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Heavy Metals Concentrations in Water, Sediment and Fish in River Sutlej at Sulemanki Headworks

Amtul Bari Tabinda*, Sidra Bashir, Abdullah Yasar and Saleha Munir
Sustainable Development Study Centre, GC University, Katchery Road, Lahore-54000

Abstract.- Contaminants residues in biota are reflective of environmental quality. In the present study heavy metals (HMs) Fe, Zn, Cu, Cr and Ni concentrations were determined in water, sediment and fish in River Sutlej at Sulemanki Headworks. Order of HMs concentrations in water, sediments and fish species was Fe > Zn > Cu > Cr > Ni. HMs concentration in water, sediment and fish were significantly greater ($P<0.01$) during the winter season as compared to summer season. Significantly higher concentrations of HMs were found in sediments as compared to water ($P<0.05$) and fish ($P<0.05$). Concentrations of Fe, Cu, Cr and Ni in sediments were significantly correlated ($P<0.05$) with concentrations of these HMs in water which shows that these HMs re-suspend from sediments into water. Similarly concentrations of HMs in water were significantly correlated ($P<0.05$) with their concentrations in fish which indicates accumulation of HMs from water in fish tissues through its gills and skin.

Keywords: Heavy metals, water, sediment, fish, iron, copper, chromium, nickel.

INTRODUCTION

Rivers are a good source of drinking water and support many types of aquatic life. In industrialized countries contamination of water resources, sediments and biota with heavy metals (HMs) is alarming due to their bioaccumulation, persistence and toxicity. (Al-Yousuf *et al*., 2000; Grosheva *et al*., 2000; Ikem *et al.*, 2003; Rashed, 2001; Storelli and Marcotrigiano, 2001). The HMs concentration in sediments is several times higher than the surrounding water (Mendil and Uluozlu, 2007). Sediments being sink for HMs have a significant role in contaminant remobilization in aquatic system (Zoumis *et al*., 2001). HMs are released from sediments to water and their accumulation by fish depends on several factors like solubility of HMs, adsorption or precipitation **(**Ikem *et al.,* 2003). Accumulation of HMs up to toxic concentrations can be harmful (Karadede and Unlu, 2000).

Fish has a good nutritional value. It is an excellent source of protein and contains omega 3-fatty acids which are helpful for curing different types of cancer (Paul *et al*., 2002; Terry *et al*., 2001). For humans, consumption of contaminated fish is a major route for intake of HMs and chemicals (Dougherty, 2000). In aquatic ecosystem fish are at the top of food chain. HMs present into aquatic ecosystem accumulate in fish and pose a threat to fish, birds and human health (Bervoets and Blust, 2003). The HMs bioavailability in aquatic environment is determined by biotic (feeding habits, exchange surfaces) and abiotic factors (pH, temperature and complexation reactions) (Chowdhury and Blust, 2002; Clearwater *et al.*, 2002). In fish HMs can also be accumulated by food chain (Tabinda *et al*., 2013) or overlying water (Fernandes *et al*., 2008). Some HMs like Zn and Cu are essential for fish metabolism while others have no function (Eastwood and Couture, 2002). The present study determined the concentration of HMs in water, sediment and tissues of Indian major carps.

MATERIALS AND METHODS

River Sutlej is the longest river and flows through Punjab in northern India and Pakistan. It is located in east of the Central Suleman Range in Pakistan. Sulemanki Headworks is on the River Sutlej in the Punjab province of Pakistan and is used for irrigation and flood control. Numerous industries are present in region *i.e.* sugar mill, oil mill and paper mill (Irrigation and Power Department, 2004). Industrialization has introduced the water pollution problem in rivers. River pollution first deteriorates its physical quality and then the community is destroyed as a consequence disturbing its food web.

* Corresponding author: amtulbaritabinda64@yahoo.com
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The assessment of water quality of river helps in predicting future alterations in water quality due to developmental activities.

Water, sediment and fish samples were collected from three different locations of River Sutlej at Sulemanki Headworks during both summer and winter seasons. Water samples were collected from different depths. Water samples were collected with the help of Van Dorn Bottle Sampler and sediment samples with the help of Ekmann dredge. Three specimen of each *Labeo Rohita*, *Catla catla and Cirrhina mrigala* were collected from each location in both summer and winter seasons.

Water samples were collected and stored in plastic bottles and acidified with highly pure analytical grade conc. HNO_3 at pH<2. Sediment and fish samples were stored in zip lock plastic bags and kept in icebox for transportation. Fish was dissected, muscular portion was separated, homogenized and stored at -20°C in deep freezer in plastic bags (Tabinda *et al.*, 2010).

