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Heavy Metal Contamination of Freshwater Fish and Bed Sediments in the River Ravi Stretch and Related Tributaries

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Abstract: Iron, zinc, lead, nickel and manganese contaminations in the river bed sediments and organs viz., scale, skin, muscle, gills, liver and kidney of freshwater fish, *Catla catla, Labeo rohita* and *Cirrhina* in the stretch of river Ravi (from Baloki headworks to Sidhnai barrage) and the related effluent discharging tributaries have been studied. Suspended matter and the soluble metallic ions had affected the quality of bed sediments significantly that resulted in the accumulation of metals in fish organs. Three fish species showed non-significant differences for the accumulation patterns of all metals except lead. The fish at Baloki headworks accumulated significantly higher quantities of iron and nickel in their bodies than those captured from Sdhnai barrage. However, the fish collected from Baloki headworks and Sidhnai barrage showed direct relationship ($r = 0.8997$) with the intensity of metal pollution in the bed sediments. Accumulation of iron in all the four fish organs showed statistically significant differences. Lead accumulation in both gills and liver were significantly higher than that in fish muscle and kidney. Fish liver was the organ that accumulated significantly higher quantities of nickel followed by that of kidney, gills and muscle. Both fish liver and kidney were the organs that accumulated significantly higher quantities of manganese than that of gills and muscle. Among the three fish species, *Cirrhina mrigala* showed significantly lower ability to accumulate lead in its body than that of *Catla catla* and *Labeo rohita.* Fish liver was the organ that accumulated significantly higher quantities of nickel, followed by that of kidney, gills and muscle.

Key words: River Ravi, *Catla catla, Labeo rohita, Cirrhina mrigala,* bed sediments, bio-accumulation

INTRODUCTION

Human destructive influence on the aquatic environment is in the form of sublethal pollution, which results in chronic stress conditions that have a negative effect on aquatic life. Under normal circumstances, metals which are mainly beneficial, indeed essential, such as copper and zinc, may become pollutants when present in excess by exhibiting toxic effects on aquatic organisms[1,2]. In aquatic ecosystem, heavy metals have received considerable attention due to their toxicity and accumulation in biota[2,3] and fish[4]. In fish, the toxic effects of heavy metals may influence physiological functions, individual growth rates, reproduction and mortality[5,6]. Heavy metals may enter fish bodies in three possible ways; through the body surface, gill or the digestive tract[7-9]. Food may also be an important source for heavy metal accumulation in fish[10-11] due to polluted water[12], sediments and potentially leading to bio-magnification, the increase of pollutants to the food chain[2]. With the rapid increase in industrialization in Pakistan, the water pollution has become a serious problem as the industrial effluents and domestic sewage, containing bulk quantities of toxic heavy metals, are being continuously discharged into the rivers. Heavy discharge of metals and their compounds into the river system of Pakistan in general and of the Punjab province in particular has adversely affected the freshwater fisheries. This points towards desperate need for assessing the problem and to develop methods for eliminating the ill-effects of the pollutants like zinc, iron, manganese, cadmium, lead and nickel in the natural freshwaters.

MATERIALS AND METHODS

The stretch of river Ravi, from Baloki headworks to Sidhnai barrage, was monitored at five sampling sites viz. Baloki headworks, Syed wala, Marii pattan, Kamalia-Chichawatni (KC) bridge and Sidhnai barrage and, three effluent discharging tributaries, Degh nulla, Samundri and Sukhrawa main drains at their discharging points into the river. Sediment samples were collected on fortnightly basis. This research work was conducted for a period of one year i.e. from September, 2003 to August 2004. Each sampling station was divided into three sub-sampling stations within a diameter of 100 m by following the proportionate sampling procedure. Samples were collected with the help of a iron pipe (dia = 2 inches) pressed with pressure through the water column to obtain a sediment layer of about one foot. Sediment samples collected from the three sub-sampling stations, at each of the station, were mixed to have a composite sample. Concentration of metals viz., iron, zinc, lead, nickel and manganese in bed sediments were determined by following the methods of SMEWW[13]. Fish samples were collected on monthly basis with the sample size of five for each fish species from the river stretch at Baloki headworks and Sidhnai barrage as fish were only available at these two points. Fish were dissected and their organs viz., kidney, liver, gills and muscle were taken for the determination of metals. After wet digestion of the samples, in Perchloric acid, Hydrochloric acid and Nitric acid, the volumes were prepared for the detection of heavy metals. The samples of sediments for heavy metals determination by Atomic Absorption Spectrophotometer were prepared according to Parker[14], Harding and Whitton[15] and SMEWW[13] methods. Analysis of variance and DMR tests were performed to find-out statistical differences among various parameters[16].

