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Concentration of heavy metals in the water and fish tissues of the river ravi, Pakistan

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Abstract

The River Ravi has subject to severe disturbances due to contaminants discharge of untreated industrial wastes and domestic sewage. This study was planned to assess the status of heavy metals Copper (Cu), chromium (Cr), cadmium (Cd) and cobalt (Co) in water and indian major carp (*Catla catla)* collected from the sampling station, Baloki Headworks. The results showed significant differences among six fish organs viz. Gills, kidney, liver, skin, muscle and scales. Accumulation of Cu in all the six fish organs showed significant difference. Fish liver was the organ that accumulated significantly higher quantities of these metals followed by that of kidney and scales. The magnitude of heavy metals in both river stretch and tributary waters were Cu > Cr > Cd > Co while in the fish tissue the elements decreased in the order Cu > Cr >Co> Cd. The correlation coefficient between the metals toxicity of *Catla catla* body organs and water was positively significant. The result of this study indicated that the metals present in the river system were taken up by *Catla catla* through water, sediments and food, regardless of their biological needs, showed higher metal concentrations.

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Introduction

Human activities have increased the concentration of metals in many of the natural water systems which have raised concerns regarding metal bioaccumulation and human health hazards. In aquatic environment, larger animals such as fsh have been exposed to heavy metals as a direct significance of biomagnifications (Ekwanyanwu *et al.*, 2011; Javed and Usmani, 2011). The danger is that heavy metals even at low concentrations in fsh and water have a particular importance in ecotoxicology and their toxic effects have been widely published for a number of water bodies (Obasohan, 2008;Ubaidullah, 2003;Oronsaye *et al.*, 2010). Among aquatic species, fishes are the inhabitants that cannot escape from the harmful effects of heavy metal pollution. This is because of their very close contact with water that carries the heavy metals and also fish have to extract oxygen from water by passing water over their gills. The gills particularly are therefore a potential site of absorption of heavy metals and can be considered as one of the most significant indicators in water systems for the estimation of metal pollution level (Dural *et al.*,2007; Ekwanyanwu *et al.*, 2011). It is meaningful noting too that other fsh organs including the muscles, liver and kidney have also been studied for heavy metal accumulation (Begum *et al.*, 2009; Ekwanyanwu *et al.*, 2011; Javed and Usmani, 2011).

With the rapid increase in industrialization in Pakistan, the water pollution has become a serious problem as the industrial effluent and domestic sewage, containing bulk quantities of toxic heavy metals, are being continuously discharged into the rivers especially in the river Ravi (Javed, 2005). Therefore in the present study, it was aimed to evaluate the pollution level of aquatic ecosystem via determing the accumulation of metals in water and *Catla catla*.

Materials and methods

Four sampling stations viz. Shahdera Bridge, Mohnalwal, Sunder and Baloki headworks along the stretch of river Ravi and four effluent discharging tributaries viz. Mehmood Booti nulla, Shad Bagh nulla, Bakar Mandi nulla and Hudiara nulla were fixed to study the toxicity of metals.

Sample collection

Water

Water samples were filtered through 0.45 µm Millipore membrane filters (Type HV). Cadmium, chromium, cobalt and copper concentrations in water were determined through Atomic Absorption Spectrophotometer (Perkin Elmer, AAnalyst-400) by following the method Nos. 3500-Cd B, 3500-Cr B, 500-Co B and 3500-Cu B of A.P.H.A. (1998), respectively.

Fish

Samples of fish organs viz. gills, kidney, liver, skin, muscle and scales of *Catla catla* fish species were digested, separately, with concentrated HNO_3. Each sample was taken in a 100 ml quartz tube and extra pure 10 ml concentrated HNO_3 (Riedel) was added. Samples in quartz tubes were heated at 100, 150, 200 and 250°C on a hot plate continuing until sample was completely digested. The sample was cooled and 10 ml of 1N HNO_3 was added again. Digested sample was transferred to 500 volumetric flasks to make the volume by using the double distilled water. The digested sample volume was filtered through 0.45 µm Millipore membrane filter (Type HV). The filtrate was analyzed for Cd, Cr, Co and Cu according to A.P.H.A. (1998) on Atomic Absorption Spectrophotometer.

