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Occurrence of heavy metals in fish: a study for impact assessment in industry prone aquatic environment around Kolkata in India

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Abstract A study was conducted during November 2005–October 2006 for determining the heavy metal contamination in surface water and sediments and giving prime thrust to determine the heavy metal concentrations fish samples collected from various points of the river Ganga at different time interval. Fish samples (viz., *Channa marulius* and *Aorichthys seengala*) were analyzed for heavy metals using standard laboratory procedures by AAS method. In impact points the annual average values for Cu, Cr, Cd, Pb and Zn were 0.15, 0.04, 0.03, 0.02 and 0.29 ppm, respectively. The concentrations of heavy metals in the riverine water collected from middle point had the order Zn > Cu > Cr > Cd > Pb. The data indicated that copper was maximally accumulated in the riverine sediments whereas least annual average concentration was obtained for lead. The trend of accumulation suggested deposition was maximum for zinc and minimum for cadmium in the muscles of both fish species. Only zinc has shown some significant seasonal variation in relation to metal deposition in fish muscles (minimum in monsoon and maximum in summer). The heavy metal contamination to fish may be due to indiscriminate discharge of polluted and untreated sewage sludge to the river. The heavy metal contents in fish at some places are alarming.

Keywords Heavy metals · Fish · Ganga water · Contamination · AAS · Spatial and temporal changes · West Bengal

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Introduction

Heavy metal contamination of aquatic ecosystems has been recognised as a serious pollution problem. Heavy metals are defined as the metallic chemical element that has a relatively high density and are toxic or poisonous at low concentrations (Connell 1984). All heavy metals are potentially harmful to most organisms at some level of exposure and adsorption. They are released in aquatic environments in different ways, i.e., from different natural and anthropogenic sources, including industrial or domestic sewage, storm runoff, leaching from landfills, shipping and harbor activities and atmospheric deposits (Yilmaz 2003; Marcovecchio 2004) and tend to bioaccumulate. In fact, contamination of aquatic environments with potentially harmful and non-degradable substances like heavy metals, and its subsequent impact on organisms, is more dramatic within estuaries and semiclosed coastal zones, especially when they are situated near highly populated or industrial areas. The possible entrance of heavy metals in aquatic biota is schematically represented in Fig. 1.

Fish are vital sources of digestible protein, vitamins, minerals and polyunsaturated fatty acids (Irwandi and Farida 2009). They lie at the top of the aquatic food chain and may concentrate large amounts of some metals from the water. In addition, fish are most indicative factors in freshwater systems, for the estimation of trace metal pollution and risk potential of human consumption (Rashed 2001). For the normal metabolism of fish, the essential metals like copper and zinc must be taken up from water, food or sediment. However, similar to the route of essential metals, non-essential ones are also taken up by fish and accumulate in their tissues (Yilmaz 2006; Canli and Atli 2003).

The objective of the present study was to determine the levels of certain heavy metals in riverine water, sediment and muscles of two different fish species, *Channa marulius* and *Aorichthys seengala*. Both of the fish species live and search for food in the mud and sand at the bottom of the river; however, *C. marulius* occasionally feeds on water surface also. The species from Ganges were selected because it originates very pure water resource Gangotri glacier located at Himalayan range and flows across major industrial areas along the riverside of the country. The emergence and course of flow of the river over West Bengal

