

# Impact of anthropogenic activities on physico-chemical parameters of water and mineral uptake in *Catla catla* from river Ravi, Pakistan

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**Abstract** The river Ravi, while passing through Lahore, the second largest city of Pakistan, gets highly polluted owing heavy loads of untreated municipal sewage and industrial effluents of diverse kinds. The fish, *Catla catla* sampled in two different seasons from three downstream polluted sites were compared with the samples of the same fish from an upstream, a less polluted site, for their physico-chemical parameters. The data were statistically analysed to study the effect of sites, seasons and their interaction on the physico-chemical parameters of waters and mineral uptake in fish muscles. Significant differences ( $P < 0.001$ ) among the sampling sites and seasons were observed. The river appeared to be polluted as indicated by the high values of total suspended solids (909 mg/l) and sulphate (964 mg/l) in comparison to the respective values of 150 and 600 mg/l being suggested as the safer values of drinking water of the National Environmental Quality Standards. Most trace and macro elements in fish muscles were increased with the increasing pollution loads from the upstream to the downstream sites of this river. The remarkable increases in the levels of all the

investigated minerals in fish muscles from the polluted sites raise concerns about the long-term health of the river Ravi ecosystem and consequently the fish and its consumer's health. The results contradict the opinion of the local population that the riverine fish are natural, more health-promoting and precious than the pond fish. Therefore, we strongly argue for the utilization of an effect-based monitoring approach to alleviate the detrimental effects of anthropogenic activities on fish and the fish consumers' health.

**Keywords** River Ravi · Urban sewage · Carp · Mineral bioaccumulation · ICP-OES

## Introduction

Rivers are important components of freshwater ecosystems. The availability of these natural water systems has been a directional factor in the development of various civilizations in their vicinities (Benjamin et al. 1996). Accordingly, historic and major cities are mostly located alongside rivers. Rivers have been providing water for drinking, irrigation, soil fertility and transport alongside food to humans. Unfortunately, the cities in return have been dumping their solid and water waste into these rivers. Initially, these wastes were of domestic origin to which soon joined the industrial activities. In developing countries, heavy industrial development to meet the needs of increasing populations, have been contaminating rivers through

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effluents loaded with different chemicals. For these reasons, awareness about the effects of anthropogenic pollution on freshwater ecosystems has gradually increased and has become a matter of concern over the last few decades (Mahmood 2003; Vutukuru 2005).

The river Ravi originates in the mid-Himalayas of Himachal Pradesh, India from the glaciers from where it follows the north western path in India. The river Ravi is a trans-boundary river entering Pathankot at Chaundh and forms a boundary between India and the state of Jammu and Kashmir for 23 miles and then enters in Pakistan through the village Tadyal, Kot Naina, Shakargarh Tehsil of Sialkot from where it joins the Ujh river. The river Ravi while flowing through Lahore becomes just like a wastewater carrier with high discharge variation of 270–81,000 ft<sup>3</sup>/s. The flow in river Ravi is highly variable and seasonal variation in waste water is less as compared to the river water fluctuations which result in higher concentration of contaminants during low-flow periods of the river. There are more than seven pumping stations along the river discharging the municipal sewage of Lahore city into the river. Furthermore, there are two drains (Hudiarra drain and Deg Nullah) which dispose of industrial effluents into the river Ravi. Hudiarra drain is one of the major sources of pollution for the river. It enters Pakistan loaded with pollutants of around 100 industries located adjacent to the Hudiarra drain on the 55 km Indian side and more than 112 industries located next to the drain as it travels 63 km through the Punjab, Pakistan. Deg Nullah carries the effluents from Kala Shah Kaku industrial complex, which has more than 149 industrial units. Some industries on Lahore-Sheikhupura road also discharge their wastewater into the drain (Saeed and Bahzad 2006). The untreated industrial effluents are adding reasonable amount of toxic metals into the river Ravi (Rauf et al. 2009).

This study was aimed at analyzing the bioaccumulation of Cd, Pb, Cr, Mn, Zn, Cu, Fe, Ni and Na, K, Ca, P and Mg in the fish *Catla* (*C.*) *catla* (thaila) sampled from an upstream and three downstream locations for verifying the effects of urban pollutants on these fish as a representative of the fauna of the river Ravi.

