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Copper-toxicity to Water and Plankton in the River Ravi, Pakistan

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ABSTRACT

Copper (Cu) toxicity of water and plankton in the river Ravi stretch from Lahore siphon to Baloki head works, Pakistan and related effluent discharging tributaries has been studied. The effluents from tributaries had an adverse effect the planktonic biota of the river Ravi. Among nine tributaries, Taj Company nulla exhibited significantly higher contaminated plankton, due to uptake and accumulation of Cu from water. Maximum concentration of Cu (281.60 µg g^{-1}) was recorded in Taj Company nulla, while it was minimum (9.80 µg g^{-1}) in Lahore siphon Right Bank (R B). Average maximum and minimum value of Cu concentration in water samples were 5.33 and 0.10 mg L^{-1} at Farrukhabad nulla and Lahore siphon Left Bank (L B), respectively. The relationships between accumulation of Cu in plankton and the physico-chemistry of water were significant. Data revealed that plankton had a greater tendency to accumulate Cu than that retained in water.

Key Words: River ravi; Cu-toxicity; Metal pollution; Plankton; Biological indicator

INTRODUCTION

Copper (Cu), a trace metal and essential for cellular metabolism, may becomes extremely toxic for aquatic animals as its concentration increases in water (Carvalho & Fernandes, 2006). The presence of heavy metals in the environment is partially due to natural processes, but mainly as a result of industrial waste (Mansour & Sidky, 2002). Majority of the heavy metals that were previously occurring at very low concentrations in water are now found in high concentrations, creating deleterious effects on aquatic life including fish (Adeyeye, 2000; Asaolu, 2002; Patil & Shrivastava, 2003). Food may be an important source for heavy metal accumulation in fish from polluted water and sediments and potentially leading to bio-magnification (Javed & Hayat, 1995 & 96; Clearwater, 2002; Javed, 2004).

The impact of Cu on the aquatic environment is complex and depends on the physicochemical characteristics of water (Laure´n & McDonald, 1986; Mazon & Fernandes, 1999; Tao *et al*., 1999; Takasusuki *et al*., 2004). Alkalinity, hardness and pH strongly influence Cu speciation in water and consequently its bioavailability to fish (Florence *et al*., 1992; Playle *et al*., 1992; Erickson *et al*., 1996; Tao *et al*., 2000, 2001). Heavy metal toxicity may decrease the oxygen consumption by the fish, while water hardness has a significant effect on heavy metals toxicity (Rathore & Khangarot, 2003). Environmental conditions such as oxygen concentration, temperature, hardness, salinity and presence of other metals may also affect metals toxicity to the fish. Hypoxic conditions like temperature increase and acidification usually renders the fish more susceptible to intoxificant (Witeska & Jezierska, 2003). Distribution of aquatic organisms may be influenced by factors that co-occur with higher toxicities, such as temperature, pH, oxygen concentration, food and habitat-availability.

With the rapid increase in industrialization in Pakistan, the water pollution has become a devastating issue as the industrial effluent and domestic sewage, containing bulk quantities of toxic heavy metals, are being continuously discharged into the rivers especially in river Ravi (Javed, 2005). In view of this, the present study evaluates the pollution level of aquatic ecosystem via determining the accumulation of Cu in water and plankton samples of the river Ravi (from Lahore Siphon to Baloki head works) and its related tributaries.

MATERIALS AND METHODS

The stretch of the river Ravi under study i.e., from Lahore siphon to Baloki headworks (about 70 km long) was extensively surveyed and ten sampling stations, along both right and left banks of the river viz. Lahore siphon (L B), Lahore siphon (R B), Shahdera bridge (L B), Shahdera bridge (R B), Mohlanwal, Purani Bheni, Sunder, Chakkighera, Baloki headworks (L B), Baloki head works (R B) and nine (9) effluent discharging tributaries viz. QB link canal, Degh nulla, Farrukhabad nulla, Mehmood Booti nulla, Shad Bagh nulla, Munshi Hospital nulla, Taj Company nulla, Baker Mandi nulla and Hudiara nulla were chosen to study the toxicity of Cu. Each sampling station was divided in to three sub-stations at equal distance from the coming sources (within a diameter of 100 m) to collect water and plankton samples by following proportionate sampling procedure (Steel *et al*., 1996).