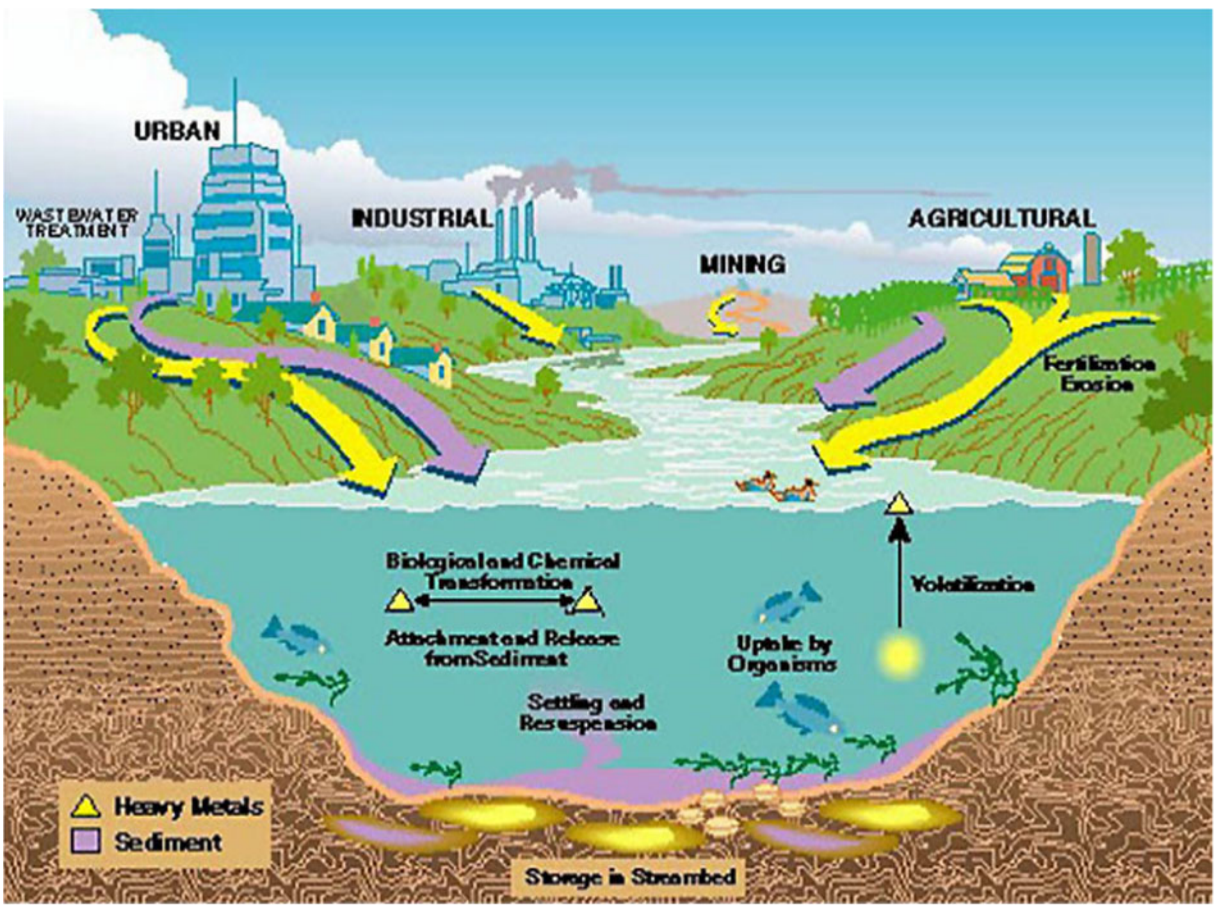

Fig. 1 The possible entrance of heavy metals in aquatic biota (www.embryology.med.unsw.edu.au/Defect/metal.htm)

is shown in Fig. 2. As a result, it receives not only municipal or urban sewage discharge but also untreated industrial effluents and agricultural run off, considered as prime sources of heavy metal pollution in river water.

Heavy metals selected for the present study were copper (Cu), chromium (Cr), cadmium (Cd), lead (Pb) and zinc (Zn). Among them Cu and Zn are required in trace amounts for smooth function of different biological systems (Bowen 1966; Sorensen 1976). Pb and Cd, however, have no known biological functions and generate adverse effects in all forms (Tort et al. 1987). They were found at high concentration levels in fish tissues close industrial area (Thompson et al. 2000). The results from this study indicated significant accumulation of these heavy metals in the riverine water, sediment and muscles of *C. marulius* and *A. seengala* collected from different points on Ganges flowing at Kolkata, West Bengal, India.

Material and methods

Description of the site

The River Ganges in West Bengal is flowing through industrial zone of Howrah in its east bank and the capital city of the state, Kolkata to the west before meeting Bay of Bengal near Dimond Harbour. The huge sewage water from the two regions, produced as a result of regular municipal and industrial activities, ultimately disposed of river Ganga. Presently, the treatment plants operating near Howrah are Bally and Howrah Sewage Treatment Plants (STPs). The final effluents are released at two different points and they are selected as the impact points near Howrah side. The other two impact points, located near Kolkata, where effluents from Maheshtala and CETP STPs in Kolkata were discharged into the river Ganga. In this paper, the impact points were denoted

Fig. 2 The emergence and course of flow of the river Ganga over West Bengal (www.gits4u.com/water/ganga.htm)