Data Analysis

Data on all the above mentioned variables were collected on fortnightly basis and statistically analyzed by following two-way classification (Factorial Experiment). Mean values and standard deviations were computed for each sample size and variables separately. Data were analyzed by following Steel *et al.* (1996).

Results and discussion

Fish is considered as one of the main protein sources of human diet. River pollution leads to the fish affected by toxic materials from many sources i.e.

domestic and industrial wastewaters and surface runoff (Ahmed *et al*., 2011). The present study reveals that the effluents discharging tributaries have contributed significantly towards metals (cadmium, chromium, cobalt, and copper) toxicity in the river up to Sunder while the quality of river water improves at Baloki headworks due to mixing of Q. B. Link Canal water. However, the continues influx of river water at Baloki headworks deteriorated the quality of water, plankton, sediments and fish (Ubaidullah, 2003)

In the river, the mean annual cadmium concentrations varied between a maximum mean value of 0.59±0.43 mgL^{-1} (Sunder) and a minimum mean concentration of 0.39±0.23 mgL^{-1} recorded at Baloki headworks. (Table 1). Among the tributaries, Mehmood Booti nulla showed the highest mean cadmium concentrations of 0.53±0.19 mgL^{-1}. The water in Bakar Mandi nulla had the mean annual lowest concentration of 0.45±0.14 mgL^{-1}. Cobalt, copper, cadmium and chromium concentrations in the river water represent a potential hazard to the aquatic environment and exceeded the permissible limits for sustainable conservation of aquatic habitats (Javed, 2004; Yayintas *et al*., 2007).

In the river, the highest mean chromium concentration of 3.34±0.86 mgL^{-1} was recorded at Sunder while it was the lowest (2.11±0.74 mgL^{-1}) at Baloki headworks. In the tributaries, the mean chromium concentrations fluctuated between a maximum value of 3.89±0.85 mgL-1 to a minimum concentration of 2.66±0.68 mgL-1 recorded at Mehmood Booti nulla and Bakar Mandi nulla, respectively. Koukal *et al.* (2004) assessed the water quality and toxicity of polluted rivers "Fez and Sebou" in the region of Fez (Morocco) and reported severe chromium and copper pollutions in the river water that has resulted in the loss of aquatic life.

Table 1. Analysis of variance on metal concentrations in the river and tributary waters during the study period.

S.O.V	**D.F**	**MEAN SQUARES**			
		Cadmium	**Chromium**	**Cobalt**	**Copper**
Fortnights	23	0.214 $^{p<0.001}$	5.078 $^{p<0.001}$	0.040 $^{p<0.001}$	6.130 $^{p<0.001}$
Samplng Stations	07	0.724 $^{p<0.001}$	25.125 $^{p<0.001}$	0.125 $^{p<0.001}$	65.548 $^{p<0.001}$
Error	161	0.063	0.330	0.003	0.696
S.E. for					
Fortnights		0.0437	0.1217	0.0135	0.2010
Sampling Stations		0.0419	0.1172	0.0110	0.1238
COMPARISON OF HEAVY METALS (±SD)					
Sampling Stations		**Cadmium (mg L^{-1})**	**Chromium (mg L^{-1})**	**Cobalt (mg L^{-1})**	**Copper (mg L^{-1})**
RIVER SITES					
Shahdera Bridge		0.59±0.29 c	3.31±1.22 b	0.34±0.10 d	5.07±1.65 a
Mohnalwal		0.54±0.35 c	2.89±0.64 b	0.33±0.07 d	4.16±1.24 a
Sunder		0.59±0.43 c	3.34±0.86 b	0.32±0.14 d	4.32±0.17 a
Baloki headworks		0.39±0.23 c	2.11±0.74 b	0.19±0.05 d	3.00±0.98 a
TRIBUTARIES					
Mehmood Booti nulla		0.53±0.19 c	3.89±0.85 b	0.25±0.04 d	4.56±1.30 a
Shad Bagh nulla		0.51±0.14 c	3.56±0.84 b	0.28±0.06 d	4.54±1.33 a
Bakar Mandi nulla		0.45±0.14 c	2.66±0.68 b	0.20±0.08 d	3.67±1.21 a
Hudiara nulla		0.46±0.09 c	3.87±1.13 b	0.29±0.05 d	4.72±1.05 a

(Mean values with similar letters in a single column are statistically similar at $p<0.05$).