Collection of samples. Water samples were collected, on fortnightly basis between 9:00 to 14:00 h for a period of one year from the selected sampling stations of the river and its tributaries. Water samples were collected from just below the surface and column (maximum two meters below the surface). Three sub-samples collected from each station were mixed to have a composite sample. From each sampling station the plankton samples were collected both from surface and column by filtering nearly 70 - 80 L of water through plankton net (pore size = 10 µm). Water samples containing plankton were filtered through pre-weighed filter paper. Filter papers along with filtrates were dried to calculate the dry weights of plankton.

Determination of heavy metals in water and plankton samples. For the determination of Cu concentrations the water and plankton samples were wet digested and quantities determined using Atomic Absorption Spectrophotometer (Model Varian 240 S S, USA) with the methods of APHA (1989).

Determination of physico-chemical parameters. Physico-chemical parameters were recorded on fortnightly basis. Water temperature, dissolved oxygen, pH, electrical conductivity and turbidity were determined using qequsite instruments from HANNA (Models HI-8053, HI-9143, HI-8520, HI-8733, USA) and Jenway (Model 6035, UK) companies, while total ammonia, chlorides, sodium, potassium, total hardness, total alkalinity and planktonic biomass were determined as described by of APHA (1989). The data was analyzed statistically for analysis of variance and Duncan's Multiple Range was performed to find significant differences among various parameters (Steel *et al.*, 1996).

RESULTS

Copper concentrations in water and plankton showed significant differences ($p < 0.05$). Differences among sampling stations for the Cu concentrations in water and plankton were also significant ($p < 0.01$) (Table I). A maximum Cu concentration (5.07 mg L^{-1}) in water was recorded at Shahdera bridge (L B) and minimum (0.10 mg L^{-1}) at Lahore siphon (L B) along the river site. Among the tributaries, the highest and lowest value of Cu was recorded at Farrukhabad nulla and QB. link canal respectively (Table I; Fig. 1). Among river site sampling stations, maximum Cu concentrations (138.71 µg g^{-1}) in plankton was recorded at Shahdera bridge (L B) and minimum at Lahore siphon (R B). However, among tributaries this value was maximum at Taj Company nulla and minimum at QB link canal (Table I; Fig. 2).

Data revealed that correlation coefficient of Cu in water with plankton was positive ($r = 0.697$). Cu showed a positive correlation of water with temperature, electrical conductivity, total ammonia, chlorides, sodium, potassium, total hardness, total alkalinity, water turbidity and planktonic biomass. However pH and dissolved oxygen were negatively significant with copper concentrations in water (Table II). Cu concentration in plankton showed a positive relationship with temperature, electrical conductivity, total ammonia, chlorides, sodium, potassium, total hardness, total alkalinity, water turbidity and planktonic biomass but negative with pH and dissolved oxygen.

Table I. Comparison of water and plankton samples collected from Ravi River and tributaries for copper concentrations

Sampling Stations	Water (mg L^{-1} ± SD)	Plankton (µg g^{-1} ± SD)
River		
Lahore siphon (L.B.)	0.10±0.04 j	11.96±02.53 k
Lahore siphon (R.B.)	0.10±0.06 j	9.80±02.95 k
Shahdera bridge (L.B.)	5.07±1.65 ab	138.70±30.54 e
Shahdera bridge (R.B)	1.23±0.88 i	37.33±10.59 ijk
Mohlanwal	4.16±1.24 ef	91.66±28.72 fg
Purani Bheni	2.46±0.93 h	83.91±24.83 fgh
Sunder	4.32±0.17 de	105.40±22.61 f
Chakkighera	3.72±1.21 f	88.54±22.66 fg
Baloki headworks (L.B.)	3.13±0.97 g	64.58±19.15 ghi
Baloki headworks (R.B.)	3.00±0.98 g	56.67±22.64 hij
Tributaries		
Q. B. link canal	1.21±0.53 i	31.80± 09.96 jk
Degh nulla	3.15±0.90 g	74.06± 25.70 gh
Farrukhabad nulla	5.33±1.46 a	241.40± 75.80 b
Mehmood Booti nulla	4.56±1.30 bcde	225.40±118.79 bc
Shad Bagh nulla	4.54±1.33 cde	194.00± 83.72 d
Munshi Hospital nulla	4.87±1.53 abc	251.30± 89.89 b
Taj Company nulla	4.83±1.32 abcd	281.60±110.79 a
Bakar Mandi nulla	3.67±1.21 f	184.00± 78.39 d
Hudiara nulla	4.72±1.05 bcd	199.90± 91.27 cd