Table 1 Monthly occurrence of copper, chromium, cadmium, lead and zinc in water

Location	Metals	Concentration of heavy metals (in ppm)											
		Nov. 2005	Dec. 2005	Jan. 2006	Feb. 2006	Mar. 2006	April 2006	May 2006	June 2006	July 2006	Aug. 2006	Sep. 2006	Oct. 2006
Bally (Im)	Cu	0.20	0.22	0.18	0.16	0.05	0.10	0.06	0.08	0.15	0.19	0.22	0.18
	Cr	0.05	0.02	0.04	BDL	0.06	0.05	0.04	0.02	0.10	0.14	0.10	BDL
	Cd	BDL	BDL	0.08	0.06	0.03	0.05	0.06	0.02	BDL	0.02	0.01	0.01
	Pb	BDL	0.04	BDL	0.02	BDL	BDL	0.03	0.06	0.05	BDL	BDL	0.02
	Zn	0.22	0.35	0.25	0.30	0.33	0.24	0.25	0.32	0.26	0.22	0.24	0.28
Howrah (Im)	Cu	0.15	0.20	0.17	0.18	0.08	0.04	0.04	0.05	0.20	0.18	0.16	0.15
	Cr	0.02	BDL	0.06	0.03	0.05	0.01	0.07	0.12	0.15	0.12	0.08	0.01
	Cd	BDL	0.02	0.05	0.05	0.02	0.02	0.04	BDL	0.01	0.05	0.02	BDL
	Pb	0.05	0.02	0.01	0.02	0.01	BDL	BDL	0.02	0.02	0.01	0.01	BDL
	Zn	0.25	0.21	0.33	0.22	0.25	0.32	0.38	0.20	0.28	0.32	0.30	0.32
Maheshtala (Im)	Cu	0.20	0.22	0.25	0.24	0.18	0.14	0.10	0.08	0.15	0.18	0.15	0.16
	Cr	0.02	0.10	0.02	BDL	0.06	0.06	0.02	BDL	0.04	0.08	BDL	0.05
	Cd	0.04	BDL	BDL	0.01	BDL	BDL	0.03	0.01	0.06	0.08	0.03	0.02
	Pb	BDL	0.03	0.03	0.01	0.02	0.01	0.02	0.01	0.03	0.02	0.04	0.04
	Zn	0.48	0.44	0.56	0.40	0.18	0.10	0.13	0.15	0.26	0.25	0.30	0.52
CETP (Im)	Cu	0.25	0.20	0.17	0.20	0.12	0.10	0.05	0.05	0.17	0.14	0.20	0.18
	Cr	BDL	0.06	0.05	0.01	0.02	0.01	0.02	BDL	0.04	0.03	0.01	BDL
	Cd	BDL	0.02	0.02	BDL	BDL	0.03	0.02	0.01	0.05	0.05	0.10	0.01
	Pb	BDL	0.06	0.02	0.01	0.02	0.03	0.05	BDL	0.02	BDL	0.02	BDL
	Zn	0.44	0.50	0.42	0.45	0.14	0.16	0.12	0.15	0.25	0.20	0.22	0.48
Middle 1	Cu	0.12	0.08	0.14	0.11	0.02	0.03	BDL	0.04	0.07	0.13	0.20	0.10
	Cr	0.02	0.03	0.04	BDL	0.02	0.02	0.03	0.01	0.04	0.05	0.10	BDL
	Cd	0.01	BDL	BDL	0.02	BDL	0.02	0.04	BDL	BDL	BDL	0.01	0.02
	Pb	0.02	0.02	BDL	0.01	BDL	0.02	0.01	0.02	0.05	0.02	BDL	0.01
	Zn	0.24	0.25	0.24	0.20	0.32	0.23	0.26	0.25	0.22	0.23	0.22	0.20
Middle 2	Cu	0.22	0.16	0.15	0.18	0.08	0.12	0.08	0.10	0.14	0.16	0.22	0.15
	Cr	0.02	0.01	0.03	0.02	0.05	0.03	0.02	BDL	0.02	0.04	0.01	0.02
	Cd	BDL	0.02	0.02	0.04	0.03	0.04	0.02	0.01	0.02	0.06	0.08	0.03
	Pb	BDL	0.01	0.03	BDL	0.02	0.01	0.02	0.04	0.02	0.03	0.01	0.02
	Zn	0.32	0.45	0.32	0.43	0.16	0.12	0.14	0.10	0.22	0.26	0.24	0.38

as Im (name of corresponding STP) such as Im (Bally). Two spots situated in the midstream between between Im (Bally) and Im (Howrah; Middle 1) and between Im (Maheshtala) and Im (CETP; Middle 2) was additionally decided for sampling. The sediment samples were collected only from middle points.