*C. catla* is a eurythermal species that grows best at water temperatures between 25–32 °C. The fry and adult fish are planktophagic with their specific surface feeding habits. The human inhabitants of the river's

surrounding area prefer this fish due to its rapid growth, size and taste. Since the carp's natural breeding requires a riverine environment and it does not occur within ponds, it is vital for the concerned authorities to maintain fish health, reproduction and meat quality through regular assessment of the bioaccumulation of pollutants in tissues of this species inhabiting different river water systems in Pakistan. The present study reports the effects of urban pollution loads in the form of different minerals on minerals uptake in muscle of *C. catla* collected from different sites during low- and high-flow seasons of the same year.

## Materials and methods

### Brief description of sampling sites

Four sampling sites as low, medium, moderate and high polluted alongside the upstream and downstream sites of the river Ravi were selected to evaluate the pollution levels in water and fish samples as described below:

#### *Site A: Lahore Siphon as the upstream and low polluted site*

This upstream sampling site, situated near village Talwara Par (31° 41' N and 74° 25' E) was least disturbed and polluted with relatively good water quality. Marala Ravi Link canal joins the river Ravi approximately 15 km upstream of this sampling site which diverts the water from river Chenab and minimizes anthropogenic impacts on water quality. No point source pollution at this site was identified. However, the locality does receive some contaminants from the agricultural runoff. The river bed at this site is made of predominantly sand whereas this site had turbid water which did not allow the determination of its surface current.

#### *Site B: Shahdera as the first downstream and medium polluted site*

This downstream sampling site is situated near old Ravi Bridge, Lahore (31° 36' N and 74° 18' E). Up to this site, the river Ravi receives untreated municipal sewage effluent of Lahore city from three major pumping stations (North East and Shad bagh on the left and Shahdera on the right side of the river). This

site is under considerable stress due to the solid waste dumping on the bank where the urbanized over-crowded towns are located. This site was muddy and sandy and its water was blackish, smelly and slow moving especially at the low-flow time of the year.

*Site C: Sunder as the second downstream and high polluted site*

This sampling site is situated near village Nano Dogar (31° 21'N and 74° 3'E) where it receives untreated municipal wastewater from four major pumping stations of Lahore city. Besides, there are two main drains namely Hudiana Drain and Deg which dispose off their urban and industrial effluents into the river Ravi. Inflow of previously sewage-polluted water plus the drains effluents together make it a highly polluted site. The bed of the river was represented by mosaic mud and sand. The river water at this site was very slow moving, blackish and smelly, especially during the low-flow time.

*Site D: Balloki headworks as the third downstream and moderate polluted site*

This site is located near Head Balloki (31° 13' N and 73° 52' E) where the Qadirabad (Q.B.) Link Canal joins the river Ravi downstream between sites C and D. No point source pollution at this site was identified; however, this segment does receive some contaminants from agricultural runoff. The bed of the river at this site consisted of sand and contained turbid water.

#### Water sampling

Each sampling site was divided into three sub-sampling sites (radius ~40 m) at mostly equal distance from each other. Water samplings were carried out 1 day before fish sampling. The water samples were collected from each of these sites during low- (Nov–Dec 2009) and high-flow (Sep–Oct 2010) seasons of the river in labelled clean plastic bottles. Duplicate water samples for physico-chemical analysis were collected in sterilized screw-capped bottles from 30–40 cm below the water surface from the mid of river with the help of a wooden boat. The bottles were opened under water after immersing them to the desired depths and after sampling they were immediately capped. All water samples were then transported to the

laboratory in the ice box and stored at 4 °C in refrigerator.

#### Fish sampling

Fish specimens of *C. catla* were collected from the above mentioned sampling sites of the river during the low- and high-flow seasons. Services of the professional fishermen were hired for the fish collection by using locally made patti (Gill nets) of about 6 feet wide and 40 feet long with a cork line at the top rope and metal line with the ground nylon rope. The four fishermen on two manually driven wooden boats shared a single gill net. Nine fish specimens of similar sizes were saved out of the fish collected from triplicate nettings per site. Each fish specimen was washed with water and drained before their transfer to separate polythene bags which were then immediately placed in ice and transported to the laboratory. After morphometric measurements, the fish were dissected to collect muscle tissues into labelled sterilized polythene bags for their storage in a freezer at –20 °C until further analysis.