0.5g sediment sample was taken in digestion tube. 4 mL highly pure analytical grade conc. HNO_3 was added, sample was heated for 1hr at 120°C (Yilmaz *et al.*, 2007), 4mL H_2O_2 was added and digested until it was colorless (Tan 2005). 5g fish muscle was digested in 10ml conc. HNO_3 for HMs analysis. HMs were analyzed by Atomic Absorption Spectrophotometer Perken-Elmer model AA-400.

Statistical analysis

Differences in the HMs concentrations during summer and winter seasons were analyzed using t-test. Correlation of HMs concentrations between water and sediments, water and fish was computed by Pearson's correlation using SPSS software version 16.0.

RESULTS

Order of the HMs concentration in water, sediment and fish was Fe> Zn> Cu> Cr>Ni. The range of Fe, Zn, Cu, Cr and Ni in water (µg ml^{-1}) during winter was 0.76-0.78, 0.38-0.40, 0.24-0.26, 0.21-0.23 and 0.06-0.07 but in summer 0.59-0.61, 0.09-0.11, 0.08-0.11, 0.09-0.10 and 0.01-0.02, respectively (Table I). In sediments range of these HMs (µg g^{-1}) during winter was 1837-1859, 124-128, 45.3-49.1, 38.7-41.6 and 22.9-28.1 but in summer 1788-1828, 119-129, 28.7-34.7, 26.4-33.2 and 17.1-19.0, respectively (Table II).

Range (µg g^{-1}) of Fe, Zn, Cu, Cr and Ni in *Cirrhina mrigala* during winter season was 38.4-42.6, 26.5-33.3, 5.73-6.13, 2.43-2.55 and 1.64-1.88 but in summer season 30.3-36.0, 25.3-31.5, 4.53-5.46, 1.37-1.49 and 0.63-0.97, respectively. In *Labeo rohita* this range (µg g^{-1}) was 31.7-38.1, 20.1-29.1, 4.14-5.54, 2.32-2.50 and 1.58-1.78 during winter season but 19.7-29.1, 19.9-24.8, 3.48-3.98, 1.17-1.21 and 0.82-1.09 during summer season, respectively. Similarly in *Catla catla* these HMs ranged (µg g^{-1}) in winter as 25.5-30.8, 21.8-28.1, 3.82-3.96, 1.22-2.42 and 1.57-1.63 but in summer 18.2-21.5, 14.8-19.9, 2.00-2.46, 1.08-1.15 and 0.54-0.60, respectively (Table III).

DISCUSSION

Fe, Zn, Cu, Cr and Ni concentrations in water, sediment and fish at Sulemanki Headworks were significantly greater (P<0.01) during the winter season as compared to summer. Lower concentrations of HMs in summer may be due to monsoon rains that diluted the River water. Average concentration of Fe in river water was 3.4 times higher than its permitted value of 0.2 mg L^{-1} (WHO, 1993). Zn concentration was 2.5 times greater than its' permitted limit of 0.1 mg L^{-1} (NEPA, 1989). Cu and Cr average concentrations were 17.5 and 15.7 times in excess as compared to their permitted limit of 0.01 mg L^{-1} (WHO, 1993; NEPA, 1989). Similarly the Ni concentration was 2.2 times higher than its permissible limit value of 0.02 mg L^{-1} (WHO, 1993).

Concentrations of Fe, Zn, Cu, Cr and Ni in sediments were about 2669, 523, 232, 233 and 496 folds higher as compared to water. Average concentration (µg g^{-1}) of Cu in sediments was 1.2 times higher than NOAA ERL permissible limit of 34 (Wang *et al.*, 2010). The concentrations of Zn, Cr and Ni in sediments were within Dutch permitted limit (µg g^{-1}) of 150, 100 and 35 respectively (Tabinda *et al.*, 2013).

Fish is consumed by humans as one of the main protein source and is a major part of human diet (Rashed, 2001). HMs contamination in water

Table I.- Heavy metals concentration in water from River Sutlej at Sulemanki Headworks (µg mL^{-1}).