Table II. Correlation coefficients (r) of various variables under study

	Temp.	pH	E.C.	DO	NH_3	Cl	Na	K	T.H.	T.A.	Tur	P.B	Cu. W
pH	-0.04309												
E.C.	0.30297	-0.48307											
OD	-0.27799	0.54678	-0.84507										
NH_3	-0.05608	-0.47615	0.73513	-0.73465									
Cl	0.38747	-0.42058	0.85739	-0.73739	0.60539								
Na	0.19383	-0.35007	0.78854	-0.71440	0.62077	0.67785							
K	0.28496	-0.44197	0.88886	-0.810770	0.72162	0.77657	0.75711						
T.H.	-0.12009	-0.40761	0.66258	-0.67067	0.64096	0.52948	0.63255	0.63517					
T.A.	0.07566	-0.44120	0.84955	-0.78786	0.75679	0.65715	0.72688	0.80131	0.74192				
Turb	0.29300	-0.39283	0.73200	-0.73117	0.67306	0.60966	0.62624	0.71119	0.54784	0.69132			
P.B.	0.21470	-0.37865	0.57824	-0.58582	0.54644	0.55181	0.60159	0.52241	0.44295	0.48687	0.53318		
Cu.W	0.42772	-0.32478	0.52419	-0.62292	0.37994	0.48703	0.41773	0.55165	0.33552	0.40899	0.54991	0.40948	
Cu plk	0.50904	-0.43378	0.72253	-0.73056	0.44120	0.67798	0.56118	0.71945	0.48302	0.60839	0.62274	0.39832	0.69694

Critical value (2-tail, 0.05) = + or – 0.09185

Cu.W. = Copper concentrations in water (mgL^{-1}); Cu. Plk = Copper concentrations in plankton (μgg^{-1}); Temp. = Temperature (°C); E.C. = Electrical conductivity (μScm^{-1}); DO = Dissolved oxygen (mgL^{-1}); NH_3 = Total ammonia (mgL^{-1}); Cl = Chlorides (mgL^{-1}); Na = Sodium (mgL^{-1}); K = Potassium (mgL^{-1}); T.H. = Total hardness (mgL^{-1}); T.A = Total alkalinity (mgL^{-1}); Turb. = Turbidity (NTU); P.B. = Planktonic biomass (mgL^{-1})

Fig. 1. Fluctuation in copper concentrations in water (mg L^{-1}) at various sampling stations