#### Physico-chemical analysis

Water temperature was measured at the time of sampling by immersing a mercury glass thermometer (°C). Standard methods (APHA 1985) were followed for the estimation of various physico-chemical parameters of the sampled water. For estimating total suspended solid, about 100 ml of each water sample was filtered thrice through a dried pre-weighed filter paper (Whatman No. 541). The filter papers were then dried in an oven at 105 °C for 1 h and re-weighed after cooling in a desiccator to determine the total suspended solids as milligrams per liter. For assessing total dissolved solids, 100 ml of a given water sample was filtered through a pre-weighed filter paper and the filtrate added to a pre-weighed evaporating dish. The filtered sample was evaporated to dryness on water bath and then dried in an oven at 105 °C for 1 h. The dish was weighed after cooling in a desiccator. Total dissolved solids were then determined and reported as milligrams per liter. Parameters like dissolved oxygen (DO) were analysed by Winkler's method while Ca, Mg and total hardness were worked out by standard EDTA titration method (APHA 1985). The chloride contents were measured by argentometric method whereas total alkalinity and ammonia were determined

by titrimetric and Nessler's methods, respectively. Stannous chloride colorimetric method was used for the phosphate estimation while sulphate and nitrite contents were analysed by EDTA titrimetric and diazotization methods (APHA 1985). Phenoldisulfonic acid method was used for the estimation of nitrate (Garg et al. 2000).

#### Analysis of fish muscles

Frozen fish muscle samples were carried out at the Newcastle University, UK by the prior authorisation of the Secretary of State for DEFRA under regulation 4, products of Animals Origin Regulation in July, 2011. The muscle samples were stored at  $-20^{\circ}\text{C}$  on arrival. Before the analysis, the tissues were freeze dried and ground and about 1 g of each freeze dried muscle tissue was mixed with about 10 ml of 55 % nitric acid in a flask at room temperature. The flasks were then placed on a hot plate to digest the tissues. Dense white fumes after brown fumes from the flask indicated completion of the digestion process. The mixture was evaporated at  $200\text{--}250^{\circ}\text{C}$  until a clear solution was obtained, which was further evaporated up to 0.5 ml. Digested sample from each flask were cooled and diluted to 20 ml with distilled water by properly rinsing the digestion flasks and filtered through the filter paper (Whatman No 541). Finally, the solution was transferred into a plastic screw-capped container (20 ml) which was placed in a refrigerator until analysis. A Varian Vista-MPX CCD Inductively coupled plasma optical emission spectroscopy (ICP-OES Varian Inc, Australia) machine was calibrated over the relevant concentration of individually certified standards. Ca, Zn, Ni, Cu solutions (May & Baker Ltd, UK),  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$  solutions, Cd (cadmium coarse powder), Cr (chromium (III) chloride 95 %), Na (sodium chloride 99.5 %) (BDH chemicals, UK), P (sodium phosphate  $\geq 99\%$ ; Sigma-Aldrich, Gillingham, UK), K (potassium chloride 99.8 %; Fisher Scientific, Loughborough, UK) were used to prepare standard solutions. Mineral concentrations in muscle samples were then recorded in milligram per kilogram dry weight (in milligrams per kilogram DM).

#### Statistical analysis

The data were statistically analysed by using general linear model in Minitab software to find the effect of either site or season or site  $\times$  season interaction on

water quality (physico-chemical parameters) and mineral profiles in fish muscles. The effect of these factors were declared highly significant if  $P < 0.001$ , very significant if  $P < 0.01$  and significant if  $P < 0.05$ . Tukey's post-hoc test was used if there were more than two means to compare for their significant differences at  $P < 0.05$ .

#### Results

Mean values of various physico-chemical parameters of water samples from the four sampling sites for both the flow seasons are presented in Table 1. All parameters showed highly significant difference ( $P < 0.001$ ) between seasons and sites. The parameters, except temperature, dissolved oxygen, total alkalinity, Ca, Mg and total hardnesses, and ammonia showed site  $\times$  season interaction ( $P < 0.05$ ). Furthermore, all the parameters, except total suspended solids and sulphate, fell within the permissible ranges of the National Environmental Quality Standard (National Environmental Quality 2001) for municipal and liquid industrial effluents in Pakistan.