RESULTS

Iron concentrations in sediment samples fluctuated significantly at various sampling sites. However, there were non-significant differences among Baloki headworks, Syed wala, K.C. bridge, Sidhnai barrage and Samundri main drain and, between Degh nulla and Sukhrawa main drain. The sediments at both Degh nulla and Sukhrawa main drain showed the highest iron contaminations of 17639.37±4096.42 and 16082.00±3071.16 $\mu g\ g^{-1}$ respectively. However, the difference between these two tributaries was non-significant. Marii pattan showed the lowest mean iron contamination of 9343.26±2755.02 $\mu g\ g^{-1}$ (Table 1). Sediments collected from Samundri main drain showed the mean highest zinc contamination of 920.41±285.89 $\mu g\ g^{-1}$ while was minimum at Baloki headworks (167.59±23.08 $\mu g\ g^{-1}$). The sediments at Baloki headworks had the mean annual highest lead concentration of 135.97±21.81 $\mu g\ g^{-1}$ while lowest at Sidhnai barrage (40.83±11.91 $\mu g\ g^{-1}$). Sediments at Samundri and Sukhrawa main drains showed the mean annual lead contaminations of 121.91±13.73 and 122.81±16.25 $\mu g\ g^{-1}$ respectively. However, both the drains showed non-significant differences for the accumulation of lead in their sediments (Table 1). Sediment samples collected from Samundri main drain showed the mean annual highest nickel contamination of 274.02±42.98 $\mu g\ g^{-1}$ while the lowest (145.02±47.93 $\mu g\ g^{-1}$) at Sidhnai barrage. Other sampling stations showed statistically significant variations for their nickel concentrations also. Sediments collected from various sampling stations showed statistical differences for the concentration of manganese. The sediments at K.C. bridge were highly polluted with manganese having the mean annual concentration of 2389.71±794.22 $\mu g\ g^{-1}$ while lowest at Sukhrawa main drain that exhibited the mean annual contamination level of 293.01±31.04 $\mu g\ g^{-1}$.

Three fish species viz., *Catla catla, Labeo rohita* and *Cirrhina mrigala* captured from Baloki headworks and Sidhnai barrage were examined for their metallic ion concentrations. There existed highly significant differences among the fish organs for the accumulation of all the heavy metals (Table 2). However, fish species showed non-significant differences for the bio-accumulation pattern of all metals, except lead. Sites of fish collection differed significantly as far as bio-accumulation of iron and lead in fish body. The fish at Baloki headworks showed significantly higher iron and nickel in their bodies than that obtained from Sidhnai barrage. Accumulation of iron in all the four organs of fish showed statistically significant differences. However, accumulation differences of zinc in fish muscle, gills and kidney were statistically significant. Lead accumulation in both gills and liver were significantly higher than that in fish muscle and kidney. Fish liver was the organ that accumulated significantly higher quantities of nickel, followed by that of kidney, gills and muscle. Both fish liver and kidney were the organs that accumulated significantly higher quantities of manganese than that of gills and muscle. Among the three fish species,

Table 1: Metals toxicity ($\mu g\ g^{-1}$±SD) in bed sediments

Sampling station	Iron	Zinc	Lead	Nickel	Manganese
River Site					
Baloki Headworks	12206.17±3439.82a	167.59±23.08c	135.97±21.81a	180.69±62.11b	1635.99±480.29c
Syedwala	12208.33±4349.88a	396.19±202.28ab	133.29±45.87a	184.16±74.86ab	1473.41±1257.16d
Mari Pattan	9343.26±2755.02b	335.00±81.48b	78.36±18.44b	167.87±46.94cd	1802.74±664.08bc
K.C. Bridge	12744.95±4074.40a	387.21±104.75ab	89.55±17.46b	162.28±48.19cd	2389.71±794.22a
Sidhnai Barrage	11905.50±1769.32a	196.85±78.49c	40.83±11.91c	145.02±47.93d	1445.71±352.98d
Tributaries					
Degh nulla	17639.37±4096.42a	419.22±107.67b	78.73±21.67b	198.06±70.61b	1780.91±573.86a
Samundri main drain	13257.86±3297.79b	920.41±285.89a	121.91±13.73a	274.02±42.98a	1977.00±668.86a
Sukhrawa main drain	16082.00±3071.16a	294.77±55.89c	122.81±16.25a	208.80±72.54b	293.01±31.04b

Means with similar letters in a single column are statistically similar at $p<0.05$

Table 2: Metal concentrations (µg g⁻¹) in different organs of three fish species

Variable	Mean square				
SOV	Iron	Zinc	Lead	Nickel	Manganese
Fish organs	($p<0.01$) 136971.66	($p<0.01$) 2841.02	($p<0.01$) 37.42	($p<0.01$) 66.95	($p<0.01$) 91.51
Fish species	NS 895.89	NS 231.75	($p<0.01$) 31.70	N.S. 0.005	N.S. 8.15
Fish collection sites	($p<0.05$) 299.95	N.S. 189.06	N.S. 11.00	($p<0.05$) 1.68	N.S. 16.02
Comparison of means (µg g⁻¹)					
Fish Organs					
Muscle	69.49d	75.42c	7.58b	1.73c	9.02b
Gills	291.40b	83.20bc	12.55a	3.45b	11.27b
Liver	431.30a	124.90a	12.54a	9.45a	17.49a
Kidney	213.60c	91.64b	9.13b	3.97b	15.70a
Fish species:					
Catla catla	260.86a	98.90a	12.29a	4.67a	14.39a
Labeo rohita	253.52a	94.28a	10.72a	4.65a	13.35a
Cirrhina mrigala	239.99 a	88.17a	8.34b	4.62a	12.37a
Site of fish collection					
Baloki Headworks	263.45a	96.59a	11.13	4.91a	14.19a
Sidhnai Barrage	239.47b	90.98a	9.77	4.39a	12.55a

Means with similar letter in a single column are statistically similar at $p<0.05$ NS: Non-significant

Cirrhina mrigala showed significantly lower ability to accumulate lead than that of *Catla catla* and *Labeo rohita*. Accumulation of all metals in fish body organs showed positive correlation ($r = 0.8996$) with the intensity of metallic pollution in sediments at both Baloki headworks and Sidhnai barrage.