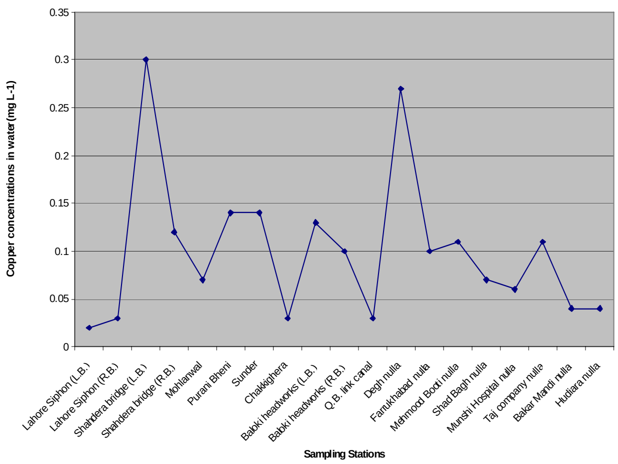
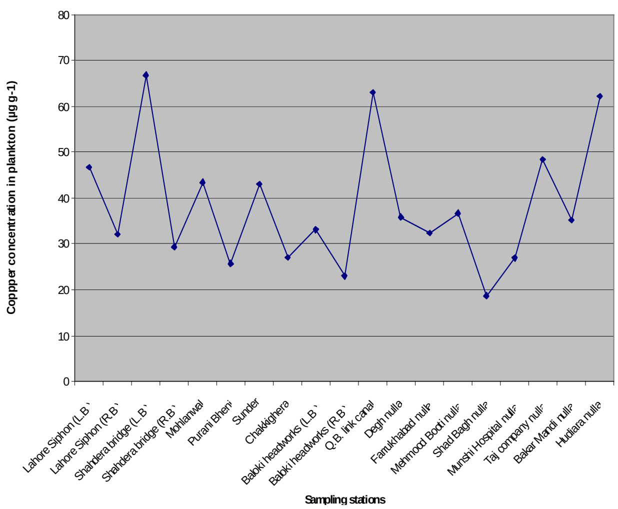


Fig. 2. Fluctuation in copper concentrations in plankton ($\mu g\ g^{-1}$) at various sampling stations



DISCUSSION

Pollutants introduced into the river are naturally carried downstream but, after initial mixing, they do not become further diluted, because of confluence with other water sources. 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 nine tributaries, into the river had adverse influence on the purity of river water. This showed significant impact of Cu toxicity in water and on its accumulation in plankton body (Table I; Fig. 1 & 2). Therefore, in aquatic ecosystem plankton show a great tendency to accumulate metals in their bodies from water and sediments (Khan *et al.*, 1981; Javed & Hayat, 1999). Wang and Tang (1998) reported that toxic water and sediments pollution had great effect on the aquatic ecosystem in Le An river in China.

Significant correlation between Cu concentration in water and plankton revealed the capability of plankton to concentrate heavy metal from their aquatic environment. (Table II). The results agree with those of Forstner and Wittman (1979) who suggested that the phytoplankton act as a bio-indicator of metals in an aquatic ecosystem, because they eliminate metals from the environment, accumulate and store them for longer periods. Many trace elements such as arsenic, cadmium, copper, lead and selenium can be toxic to aquatic biota (Eisler, 1985 & 88), because plankton has the ability to concentrate heavy metals from their aquatic environment (Harding &Whitton, 1981; Javed & Hayat, 1996).

Copper in water and turbidity showed positively non-significant correlation (Table II). In the polluted waters, the major problems are low dissolved oxygen, high turbidity, organic matter, ammonia contents and severe heavy metal toxicity (Koukal *et al.*, 2004). Dissolved metal ions create turbidity and discoloration (Frank & Cross, 1994). During present investigation Cu in water showed positive correlation with temperature and planktonic biomass. Javed and Hayat (1996) reported the uptake and accumulation of metals in planktonic biomass that was inversely dependent on water pH. They further reported positive correlation between heavy metal ions and temperature of water. However, little is known about the concomitant effects of temperature and pH on Cu toxicity (Carvalho & Fernandes, 2006). Plankton showed a direct relationship with the accumulation of Cu content of water and its temperature. Temperature changes in a given direction may change the toxicity depending upon the species (Macleod & Pessah, 1993). Jackson (1988) reported increase in metals uptake by benthos with a decrease in water temperature.

Total hardness showed positive correlation on the accumulation of Cu in the plankton. The Cu toxicity of plankton both in river and tributaries showed inverse relationships with total hardness of water. Water-borne metals are greatly toxic to aquatic to aquatic organism in soft water of pH and low dissolved organic carbon (Novelli *et al.*, 1998). This is because the hardness cations (Mg^{2+} & Ca^{2+}) compete with heavy metal ions for binding sites within the organism.