Mean temperature ranged from  $24.1^{\circ}\text{C}$  for upstream (site A) to  $24.9^{\circ}\text{C}$  for downstream sites during high-flow and  $22.9$  to  $23.5^{\circ}\text{C}$  during the low-flow season. The site C showed maximum temperature in both flow seasons. Dissolved oxygen decreased up to  $3.8\text{ mg O}_2/\text{l}$  at site C during the low-flow season. However, its values at site A (upstream) were not significantly different at both seasons ( $P > 0.05$ ). Total dissolved solids significantly varied downstream and showed higher values during low than the high-flow season ( $P < 0.01$ ). Highest value of  $948\text{ mg/l}$  at site C during low flow was 5.76-fold higher in comparison with that of the upstream location during the high-flow season. Lowest total suspended solids with a value of  $213\text{ mg/l}$  were recorded at site A during the low-flow season while the highest corresponding value ( $909\text{ mg/l}$ ) was found for the site C during the high-flow season. These values were much higher than the recommended value of  $150\text{ mg/l}$  by National Environmental Quality (2001). Total alkalinity ( $240$  to  $318\text{ mg/l}$  and  $176$  to  $254\text{ mg/l}$ ) and hardness ( $210$  to  $307\text{ mg/l}$  and  $156$  to  $271\text{ mg/l}$ ) significantly increased downstream during both low- and high-flow seasons, respectively than the corresponding values for the upstream location. Similarly, both nitrite and nitrate contents increased among downstream sites during low flow as compared to the

**Table 1** Means (mg /L, unless otherwise mentioned) of physico-chemical parameters of water from different sites of the river Ravi

Parameter	A		B		C		D		SEM and Significance		
	Low	High	Low	High	Low	High	Low	High	Site	Season	Site × season
Temperature (°C)	22.87e	24.10c	23.30d	24.67ab	23.53d	24.93a	22.83e	24.43b	0.049***	0.034***	0.068ns
Dissolved oxygen	5.23a	5.37a	4.30c	4.63b	3.80f	4.17e	4.13e	4.40d	0.031***	0.022***	0.044 ns
Total dissolved solids	580c	165g	675b	267f	948a	437d	741b	360e	10.20***	7.21***	14.43**
Total suspended solids	213f	354e	424d	564c	695b	909a	542c	734b	8.025***	5.674***	11.349*
Total alkalinity	240c	176e	260c	201d	288b	225c	318a	254c	3.224***	2.280***	4.560ns
Ca hardness	156c	109d	170c	131cd	198b	152c	234a	206b	3.798***	2.685***	5.371ns
Mg hardness	54.0c	47.7c	62.3b	51.7c	67.3ab	54.7c	72.3a	65.3ab	1.349***	0.954***	1.908ns
Total hardness	210c	156d	232.7c	182.7cd	265.3b	206.7c	306.7a	271.3b	4.310***	3.048***	6.095ns
Nitrite	1.12f	0.53f	3.68d	2.07e	6.98a	4.62c	5.47b	3.80d	0.106***	0.075***	0.150***
Nitrate	3.86f	1.63g	8.62c	4.18ef	11.17a	5.43d	10.05b	4.88de	0.130***	0.092***	0.183***
Phosphate	1.60e	0.66e	6.46b	4.16c	8.34a	6.14b	2.66d	1.96d	0.141***	0.100***	0.200**
Chloride	63.20f	29.50g	167.47c	99.50e	286.17a	179.80c	216.07b	132.20d	3.495***	2.472***	4.943**
Ammonia	0.337ef	0.217f	0.750c	0.593d	1.220a	0.940b	0.550d	0.363e	0.020***	0.014***	0.027ns
Sulphate	387d	329d	646b	488c	964a	679c	791b	620c	12.300***	8.696***	17.392***

Sites: Siphon (upstream = A); Shahdera = B; Sunder = C; and Head balloki = D; with two seasons (low and high flow)

Means within the same row with the same letters did not differ significantly ( $P > 0.05$ ); here \*, \*\* and \*\*\* represent significance at  $P < 0.05$ ,  $P < 0.01$  and  $P < 0.001$ , respectively

high-flow season. The nitrite content for the site C appeared two folds higher than the value obtained for the site B. Furthermore, the nitrate contents in water samples were higher than the nitrite contents. Similarly, phosphate, chloride and ammonia at site C during the low-flow season showed 12.6-, 9.7- and 5.6-fold increases, respectively over the respective values for the upstream site A. The sulphate contents were higher in water sampled at sites C (60.6 %) and D (31.8 %) during low flow as compared to the value of 600 mg/l proposed by National Environmental Quality (2001). The parameter, however, did not significantly differ during low- and high-flow seasons for the upstream site A (Table 1).