		Fe	Zn	Cu	Cr	Ni
Water	Winter	0.77 ±0.001* (0.76-0.78)	0.39 ±0.001* (0.38-0.40)	0.25±0.001** (0.24-0.26)	0.22±0.001** (0.21-0.23)	0.07±0.001* (0.06-0.07)
	Summer	0.60 ± 0.003* (0.59-0.61)	0.10±0.001* (0.09-0.11)	0.09±0.01** (0.08-0.11)	0.09±0.001** (0.09-0.10)	0.02±0.001* (0.01-0.02)
	Average	0.69 ±0.12	0.25±0.20	0.17±0.10	0.16±0.89	0.04±0.03
Standard value	NEPA (1989)	-	0.10		0.01	
	WHO (1993)	0.20	-	0.01	-	0.02
Other studies	Lake Beysehir, Turkey (Altındag and Yigit, 2005)	-	-	-	28.0 (27.0–28.0)	-
	Buriganga River Bangladesh (Ahmad *et al*., 2010)	-	-	163±33.5	587±44.1	8.80±1.02
	San Carlos, Spain (Usero *et al.*, 2003)	8.00±1.00	12.0±2.00	1.60±0.20	0.50±0.10	2.30±0.20
	Lake Tanganyika, Tanzania (Chale, 2002)	0.01-0.04	<0.001	<0.006	-	-

*P<0.05 **P<0.01 ***P<0.001

Table II.- Heavy metals concentration in sediments from River Sutlej at Sulemanki Headworks (µg g^{-1}).

		Fe	Zn	Cu	Cr	Ni
Sediment	Winter	1848±10.6* (1837-1859)	127±2.29* (124-128)	47.2±1.91* (45.3-49.1)	40.1±1.49** (38.7-41.6)	25.5±2.56* (22.9-28.1)
	Summer	1808±19.9* (1788-1828)	124±5.40* (119-129)	31.7±3.03* (28.7-34.7)	29.8±3.43** (26.4-33.2)	18.1±0.95* (17.1-19.0)
	Average	1828. ±28.0	126 ±1.45	39.4±11.0	35.0±7.31	21.8±5.25
Standard value	NOAA ERL	-	150	34.0		
	Dutch Limit	-	-	-	100	35.0
Other studies	Lake Beysehir, Turkey (Altındag and Yigit, 2005)	-	-	-	10.6 (9.93–11.1)	-
	Buriganga River Bangladesh (Ahmad *et al*., 2010)	-	-	27. 9 ± 3.56	177 ±30.1	200 ± 29. 2
	San Carlos, Spain (Usero, 2003)	7480±300	98.0±6.00	31.0±1.00	67.0±1.00	30.0±1.00
	Lake Tanganyika, Tanzania (Chale, 2002)	-	2.18-28.4	3.64-20.8	-	-

*P<0.05 **P<0.01 ***P<0.001

introduces metal toxicity in fish which in turn can affect the human's health (Widianarko *et al*., 2000). Average concentrations of Zn and Cu in *Cirrhina mrigala, Labeo rohita and Catla catla* from Sulemanki Headworks were within the permitted limit of USEPA 100 µg g^{-1}. Cr concentrations in *Cirrhina mrigala*, *Labeo rohita and Catla catla* were 4.0, 3.7 and 3.0 times higher than its permissible limit of 0.491 µg g^{-1} (Papagianins *et al.*, 2004). Average concentrations of Ni in *Cirrhina mrigala*, *Labeo rohita* was 1.3 times *and* in *Catla catla* 1.1 times in excess as compared to its standard value of 1.00 µg g^{-1} (Papagianins *et al.*, 2004). Daily intake of HMs by the consumption of fish is presented in Table IV.

Fe, Cu, Cr and Ni in sediments were significantly correlated (P<0.05) with water which shows that these HMs re-suspend from sediments into water. Large amount of HMs are bound in sediments due to high surface area and content of humic substances (Tam and Wong, 2000). Due to movement of the aquatic organisms, HMs captured in sediments are re-released into water (Table V). Similarly Fe, Zn, Cu, Cr and Ni in water were

Table III.- **Heavy metals concentration in fish from River Sutlej at Sulemanki Headworks (µg g^{-1}).**