Collection of samples

Fish, water and sediment samples were collected on a monthly basis. Water samples were collected using automated water sampler (21 cc capacity) and stored in amber-coloured polyethylene bottles (1 L) pre-washed with 1 (N) HNO_3 and deionised water. To prevent further oxidation or any fungal growth 5 mL concentrated HNO_3 was added to the sampled water. At any location water was harvested from a depth 0 to 15 cm.

Sediment samples were collected using grab samples and placed in amber-coloured plastic containers. They were air dried, made free from silts using a sieve less than 2 mm prior to analysis.

During the study period, 12 fishing expeditions were carried out in middle spots between November 2005 and October 2006. Five fish samples from each spot were transported to the laboratory in a thermos flask with ice on the same day in each study period. Approximately 30 g of muscle, from each species viz.,*C. marulius* and *A. seengala*, were dissected, washed with deionized water, weighed,

Table 2 Seasonal variation of copper, chromium, cadmium, lead and zinc in water

Location	Metals	Concentration of heavy metals (in ppm)		
		Winter (Nov. 2005–Feb. 2006)	Summer (Mar. 2006–Jun. 2006)	Monsoon (July 2006–Oct. 2006)
Bally (Im)	Cu	0.19	0.07	0.19
	Cr	0.02	0.04	0.11
	Cd	0.03	0.04	0.01
	Pb	0.02	0.02	0.02
	Zn	0.28	0.29	0.24
Howrah (Im)	Cu	0.17	0.05	0.18
	Cr	0.02	0.06	0.12
	Cd	0.02	0.02	0.03
	Pb	0.02	0.01	0.01
	Zn	0.27	0.29	0.30
Maheshtala (Im)	Cu	0.21	0.13	0.16
	Cr	0.04	0.04	0.04
	Cd	0.01	0.01	0.06
	Pb	0.02	0.02	0.03
	Zn	0.48	0.14	0.27
CETP (Im)	Cu	0.20	0.08	0.17
	Cr	0.02	0.01	0.03
	Cd	0.01	0.02	0.07
	Pb	0.02	0.03	0.01
	Zn	0.46	0.14	0.22
Middle 1	Cu	0.11	0.02	0.13
	Cr	0.02	0.02	0.06
	Cd	0.01	0.02	BDL
	Pb	0.01	0.01	0.02
	Zn	0.23	0.27	0.22
Middle 2	Cu	0.17	0.10	0.17
	Cr	0.02	0.03	0.02
	Cd	0.02	0.03	0.05
	Pb	0.01	0.02	0.02
	Zn	0.38	0.13	0.24

packed in polyethylene bags, separated and stored at −20°C prior to analysis.

Preparation of samples for heavy metals analysis

The river water and sediment samples were analysed for heavy metals following the methods of APHA (1998). For the fish samples, 30 g of fish muscle was taken from each of the fish species after removing the fish scales and skin. The sample was finely chopped and kept in 25 ml concentrated nitric acid overnight followed by its digestion on heating mantle after addition of 10 ml sulphuric acid till a clear light yellow solution was obtained.

Estimation of heavy metals

Standard procedures were used for quantitative estimation of heavy metals Cu, Cr, Cd, Pb and Zn by atomic absorption spectrophotometer (AA240 FS, Varian) using different cathode lamps with air acetylene flame method. The working wavelength for the heavy metals are 213.9 nm for Zn, 324.8 nm for Cu, 228.8 nm for Cd, 357.9 nm for Cr and 217 nm for Pb. The data thus obtained were subjected to analysis of variance using SPSS 10.0 software to understand the effect of the factors like season, location or point of sampling.

Method validation

The standards of the metals samples were prepared in deionised water using the serial dilution technique in the range 0.01 to 2.00 μg g^{-1}. For all the metals calibration curves were established using these standards with $R^2 > 99\%$. The matrix effect was prominent and the matrix matched calibration standards were prepared for water, sediment and fish samples separately with $R^2 > 99\%$ for individual metal. Limit of detection (LOD) and limit of quantification (LOQ) was determined at signal to noise ratio 1:3 and 1:10, respectively. The coefficient of variation in the condition of repeatability (for five analyses in a day) and the intermediate precision (for five analyses in five different days) were evaluated at the level of LOQ for any substrate (water/sediment/fish) for each

Table 3 Monthly occurrence of copper, chromium, cadmium, lead and zinc in sediment