The data in Table 2 present mean total length (in centimeters), weight (in grams) and moisture contents of fish or their muscles for the different sites and seasons. Total lengths and weights of netted fish specimens were not significantly different ( $P>0.05$ ) between seasons and sampling sites. However, moisture contents of muscles had significant differences for the sites ( $P<0.001$ ), whereas season and site  $\times$  season interaction for the moisture contents were not significant ( $P>0.05$ ).

Table 3 shows mean concentrations of macro and trace elements in milligrams per kilogram of freeze dried muscles of *C. catla* being collected from different sites in two seasons. All macro elements (Ca, Mg, K, Na, P) showed significant differences among sites and seasons, whereas their site  $\times$  season interactions were non-significant ( $P>0.05$ ), except for the Ca, Na and P contents. All macro element mean concentrations were higher during low-flow than high-flow and pattern among the sites was site C > site B > site D > site A, except Mg. The order of mean concentration of these element was Ca > P > Na > Mg > K.

Trace element (Cd, Cr, Cu, Pb, Mn, Ni, Zn, Fe) concentrations in the muscles of *C. catla* being

collected from different sites of the river Ravi are presented in Table 3. All metals showed significant differences among the sites and seasons. However, site  $\times$  season interactions were non-significant, except for the Cd, Cr, Mn and Zn. The fish muscles showed highest concentration of Zn (50.41 mg/kg) while lowest for Cd (0.03 mg/kg). The order of metal bioaccumulation in muscle was zinc > iron > manganese > chromium > copper > lead > nickel > cadmium. The fish muscles that were sampled from site C accumulated Cd (467 %), Cr (438 %), Cu (77 %), Pb (1626 %), Mn (374 %), Ni (386 %), Zn (122 %) and Fe (78 %) as compared with the respective values for fish collected from the upstream site (A) during low-flow season (Table 3).

## Discussion

Downstream water temperature significantly increased as compared to the upstream site A but only up to the site C after which it was reduced at site D. All water bodies are subject to daily and seasonal variations due to the depth of aquatic system. The flowing water was reported to lack wide fluctuations in temperatures (Leonard 1971). Downstream changes of temperature may be attributed to the addition of sewage and industrial effluents which in turn might have contributed in enhancing the microbial activities as bacterial C.F.U. also increased likewise for the sites (unpublished data for the same sites). The reduction in temperature at site C may be a reflection of the recovery of quality of river water which improved gradually between the sampling sites C and D due partly to the merging of Q.B. link canal into the river and partly because of the microbial decomposition activities occurring during the downstream segment of the same river. In short,

**Table 2** Mean total length, weight and moisture contents of muscles of *C. catla* (Thaila) collected from different sites of the river Ravi

Parameters	A		B		C		D		SEM with significance		
	Low	High	Low	High	Low	High	Low	High	Site	Season	Site $\times$ season
Total length (cm)	34.20	34.35	34.10	34.25	34.05	34.35	34.10	33.95	0.411	0.291	0.581
Weight (g)	466	475	478	479	480	487	468	473	21.9	15.5	31.0
Muscle moisture (%)	74.69	74.92	74.13	74.78	71.41	71.98	72.75	73.38	0.281***	0.199	0.398

Sites = upstream = A; Shahdera = B; Sunder = C; and Head balloki = D; with two seasons (low and high flow)

Here \*, \*\* and \*\*\* represent significance at  $P<0.05$ ,  $P<0.01$  and  $P<0.001$ , respectively

**Table 3** Mean concentration (mg/kg) of macro and trace elements in muscles of *C. catla* (Thaila) sampled from different sites of the river Ravi