Table 2. Analysis of variance on physico-chemical concentrations in the river and tributary waters during the study period.

S.O.V	D.F	MEAN SQUARE			
		Water temperature	pH	Dissolved Oxygen	Total Hardness
Fortnights	23	598.571$^{p<0.001}$	1.601$^{p<0.001}$	9.943 $^{p<0.001}$	32890.465$^{p<0.001}$
Sampling Stations	07	464.032 $^{p<0.001}$	7.070 $^{p<0.001}$	554.569 $^{p<0.001}$	25519.928 $^{p<0.001}$
Error	161	0.037	0.013	0.016	2.273
S.E. for					
Fortnights		0.0577	0.1317	0.0135	0.2110
Sampling Stations		0.0513	0.1172	0.0120	0.1878
COMPARISON OF HEAVY METALS (±SD)					
SAMPLING STATIONS		**Water temperature (mg L^{-1})**	**pH (mg L^{-1})**	**Dissolved Oxygen (mg L^{-1})**	**Total Hardness (mg L^{-1})**
RIVER SITES					
Shahdera Bridge		23.10±5.45	7.74±0.40	6.27±1.25	136.94±35.70
Mohnalwal		23.55±.5.14	7.59±0.36	4.28±2.01	147.64±55.29
Sunder		22.91±5.40	7.56±0.45	4.56±1.76	161.11±62.49
Baloki headworks		23.28.±5.74	7.63±0.44	6.79±1.81	1 34.44±34.66
TRIBUTARIES					
Mehmood Booti nulla		28.18±4.65	7.01±0.55	0.38±0.20	209.33±51.09
Shad Bagh nulla		27.94±4.06	6.87±0.38	0.46±0.17	21 4.39±40.53
Bakar Mandi nulla		27.75±5.77	7.26±0.44	0.90±0.38	208.47±42.96
Hudiara nulla		27.74±5.33	7.42±0.37	0.33±0.22	218.33±64.78

Among the river sites, Shahdera Bridge had the mean highest annual cobalt concentration of 0.34 mgL^{-1} while it was minimum (0.19±0.05 mgL^{-1}) at Baloki headworks. Among the tributaries, Hudiara nulla had the mean highest annual cobalt concentration of 0.29±0.05 mgL^{-1} while it was significantly lowest (0.20±0.08 mgL^{-1}) at Bakar Mandi nulla. Certain metals such as Co, Cu, Fe, Mn and Pb increases in both sewage inlet drain and the lake water (Shrivastava *et al*., 2003).

In the river, the mean highest copper concentration of 5.07±1.65 mgL^{-1} was recorded at Shahdera Bridge while the concentrations recorded at Baloki headworks was the lowest (3.00±0.98 mgL^{-1}). Among the tributaries, Hudiara nulla had the highest toxicity of copper (4.72±1.05 mgL^{-1}). The Bakar Mandi nulla water was the least contaminated with copper having the mean annual lowest concentration level of 3.67±1.21 mgL^{-1}. The magnitude of heavy metals in both river stretch and tributary waters were Cu > Cr > Cd > Co. Altindag and Yigit (2005) while studying the heavy metal concentrations in the food web of lake Beysehir reported accumulation orders of heavy metals as Cd > Pb > Cr > Hg in water.

Physico-Chemical parameters of water

The physico-chemical characteristics of both river and tributary waters were determined on fortnightly basis. The mean annual values of temperature, pH, dissolved oxygen and total hardness are presented in Table.

i) *Water Temperature*

Water temperature did not fluctuate significantly among river site sampling stations. The Mohnalwal shows the mean highest water temperature of 23.55±5.14 ^{o}C while it was the minimum at Sunder (22.91±5.40) ^{o}C. Among the tributaries, Mehmood Booti nulla had the mean annual highest water temperature value of 28.18±4.65 ^{o}C. Water temperature appeared as an important factor that exerted significant impact on the toxicity of metals in both river and tributary waters. (Javed, 2004).