Location	Metals	Concentration of heavy metals (in ppm)											
		Nov. 2005	Dec. 2005	Jan. 2006	Feb. 2006	Mar. 2006	April 2006	May 2006	June 2006	July 2006	Aug. 2006	Sep. 2006	Oct. 2006
Middle 1	Cu	20.21	26.23	18.25	24.40	30.28	25.02	26.30	32.06	30.02	44.20	36.00	22.23
	Cr	18.55	18.02	15.06	22.52	20.60	30.50	28.04	20.01	26.08	22.45	25.02	20.05
	Cd	26.08	32.02	27.53	16.04	35.26	32.00	30.08	25.03	36.05	40.16	26.05	28.50
	Pb	0.25	0.68	0.40	0.58	0.22	0.20	0.20	0.36	0.44	0.30	0.28	0.32
	Zn	40.05	44.28	60.08	48.05	36.85	40.12	38.25	46.05	50.08	52.26	50.15	55.26
Middle 2	Cu	225.30	276.06	270.01	245.52	210.05	230.08	223.55	233.02	240.80	232.01	235.50	250.26
	Cr	3.05	3.02	2.01	1.25	4.80	3.55	2.05	5.65	2.20	4.50	5.02	2.36
	Cd	0.66	0.80	1.25	1.10	0.68	0.56	0.90	0.80	0.75	1.02	0.66	1.05
	Pb	8.06	8.00	6.02	9.85	5.02	7.56	6.82	5.25	4.89	6.28	12.08	10.05
	Zn	10.60	12.45	10.05	8.20	12.25	16.50	12.05	13.24	16.55	13.06	18.50	14.22

metal. Horwitz ratio (HorRat) pertaining to intralaboratory precision, indicating reproducibility of the method was calculated based on the equation:

HorRat = RSD/PRSD, here RSD is the relative standard deviation and PRSD ($= 2C^{-0.15}$) where C is the concentration (in general LOQ) expressed as a mass fraction, i.e. 50 ng g^{-1} = 50×10^{-6}.

Result and discussions

Heavy metal at impact points

The monthly variation of different heavy metals obtained near impact points located at Bally, Maheshtala, Howrah and Kolkata is presented in Table 1. The concentration of Cu, Cr, Cd, Pb and Zn were in the range of 0.04 to 0.25, below detectable limit (BDL) to 0.015, BDL to 0.010, BDL to 0.06 and 0.10 to 0.56 ppm, respectively. The annual average values for all the above metals were 0.15, 0.04, 0.03, 0.02 and 0.29 ppm, for Cu, Cr, Cd, Pb and Zn, respectively. The order of heavy metals accumulation at the impact points was Zn > Cu > Cr > Cd > Pb.

Heavy metal in riverine water (middle points)

The seasonal variation of different heavy metals in the riverine water of middle points between Bally and Howrah and CETP and Maheshtala is presented in Table 2. Lower and upper detection levels of heavy metals in the riverine water and their annual average values were as follows: BDL to 0.22 ppm, mean 0.12 ppm (Cu); BDL to 0.10 ppm, mean 0.03 ppm (Cr); BDL to 0.08 ppm, mean 0.02 ppm (Cd); BDL to 0.05 ppm, mean 0.02 ppm (Pb) and 0.10 to 0.45 ppm, mean 0.25 ppm (Zn). The concentrations of heavy metals in the riverine water collected from middle point had the order Zn > Cu > Cr > Cd > Pb.

Heavy metals in sediment

Table 3 represents the monthly variation of different heavy metals in sediment from Ganges at Middle 1 and Middle 2 location of sediment samples. The concentration of Cu, Cr, Cd, Pb and Zn were in the range of 18.25 to 276.06, 1.25 to 30.50, 0.56 to 40.16, 0.20 to 12.08 and 8.20 to 60.08 ppm for Cu, Cr, Cd, Pb and Zn, respectively. The mean values for all the above metals were 133.64, 30.50, 40.16, 12.08 and 60.08 ppm, respectively. The order of heavy metal accumulation in sediment was Cu > Zn > Cd > Cr > Pb. The data indicated that copper was maximally accumulated in the riverine sediments where as least annual average concentration was obtained for lead (Table 4).

According to Connell (1984), the behavior of metals in natural waters is a function of the substrate sediment composition, the suspended sediment composition and the water chemistry. Sediment composed of fine sand and silt will generally have higher levels of adsorbed metal than quartz, feldspar and detrital carbonate-rich sediment. Metals also have a high affinity for humic acids, organo-clays and oxides coated with organic matter.