Copper concentration in plankton was positively correlated with water temperature, electrical conductivity, total alkalinity and total hardness. However, the correlation coefficient between Cu concentration in plankton and dissolved oxygen was negative. High water temperature, oxygen concentration, pH and hardness of lake water increased the heavy metal toxicity in plankton (Forstner & Wittman, 1979).

CONCLUSION

Water and plankton collected from the River Ravi contain concentration of Cu shown to be toxic. However toxicity assessments at Lahore siphon (Right & Left Bank) revealed little to no toxicity, indicating that the Cu was not bio-available to the plankton. Polluted water also represents a potential hazard to the aquatic environment. If periodic accidental spills continue, accumulation of Cu in River Ravi will persist, posing a continuous hazard to the river.

REFERENCES

APHA, 1989. *Standard Methods for the Examination of Water and Wastewater*, 17th edition. Washington, D.C

Adeyeye, E.I., 2000. Determination of major elements in fish, associated water and soil sediments from some freshwater ponds. *Ghana J. Chem*., 43: 367–73

Asaolu, S.S., 2002. Determination of some heavy metals in *Oreochromis niloticus*, *Clarias gariepinus* and *Synodontis* spp. from the coastal water of Ondo state, Nigeria. *Pakistan J. Sci. Ind. Res*., 45: 17–9

Carvalho, C.S. and M.N. Fernandes, 2006. Effect of temperature on copper toxicity and hematological responses in the neotropical fish *Prochilodus scrofa* at low and high pH. *Aquaculture*, 251: 109–17

Clearwater, S.I., A.M. Farag and J.S. Meyer, 2002. Bioavailability and toxicity of dietborne copper and zinc to fish. *Physiol. Toxicol*., 132: 269–313

Eisler, R., 1985. Selenium hazards to fish, wildlife and invertebrates; A synoptic review. *US Fish and Wildlife Service Biological Report*, 85: 157

Eisler, R., 1988. Lead hazards to fish, wildlife and invertebrates; A synoptic review. *US Fish and Wildlife Service Biological Report*, 85: 134

Erickson, R.J., D.A. Bernoit, V.R. Mattson, H.P. Jr. Nelson and E.N. Leonard, 1996. The effects of water chemistry on the toxicity of copper to fathead minnows. *Environ. Toxicol. Chem.*, 15: 181–93

Florence, T.M., G.M. Morrison and J.L. Stauber, 1992. Determination of trace element speciation and the role of speciation in aquatic toxicity. *Sci. Total Environ*., 125: 1–13

Forstner, V. and G.T.W. Wittman, 1979. *Metal Pollution in the Aquatic Environment*. Berlin Hedelburg, New York

Frank, L. and P.E. Cross, 1994. *Management Primer on Water Pollution Control*, pp: 23–7. Technomic Publishing Co., Inc. West Port

Harding, J.P.C. and B.A. Whitton, 1981. Accumulation of zinc, cadmium and lead by field population of Lamanea. *Water Res*., 15: 301–19

Jackson, T.A., 1988. Accumulation of mercury by plankton and bentjic invertebrates in riverine lakes of northern Manitoba (Canada): Importance of regionally and seasonally varying environmental factors. *Canadian J. Fish Aqua. Sci*., 45: 1744–57

Javed, M., 2004. Comparison of selected heavy metals toxicity in the planktonic biota of the river Ravi. *Indus J. Biol. Sci*., 1: 59–62

Javed, M., 2005. Heavy metal contamination of freshwater fish and bed sediments in the river Ravi stretch and related tributaries. *Pakistan J. Biol. Sci*., 8: 1337–41

Javed, M., 2006. Studies on metal contamination levels in Pakistan and their role as biological indicator of water pollution in the river Ravi. *Pakistan J. Biol. Sci.*, 9: 313–7

Javed, M. and S. Hayat, 1995. Effect of waste disposal on the water quality of river Ravi from Lahore to head Baloki, Pakistan. *Proc. Pakistan Cong. Zool.*, 15: 41–51

Javed, M. and S. Hayat, 1996. Planktonic productivity of river water as a bio-indicator of freshwater contamination by metals. *Proc. Pakistan Cong. Zool*., 16: 383–98

