 \pm 3.26	c	77.11 \pm 1.98	e	77.96 \pm 6.12	d
May, 2010	96.94 \pm 1.90	b	50.64 \pm 2.55	g	88.86 \pm 1.60	b	78.81 \pm 24.73	d

(Single column means are nonsignificant at $p < 0.05$)

Sampling Stations	71.36 \pm 21.20	a	57.06 \pm 25.69	c	70.36 \pm 21.98	b		
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Chromium in Plankton

The plankton samples collected from Shahdara bridge, Baloki headworks and Sidhnai barrage showed statistically significant differences for their chromium contents during various months of the study period. The plankton at Shahdara bridge had significantly higher chromium ($45.47 \pm 10.62 \mu\text{g g}^{-1}$) than that of Baloki headworks and Sidhnai barrage with the chromium contamination levels of 35.68 ± 7.32 and $34.94 \pm 6.39 \mu\text{g g}^{-1}$, respectively. However, the plankton collected from Baloki

headworks and Sidhnai barrage did not show any significant difference for their chromium contents.

At Shahdara bridge, Baloki headworks and Sidhnai barrage the lower mean chromium concentrations of 32.35 ± 1.42 , 19.60 ± 2.32 and $25.10 \pm 1.94 \mu\text{g g}^{-1}$ were recorded during the months of May, August and June, respectively while these were maximum as 62.42 ± 2.38 , 48.17 ± 3.62 and $45.00 \pm 1.98 \mu\text{g g}^{-1}$ during January (for both Shahdara bridge and Baloki headworks) and November, respectively (Table 3).

Table 3. Chromium concentrations ($\mu\text{g g}^{-1}$) in the plankton of the river Ravi.

Source of Variation	Degree of Freedom	Mean Square	Standard Error	Probability
Replications	5	9.209	0.4307	N.S.
Sampling Stations	2	2487.073	0.3045	$p < 0.001$
Months	11	896.945	0.6091	$p < 0.001$
Sampling Stations x Months	22	173.120	1.0549	$p < 0.001$
Error	175	6.677		
Total	215			

MEANS (\pm SD)								
Months	Sampling Stations						Overall mean concentrations for three Sampling Stations	
	Shahdera bridge	Balokihheadworks	Sidhnai barrage					
June, 2009	35.56 \pm 4.37	h	39.12 \pm 2.64	d	25.10 \pm 1.94	i	33.26 \pm 7.29	F
July	41.46 \pm 1.97	f	31.05 \pm 1.93	h	29.58 \pm 2.48	h	34.03 \pm 6.48	F
August	33.05 \pm 1.88	i	19.60 \pm 2.32	j	23.33 \pm 1.86	i	25.33 \pm 6.94	G
September	42.31 \pm 3.06	e	35.43 \pm 2.57	efg	39.19 \pm 2.03	bcf	38.98 \pm 3.44	D
October	48.03 \pm 1.85	d	34.96 \pm 4.13	fg	35.12 \pm 2.02	fg	39.37 \pm 7.50	Cd
November	58.56 \pm 2.28	b	44.78 \pm 2.32	b	45.00 \pm 1.98	a	49.45 \pm 7.89	A
December	59.19 \pm 2.97	b	40.57 \pm 2.47	cd	34.00 \pm 1.97	g	44.59 \pm 13.07	B
January	62.42 \pm 2.38	a	48.17 \pm 3.62	a	38.14 \pm 1.96	cdf	49.57 \pm 12.20	A
February	52.54 \pm 4.30	c	35.61 \pm 2.41	efg	34.69 \pm 1.91	fg	40.95 \pm 10.05	C
March	43.78 \pm 4.49	e	33.91 \pm 3.20	g	42.22 \pm 2.14	a	39.97 \pm 5.31	Cd
April	36.35 \pm 2.46	g	34.83 \pm 3.03	fg	37.12 \pm 1.80	def	36.10 \pm 1.16	E
May, 2010	32.35 \pm 1.42	i	30.15 \pm 1.01	i	35.74 \pm 1.37	efg	32.75 \pm 2.82	F

(Single column means are nonsignificant at $p < 0.05$)

Sampling Stations	45.47 \pm 10.62	a	35.68 \pm 7.32	b	34.94 \pm 6.39	b		
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Discussion

Chromium is used in metal alloys and pigments for paints, cement, paper, rubber and other materials. It has also been found to be an effective anti-fouling compound (Ackereley *et al.* 2004; Baird and Cann, 2008). The present investigation reveals that uptake and accumulation of all chromium by the sediments and plankton were dependent, positively and significantly, upon metallic toxicity of water. However, chromium uptake by the plankton showed significantly direct dependence on the metallic toxicity of sediments. The chemicals discharged into the aquatic bodies are ultimately adsorbed by the sediments that would become sink and source of pollutants/pollution. Sediments as an important component of aquatic ecosystem play an important function to sustain the trophic status (Singh *et al.*, 1995). Therefore, study of sediments is important to understand the effects of pollutants in the water

bodies as pollutants exist in sediments for a long period of time that would adversely affect the sustainability of ecological balance in the rivers (Singh *et al.*, 2002). The contaminated sediments may serve as sinks and secondary sources for other heavy metals (Hollert *et al.*, 2003) that can pose potential ecological risk to benthic and epibenthic organisms (Dekker *et al.* 2006). However, during this study the contamination levels of both sediments and plankton are indicative of their role as bio-indicator of the metallic pollutions in the river Ravi ecosystem due to their persistent ability to remove metals from the water, accumulate and store them over a long period of time even at low concentrations of chromium in the water. Among the three public fishing sites, Shahdara bridge had significantly higher metallic toxicity of water and planktonic biota attributed to the bulk discharges of untreated effluents, originated from adjacent industrial areas,

discharged through various small tributaries and drains. The pattern of chromium enrichment through water < plankton < sediments demonstrated the bio-accumulation and bio-magnification of chromium through water–plankton–bed sediments interactions. In conclusion, the toxic levels of chromium determined in water, bed sediments and plankton (Table I, II and III) are all above the tolerable limits recommended by EPA clearly depicting that that river Ravi ecosystem is severely contaminated with heavy metals which would eventually end up in aquatic food chain damaging the ecosystem. These results can be used to evaluate fish meat quality and hazards associated with its consumption and demand regular monitoring of pollution status of river Ravi to minimize public health issues.

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