Elements	SEM with significance													
	A		B		C		D		Site		Season		Site × season	
	Low	High	Low	High	Low	High	Low	High	Site	Season	Site	Season	Site × season	
<b>Macro</b>														
Ca	4562	2886 <sup>f</sup>	13782 <sup>b</sup>	7843 <sup>d</sup>	26769 <sup>a</sup>	10006 <sup>c</sup>	7382 <sup>d</sup>	5866 <sup>de</sup>	250.26 <sup>***</sup>	176.96 <sup>***</sup>	353.92 <sup>***</sup>			
Mg	571.7 <sup>ab</sup>	458.7 <sup>c</sup>	600.7 <sup>a</sup>	485.5 <sup>bc</sup>	626.8 <sup>a</sup>	612.3 <sup>a</sup>	656.3 <sup>a</sup>	594.9 <sup>a</sup>	12.43 <sup>***</sup>	8.79 <sup>***</sup>	17.58			
K	3066 <sup>cd</sup>	2560 <sup>d</sup>	3900 <sup>ab</sup>	3398 <sup>bc</sup>	4500 <sup>a</sup>	3782 <sup>abc</sup>	3365 <sup>bc</sup>	3309 <sup>b</sup>	91.74 <sup>***</sup>	64.87 <sup>**</sup>	129.74			
Na	3405 <sup>bc</sup>	2903 <sup>c</sup>	4841 <sup>b</sup>	4029 <sup>bc</sup>	7502 <sup>a</sup>	4555 <sup>bc</sup>	3934 <sup>bc</sup>	3811 <sup>bc</sup>	231.72 <sup>***</sup>	163.85 <sup>**</sup>	327.70 <sup>*</sup>			
P	6005 <sup>de</sup>	4724 <sup>e</sup>	9686 <sup>b</sup>	7300 <sup>cd</sup>	15613 <sup>a</sup>	8348 <sup>bc</sup>	7064 <sup>cd</sup>	6690 <sup>d</sup>	191.17 <sup>***</sup>	135.18 <sup>***</sup>	270.36 <sup>***</sup>			
<b>Trace</b>														
Cd	0.03 <sup>e</sup>	0.03 <sup>e</sup>	0.07 <sup>c</sup>	0.06 <sup>cd</sup>	0.17 <sup>a</sup>	0.11 <sup>b</sup>	0.04 <sup>de</sup>	0.04 <sup>de</sup>	0.003 <sup>***</sup>	0.002 <sup>***</sup>	0.005 <sup>***</sup>			
Cr	1.06 <sup>e</sup>	0.96 <sup>e</sup>	2.22 <sup>c</sup>	1.93 <sup>c</sup>	5.70 <sup>a</sup>	2.93 <sup>b</sup>	1.49 <sup>d</sup>	1.21 <sup>de</sup>	0.053 <sup>***</sup>	0.037 <sup>***</sup>	0.075 <sup>***</sup>			
Cu	3.20 <sup>de</sup>	2.87 <sup>e</sup>	4.21 <sup>bc</sup>	4.07 <sup>c</sup>	5.65 <sup>a</sup>	4.79 <sup>b</sup>	3.79 <sup>cd</sup>	3.27 <sup>de</sup>	0.087 <sup>***</sup>	0.062 <sup>**</sup>	0.123			
Pb	0.19 <sup>ef</sup>	0.18 <sup>f</sup>	1.07 <sup>de</sup>	0.93 <sup>def</sup>	3.28 <sup>a</sup>	2.84 <sup>ab</sup>	2.05 <sup>bc</sup>	1.50 <sup>cd</sup>	0.111 <sup>***</sup>	0.079 <sup>*</sup>	0.157			
Mn	2.62 <sup>f</sup>	1.44 <sup>g</sup>	3.40 <sup>e</sup>	3.06 <sup>ef</sup>	12.42 <sup>a</sup>	9.34 <sup>b</sup>	5.23 <sup>c</sup>	4.38 <sup>d</sup>	0.092 <sup>***</sup>	0.065 <sup>***</sup>	0.130 <sup>***</sup>			
Ni	0.37 <sup>ef</sup>	0.28 <sup>f</sup>	0.58 <sup>d</sup>	0.45 <sup>de</sup>	1.80 <sup>a</sup>	1.61 <sup>b</sup>	0.79 <sup>e</sup>	0.73 <sup>c</sup>	0.018 <sup>***</sup>	0.013 <sup>***</sup>	0.025			
Zn	22.68 <sup>e</sup>	17.85 <sup>f</sup>	34.65 <sup>c</sup>	28.52 <sup>d</sup>	50.41 <sup>a</sup>	45.45 <sup>b</sup>	37.35 <sup>c</sup>	36.40 <sup>c</sup>	0.453 <sup>***</sup>	0.320 <sup>***</sup>	0.640 <sup>*</sup>			
Fe	27.95 <sup>de</sup>	25.93 <sup>e</sup>	31.12 <sup>cde</sup>	32.81 <sup>cde</sup>	49.85 <sup>a</sup>	42.50 <sup>ab</sup>	38.17 <sup>bc</sup>	34.73 <sup>bcd</sup>	1.014 <sup>**</sup>	0.717 <sup>*</sup>	1.434			