Javed, M. and S. Hayat, 1999. Heavy metal toxicity of river Ravi aquatic ecosystem. *Pakistan J. Agric. Sci*., 36: 81–9

Khan, N.A., A. Ahmad, A.A. Nomani and M. Ajmal, 1981. Atomic Absorption Spectro-photometric studies on commercial fertilizers as a source of Cd and Zinc in soil and river water. *Environ. Pollut.*, 13: 259–64

Koukal, B., J. Dominik, D. Vignati, P. Arpagaus, S. Santiago, B. Ouddane and L. Benaabidate, 2004. Assessment of water quality and toxicity of polluted rivers Fez and Sebou in the region of Fez, Morocco. *Environ. Pollut*., 131: 163–72

Laure´n, D.J. and D.G. McDonald, 1986. Influence of water hardness, pH and alkalinity on the mechanism of copper toxicity in juvenile rainbow trout, Salmo gairdneri. *Canadian J. Fish Aqu. Sci*., 43: 1488–96

Macleod, J.C. and E. Pessah, 1993. Temperature effects on mercury accumulation, toxicity and metabolic rate in rainbow trout (*Salmo gairdneri*). *J. Fish Res. Bd. Canada*, 30: 485–92

Mansour, A.A. and M.M. Sidky, 2002. Ecotoxicological studies: heavy metals contaminating water and fish from Fayum Governorate, Egypt. *Food Chem.*, 78: 15–22

Mazon, A.F.and M.N. Fernandes, 1999. Toxicity and differential tissue accumulation of copper in the tropical freshwater fish, *Prochilodus scrofa* (Prochilodontidae). *Bull. Environ. Contam. Toxicol.*, 63: 797–804

Novelli, E.L.B., E.P. Vieria, N.L. Rodrigues and B.O. Ribas, 1998. Risk assessment of cadmium toxicity on hepatic and renal tissues of rats. *Environ. Res*., 79: 102–5

Patil, P.R. and V.S. Shrivastava, 2003. Metallic Status of River Godavari- A Statistical Approach. *Indian J. Environ. Prot*., 23: 650–61

Playle, R.C., R.W. Gensemer and D.G. Dixon, 1992. Copper accumulation on gills of fathead minnows: influence of water hardness, complexation and pH of the gill micro-environment. *Environ. Toxicol. Chem.*, 11: 381–91

Rathore, R.S. and B.S. Khangarot, 2003. Effects of water hardness and metal concentration on a freshwater muller (*Tubifex tubifex*). *Water Air Soil Pollut*., 142: 341–56

Steel, R.G.D., J.H. Torrie and D.A. Dinkkey, 1996. *Principles and Procedures of Statistics A Biometrical Approach,* 2nd edition. McGraw Hill Book Co., Singapore

Takasusuki, J., M.R.R. Araujo and M.N. Fernandes, 2004. Effect of water pH on copper toxicity in the neotropical fish, *Prochilodus scrofa* (Prochilodondidae). *Bull. Environ. Contam. Toxicol.*, 72: 1075–82

Tao, S., A. Long, C. Liu and R. Dawson, 2000. The influence of mucus on copper speciation in the gill microenvironment of carp (*Cyprinus carpio*). *Ecotoxicol. Environ. Saf.*, 47: 59–64

Tao, S., T. Liangt, J. Cao, R. Dawson and C.F. Liu, 1999. Synergistic effect of copper and lead uptake by fish. *Ecotoxicol. Environ. Saf.*, 44: 190–95

Tao, S., Y. Wen, A. Long, R. Dawson, J. Cao and F. Xu, 2001. Simulation of acid–base condition and copper speciation in fish gill microenvironment. *Comp. Chem.*, 25: 215–22

Wang, Z.J. and H.X. Tang, 1998. The chemical, toxicological and ecological studies in assessing the heavy metal pollution in Le An river, China. *Water Res.*, 35: 510–8

Witeska, M. and B. Jezierska, 2003. The effect of environmental factors on metal toxicity of fish. *Fresen. Environ. Bull.*, 12: 824–9

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