DISCUSSION

In comparison to stagnant waters, flowing water is a particularly complex situation for rivers, alter not only through cyclic, seasonal progressions, but also along their lengths, according to their depth, gradient rate of flow, geology, salt concentration, turbidity etc. Thus, there is a multitude of biological habitats. Pollutants introduced into the river are naturally carried downstream but, after initial mixing, do not become further diluted except because of confluence with other water source. Removal of pollutants then depends upon their biological degradation or decomposition. The present study revealed that bulk discharge of industrial wastes and domestic sewage, through three main tributaries, into the river has adversely affected the quality of river bed sediments. However, the maximum contribution was made by the flow of metal contaminated water received from Baloki headworks due to high discharges at river upstream through tributaries like Farrukhabad, Munshi hospital, Taj company, Bakkar mandi and Hudiara nullas and 1st Degh fall[17]. Wang and Tang[18] studied the chemical, toxicological and ecological parameters in LaAn river in China and reported that water and sediment pollution has affected the aquatic ecosystem due to effluent discharges into the river. Sediment pollution associated with the moderate biological and ecological deterioration prevailed in downstream of the river. There are numerous sources of domestic and industrial effluents leading to heavy metal enrichment of water, sediments, vegetation and fish in rivers. A knowledge of the distribution of heavy metals in water, sediments, plankton and fish play a key role in detecting sources of heavy metal pollution in aquatic system. Significantly higher concentrations of metals in water of the effluent discharging tributaries were the resultant of industrial and municipal waste water increasing the heavy metal toxicity of river bed sediments significantly. Javed and Hayat[12] and Javed[17] reported significantly higher metals toxicity of river Ravi stretch from Shahdera to Baloki headworks due to bulk discharges of untreated industrial and domestic wastes into the river Ravi. In general, the source and extent of metallic ion pollution in aquatic habitat are dependent upon the toxicity of heavy metals in sediments[19]. Significantly higher contaminations by all metals was found at the three effluent discharging tributaries than that in the river. The occurrence of such quantities of heavy metals in sediments have resulted to the precipitation of their hydroxide, carbonates and sulfides which settled down and form the part of sediment. However, the composition of these precipitations is greatly influenced by various hydrochemical conditions of the water body.

Muscle, gills, liver and kidney of three fish species (*Catla catla, Labeo rohita* and *Cirrhina mrigala*), examined for the accumulation of five metals, showed significant differences due to their ability to concentrate heavy metals. However, among the three fish species, *Catla catla* showed significantly higher tendency for the accumulation of all metals in its body. The metal accumulation trends at two fish sample collection sites varied significantly for the accumulation of iron in the three fish species also. However, the fish at Baloki Headworks showed non-significantly higher metal viz., zinc, lead, nickel and manganese accumulations than those obtained from Sidhnai barrage. The heavy metal contents of the aquatic animals originates from two roots of intake, free ions and simple compounds dissolved in water or taken up directly through the epithelium of the skin, gills and elementary canal while others, having been accumulated in food organisms or incorporated by nutrition. Thus, the heavy metals when discharged into the river, enter the food chain (plankton being the major food items of the three major carps) and accumulated in the fish body as determined during this investigation. Javed and Hayat[20] reported that *Catla catla* had significantly higher ability to accumulate metals in its body than *Labeo rohita* and *Cirrhina mrigala*. Among the four fish organs, fish liver showed the highest tendency of metal accumulation. Amundsen *et al*.[21] reported that in white fish the heavy metal accumulation was usually lowest in muscle and highest in the liver or the gills. Heiny and Tale[22] observed that trace element concentrations in fish liver generally did not follow the same pattern to concentrate in bed sediments. However, fish liver showed higher tendency to concentrate heavy metals in it. Seymore *et al*.[23] while working on the bio-accumulation of chromium and nickel in selected tissues and organs of the fresh water fish, *Barbus marequensis*, recorded that nickel was mainly accumulated in the blood, followed by that in vertebrae tissue. El-Shahawi and Al-Yousaf[24] reported that in fish, the levels of nickel, cobalt, lead and chromium was found to follow the order: liver > skin. Metal levels found in liver and skin followed the sequence: chromium > lead > nickel > cobalt. However, during this study the fish organs accumulated zinc, nickel and manganese followed the order: liver > kidney > gills > muscle while iron showed: liver > gills > kidney > muscle while for lead accumulation in fish was: gills > liver > kidney > muscle.

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