Sites=upstream=A; Shahdera=B; Sunder=C; and Head balloki=D; with two seasons (low and high flow)

Here \*, \*\* and \*\*\* represent significance at  $P < 0.05$ ,  $P < 0.01$  and  $P < 0.001$ , respectively

the physico-chemical parameters of running waters could have been influenced by the natural and anthropogenic activities around the sampling sites of this study.

DO has an inverse relation with water temperature (Ali 1999). Lower DO during low water flow season might be associated with direct discharge of untreated industrial effluents adjacent to the Hudiarra drain, Deg Nullah and organic substances loaded municipal sewage. The biodegradable components of the inloads require a large amount of oxygen for oxidation processes of micro-organisms which can cause depletion of DO. Safe recommended concentration of DO is 4 mg/l for fish, however, most species are distressed when it falls between 2 and 4 mg/l. Low level of DO such as less than 2 mg/l can cause fish mortality (McNeil and Closs 2007). Significant high value (range 165–948 mg /l) of total dissolved solids might have resulted from the effluents' higher concentration of soluble salts and other components. Subramanian (2004) reported TDS value of 272 mg/l for the river Cauvery, 241 mg/l for Ganges, 224 mg/l for Mahandi and 173 mg/l for river Indus. Higher value of the parameter obtained in this study clearly demonstrates the significance of the urban loads to the river Ravi while passing through the city, Lahore.

Total suspended solids at all the sampling sites of the river exceeded the recommended NEQS value. It appears that the communal effluents from the urban and industrial areas mixed heavy quantity of suspended solids. Comparable results have been reported by Yausafzai et al. (2010) for the river Kabul in Northern Pakistan.

Total alkalinity and the hardness of water depend upon the dissolved salts being present in water. Downstream high values of this parameter could also be attributed to the discharge of industrial effluents which contained dissolved cations and anions. Hardness of water is imparted by alkaline earth metal cations, mainly by calcium and magnesium (Mohan et al. 2007). Downstream elevated values of nitrate, nitrite and phosphate could be associated with agricultural fertilizer's runoff (Yang et al. 2004). Significant higher levels of these variables resulted into eutrophication that was observable in patches near the bank of the river. Lesser values of dissolved oxygen downstream might have been exerting respiratory stress for the aquatic fauna as reported by Nnaji et al. (2011) who mentioned comparable situation for the river Galma,

Nigeria. High concentration of chloride is considered to be the indicator of pollution due to organic wastes of animal and human origin. Subramanian (2004) reported values (in milligrams per liter) of the parameter as 11 for Brahamputra, 17 for Godavari and 10 for Ganges. All the South Asian rivers showed chloride values that were less than the study area of the river Ravi. Yausafzai et al. (2010) reported comparable results for the river Kabul.

Higher ammonia content of up to 1.220 mg /l at site C during low flow showed deterioration of water quality owing to untreated industrial effluents. It is extremely toxic to fish and should be present below 0.2 mg/l for better fish growth (Chapman 1992). Muhammad et al. (1998) reported 0.002 mg/l of ammonia for river Swat, Pakistan. Sulphate contents of the river water, like other variables, showed significant elevation (2.49-fold) at site C than the site A during low-flow season. The value of the present study area was much higher than the Kabul (Yausafzai et al. 2010), Cauvery, Gomti and Mahandi rivers (Subramanian 2004). For the above-referred parameters, it is concluded that urban sewage and industrial effluent loads have been deteriorating the river's natural habitat while at present the situation recovers to some extent at the last downstream site. If no prompt and strong pollution control measures were taken, more area of the river will become less inhabitable for the fish.