ii) pH

The river upstream water at Shahdera Bridge had significantly highest (7.74±0.40) mean pH value than rest of the river sites. Sunder exhibited the mean lowest water pH of 7.56±0.45. Shad Bagh nulla had the lowest mean water pH of 6.87±0.38. Widianarko *et al*. (2000) reported negative correlation between

lead contamination and pH of water. Boqomazov *et al.* (1991) observed an inverse relationship between water pH and concentration of mobile iron, mercury, zinc and cobalt.

iii) Dissolved Oxygen

The Baloki headworks exhibited significantly higher mean water dissolved oxygen level of 6.79±1.81 mgL^{-1} than rest of the river sites whiles the mean lowest was observed at Mohnalwal (4.28±2.01 mgL^{-1}). The tributary waters had significantly lower dissolved oxygen contents than that of the river stretch. Among the tributaries, Hudiara nulla exhibited the lowest content of 0.33±0.22 mgL^{-1} while it was the maximum (0.90±0.38 mgL^{-1}) at Bakar Mandi nulla. Heavy metal toxicity may decrease the oxygen consumption by the fish (Rathore and Khangarote, 2003).

iv) Total Hardness

Significantly higher mean total hardness of 161.11±62.49 mgL^{-1} was recorded at Sunder while the lowest was observed at Baloki headworks as 134.44±34.66 mgL^{-1}. Among the tributaries, mean annual water hardness was the maximum (218.33±64.78 mgL^{-1}) at Hudiara nulla while it was minimum (208.47±42.96 mgL^{-1}) at Bakar Mandi nulla. The availability of metals in water depends upon the water hardness has been reported by Van Aardt and Erdmann (2004) and Erdogrul and Ates (2006).

Trace metals in fish

The samples of fish, *Catla catla* were collected from Baloki headworks. Their average weights, fork and total lengths were measured and recorded. Fish organs viz. gill, kidney, liver, skin, muscle and scales were isolated and analyzed for cadmium, chromium, cobalt and copper concentrations.

At Baloki headworks, the maximum cadmium concentration of 5.10±1.16 μgg^{-1} was recorded in the liver while gills of *Catla catla* had the minimum cadmium contents of 1.08±0.43 μgg^{-1}, respectively.

The liver of *Catla catla* at Baloki headworks, contained the maximum chromium (7.64±1.26 μgg^{-1}) while it exhibited the minimum metal contents 1.19±0.99 μgg^{-1} in its muscle. *Catla catla* contained the least cobalt (1.09±0.83 μgg^{-1}) in its gills while liver appeared as an organ that had maximum accumulation of 5.45±1.20 μgg^{-1}, respectively. Fish species, had the maximum copper in their liver followed by that of their kidney. *Catla catla* muscle appeared the organ that had least concentrations of copper (4.03±1.04) (Table 3).

Table 3. Metals concentration in the tissues of *Catla catla*.

Fish	Metals	Gills	Kidney	Liver	Skin	Muscle	Scales
Catla catla	Cd	1.08±0.43	3.06±1.43	5.10±1.16	2.87±1.59	1.36±0.96	3.95±1.35
	Cr	1.49±0.48	6.24±2.89	7.64±1.26	4.63±0.49	1.19±0.99	5.66±1.48
	Co	1.09±0.83	4.14±1.01	5.45±1.20	3.45±1.06	1.52±0.68	4.62±1.68
	Cu	5.44±3.15	16.37±5.55	18.37±4.43	11.04±2.37	4.03±1.04	11.15±2.48

In the river, fish are often at the top of the food chain and has the tendency to concentrate heavy metals from water (Ekwanyanwu *et al.*, 2011). Dural *et al.* (2007) observed highest levels of cadmium, lead, copper, zinc and iron in the liver and gills of three fish species viz. *Sparus aurata, Dicentrachus labrax* and *Mugil cephalus*.

Conclusion

The concentration of Cd, Cr, Co and Cu in water and fish tissues were detected and was found to be higher than the WHO recommended limit. The fish collected from Baloki Headworks showed significantly high concentration of metals that could be related to industrialization and environmental contamination along the river Ravi stretch. We recommend constant

monitoring of heavy metals concentration in the Ravi River since the river serves as a source of drinking water, irrigation and fisheries for the local inhabitants.

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