		Fe	Zn	Cu	Cr	Ni
Cirrhina mrigala	Winter	40.4±2.10* (38.4-42.6)	29.9±3.41* (26.5-33.3)	5.93±0.20* (5.73-6.13)	2.49±0.06*** (2.43-2.55)	1.76±0.12** (1.64-1.88)
	Summer	33.2±2.88* (30.3-36.0)	28.4±3.09* (25.3-31.5)	4.99±0.46* (4.53-5.46)	1.43±0.06*** (1.37-1.49)	0.80±0.17** (0.63-0.97)
	Average	36.8±5.17	29.1±1.06	5.46±0.66	1.96±0.74	1.28±0.67
Labeo rohita	Winter	34.9±3.18** (31.7-38.1)	24.6±4.48* (20.1-29.1)	4.84±0.70* (4.14-5.54)	2.41±0.09** (2.32-2.50)	1.68±0.10** (1.58-1.78)
	Summer	24.4±4.70** (19.7-29.1)	22.4±2.41* (19.9-24.8)	3.73±0.25* (3.48-3.98)	1.21±0.03** (1.17-1.21)	0.86±0.13** (0.82-1.09)
	Average	29.6±7.40	23.4±1.59	4.28±0.78	1.81±0.84	1.22±0.50
Catla catla	Winter	28.2±2.62* (25.5-30.8)	24.9±3.17* (21.8-28.1)	3.89±0.07* (3.82-3.96)	1.82±0.60* (1.22-2.42)	1.60±0.03*** (1.57-1.63)
	Summer	19.9±1.64* (18.2-21.5)	17.3±2.53* (14.8-19.9)	2.23±0.23* (2.00-2.46)	1.12±0.03* (1.08-1.15)	0.57±0.03*** (0.54-0.60)
	Average	24.0±5.86	21.2±5.38	3.06±1.17	1.47±0.49	1.09±0.72
Standard value	USEPA (2000)	-	100	100	-	-
	Canadian Food Standard (Papagiannis *et al.*, 2004)	-	-	-	0.491	1.00
Other studies	*L. cephalus* (Altındag and Yigit, 2005)	-	-	-	0.24 (0.12–0.36)	-
	C. carpio (Altındag and Yigit, 2005)	-	-	-	0.30 (0.30–0.31)	-
	Channa punctatus (Ahmad *et al.*, 2010)	-	-	5.28	5.39	9.58
	Mystus vittatus (Ahmad *et al.*, 2010)	-	-	4.19	6.28	8.73
	Liza aurata (Usero *et al.*, 2003)	4.11	3.87	0.20	0.02	0.02
	L. marie (Chale, 2002)	34.0	16.0	4.04	-	-
	L. stappersii (Chale, 2002)	33.0	18.0	3.40	-	-
	L. miodon (Chale, 2002)	125	101	3.60	-	-
	S. tanganicae (Chale, 2002)	196	133	5.90	-	-

*P<0.05 **P<0.01 ***P<0.001

Table IV.- **Daily metal intake (mg/kg/day) by the consumption of fish.**

Metals	Daily metal intake
Fe	0.0028
Zn	0.0023
Cu	0.0003
Cr	0.0002
Ni	0.0001

significantly correlated (P<0.05) with fish which shows accumulation of HMs into the fish tissue from water (Table VI). HMs become part of fish tissue as the HMs contaminated water passes through its gills and skin (Sonmez *et al.*, 2012). The HMs concentration order in fish species was *Cirrhina mrigala* > *Labeo rohita* >*Catla catla.* The difference in accumulations of HMs can be explained on the basis of their habitat in water body and dietary habits (Canli and Atli, 2003). *Cirrhina mrigala* is a bottom dweller fish having a high contact with sediments contaminated with HMs had highest accumulation of HMs in its tissue. *Labeo rohita* being mid water column dweller fish having comparatively low contact with sediments had medium concentration of HMs and *Catla catla* being upper column fish had lowest concentrations of HMs.

Table V.- Correlation of heavy metals between water and sediments.

		Water				
		Fe	**Zn**	**Cu**	**Cr**	**Ni**
Sediment	**Fe**	0.88*				
	Zn		0.34			
	Cu			0.98**		
	Cr				0.93**	
	Ni					0.93**

*P<0.05 **P<0.01

Table VI.- Correlation of heavy metals between water and fish.

		Water				
		Fe	**Zn**	**Cu**	**Cr**	**Ni**
Fish	**Fe**	0.96**				
	Zn		0.86**			
	Cu			0.97**		
	Cr				0.87**	
	Ni					0.95**

*P<0.05 **P<0.01

CONCLUSIONS

Water, sediment and fish from River Sutlej were contaminated with HMs due to industrial discharges. Significantly (P<0.05) higher metal concentrations were present in winter as compared to summer season as monsoon rains diluted the river water during summer. As the sediments had high concentrations of detected HMs therefore high concentrations of these HMs in water may be due to their re-suspension from the sediments. Among fish species analyzed HMs concentrations were highest in *Cirrhina mrigala* followed by *Labeo rohita* and *Catla catla.*

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