Significant variation in macro elements of different specimens of the fish were found in this study. There is no specific recommended value for these elements in muscle of fish. Swann (2000) reported that it is unclear that elevated levels of macro elements in fish tissues are harmful for fish itself, other wildlife species and human consuming such fish. Freshwater fish are often at the top of the food chain. Elevated level of metals in fish muscle mainly originates from aquatic resources (Mansour and Sidky 2002). Metal bioaccumulation in fish provided evidences of exposure to contaminated aquatic environment. Industrial effluents and municipal sewage discharge into river may cause impaired movements, behavioural and physiological responses, histological and reproductive abnormalities, fish growth, health and even fish death (Atchison et al. 1987).

Zn accumulation (17.85–50.41 mg/Kg) was highest among the studied minerals in muscles at different sites and seasons in the present study. The results were in agreement with those of Jabeen and Chaudhry



(2010) for similar fish from the river Indus. Zn is the essential mineral as it shows protective effect against Cd and Pb toxicity. Different researchers regarded its higher content as a potential hazard that can endanger fish and fish consumer. Therefore, data about Zn bioaccumulation in fish is important (Amundsen et al. 1997). Fe is essential for animal health but it is toxic in higher amounts and inhibits enzyme function. It is not absorbed through digestive system of the vertebrate. Mn ranged from 1.44 to 12.42 mg/kg in the fish muscles. The site C sample showed 374 % increase in comparison with the site A during low-flow season. The permissible limits of 0.01 mg/kg (WHO 1985) and 0.05 mg/kg (FEPA 2003) render the present level of the metals being toxic for the fish quality and the human consumption. As high Mn content interferes with metabolic pathways such as the disruption of Na regulation in fish and central nervous system by inhibiting dopamine formation which may ultimately cause fish deaths (Jabeen and Chaudhry 2010).

The Cr concentration ranged from 0.96–5.70 mg/kg. More bioaccumulation of Cr occurred during the low-flow season. The permissible level of Cr in fish for human consumption is 0.05 mg/kg (WHO 1985). It could be inferred that consumption of these fish could lead to health hazards in fish consuming human populations. Much higher concentrations are attributable to the industries such as tanning and corrosion control plating pigment manufacturers situated along the Hudia drain both in Indian and Pakistani sides of this river (Saeed and Bahzad 2006). Jabeen and Chaudhry (2010, 2011) reported similar results for *Cyrinus carpio* and *Labeo rohita* from the Indus river of Pakistan.

Copper is an essential part of several enzymes and is necessary for the synthesis of haemoglobin, fish growth and reproduction (Sivaperumal et al. 2007) while its higher intake can cause adverse health problems. Sampled *C. catla* muscle showed 2.87–5.65 mg/kg of this metal which is much higher than that reported by Malik et al. (2010) for *Ctenopharyngodon idella* and *L. rohita*. Permissible level of Cu in fish is 30 mg/kg (WHO 1985; FEPA 2003). Ni is essential for normal growth and reproduction but carcinogenic when present in higher amounts. The mean concentration of Ni ranged from 0.28–1.61 mg/kg in the present study. The Cd levels in fish muscles reflect its bioavailability in aquatic environment and it could have carcinogenic effect on aquatic biota and humans. The highest Cd, up to 0.17 mg/kg, appeared for the site C during the low-flow season.

Cadmium is highly toxic as it can cause anomalies such as reduction in the development and growth rates as well as skeletal ossification even at lowest concentration (Wright and Welbourn 2002).

The Pb bioaccumulation concentrations in muscles that ranged between 0.18 and 3.28 mg/kg were also above the permissible limits of 2 mg/kg (WHO 1985) in fish for human consumption. Similar results were reported by Qadir and Malik (2011) for fish of the river Chenab, Pakistan. The toxic effect and bioaccumulation of Pb and Cr in fish can be highly influenced by water hardness, organic matter and development stage of fish (USEPA 1999). The results are in agreement with those reported by Malik et al. (2010) for the muscles of *L. rohita*.

Conclusively, the Lahore municipal and industrial effluents appeared to be highly contaminating the river Ravi. A considerable portion of the downstream river is likely to become soon uninhabitable for the fish at least during the low-flow periods. Further, the riverine fish at present appear to harbour higher than the permissible levels of several toxic metals. This, in conjunction with the local myth that riverine fish have health-promoting effects, may lead to the generation of worse health issues for the consumers. Proper treatment of the city sewage and immediate transfer of within-city-located industrial units to proper industrial zones with strict monitoring for treatment of their effluents is recommended for the betterment of river habitat, its fauna as well as the concerned human health.

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