Table 4 Seasonal variation of copper, chromium, cadmium, lead and zinc in sediment

Location	Metals	Concentration of heavy metals (in ppm)		
		Winter (Nov. 2005–Feb. 2006)	Summer (Mar. 2006–Jun. 2006)	Monsoon (July 2006–Oct. 2006)
Middle 1	Cu	22.26	28.42	36.74
	Cr	18.84	24.79	24.52
	Cd	26.03	30.59	34.09
	Pb	0.45	0.25	0.34
	Zn	49.54	40.32	50.83
Middle 2	Cu	253.43	224.18	236.10
	Cr	2.34	4.01	3.91
	Cd	0.97	0.74	0.81
	Pb	8.40	6.16	7.75
	Zn	11.10	13.51	16.04

Heavy metals in fish muscles

The monthly variation in the level of heavy metals found in the muscles of two different fish species, *C. marulius* and *A. seengala*, are shown in Table 5. The annual average values are shown in Table 6. Cu, Cr, Cd, Pb and Zn were obtained in the range of 0.34 to 0.86, 0.041 to 0.082, 0.024 to 0.048, 2.85 to 3.89 and 6.08 to 20.50 ppm, respectively, in case of *C. marulius* with the mean values of 0.52, 0.059, 0.048, 3.89 and 20.50 ppm, respectively. The concentrations of Cu, Cr, Cd, Pb and Zn for *A. seengala* were in the range of 0.75 to 1.44, 0.060 to 0.108, 0.034 to 0.062, 3.05 to 4.02 and 8.02 to 20.06 ppm, respectively; with the mean values of above metals were 0.96, 0.077, 0.046, 3.50 and 12.59 ppm, respectively. The above data indicated the order of heavy metals accumulation in fish muscles was found to be being Zn > Pb > Cu > Cr > Cd for both the species *C. marulius* and *A. seengala*. The trend of accumulation suggested deposition was maximum for zinc and minimum for cadmium in the muscles of both fish species.

Seasonal and spatial variation

In river water, spatial variation was exhibited by Cu [minimum concentration near middle point of Howrah and maximum concentration for Im (CETP)] and Cr [minimum and maximum concentrations were for Im (Maheshtala) and Im (Howrah)], respectively. Seasonal variations were prominent for Cu (minimum concentration in summer and maximum concentration in winter), Cr (minimum concentration in summer and maximum concentration in monsoon) and Zn (minimum concentration in summer and maximum concentration in monsoon). The concentrations of metals were at per ($\alpha = 0.05$) between impact and middle points or no spatial variation was observed for any metal based upon there average values. However, for sediment samples, no significant seasonal variation was obtained for any metal at $\alpha = 0.05$ levels but the spatial variation was significant. Only Zn has shown some significant seasonal variation in relation to metal deposition in fish muscles (minimum in monsoon and maximum in summer).

Table 5 Monthly occurrence of copper, chromium, cadmium, lead and zinc in fish

Fish	Metals	Concentration of heavy metals (in ppm)											
		Nov. 2005	Dec. 2005	Jan. 2006	Feb. 2006	Mar. 2006	April 2006	May 2006	June 2006	July 2006	Aug. 2006	Sep. 2006	Oct. 2006
C. marulius	Cu	0.38	0.40	0.42	0.34	0.53	0.76	0.82	0.86	0.54	0.48	0.38	0.35
	Cr	0.05	0.06	0.06	0.05	0.07	0.07	0.07	0.08	0.05	0.05	0.04	0.05
	Cd	0.05	0.04	0.03	0.03	0.03	0.04	0.05	0.05	0.02	0.03	0.03	0.04
	Pb	3.16	3.20	3.15	2.85	3.05	3.28	3.01	3.24	3.89	3.05	3.00	3.08
	Zn	10.42	12.20	10.08	14.22	13.80	16.24	20.50	18.23	6.08	10.06	12.10	11.65
A. seengala	Cu	0.80	0.82	0.88	1.05	0.90	1.22	1.44	1.25	0.82	0.75	0.77	0.86
	Cr	0.07	0.06	0.08	0.08	0.09	0.09	0.09	0.11	0.07	0.06	0.06	0.07
	Cd	0.04	0.04	0.05	0.04	0.05	0.06	0.05	0.06	0.05	0.03	0.04	0.04
	Pb	3.25	4.02	3.85	3.80	3.45	3.48	3.38	3.60	3.40	3.05	3.08	3.65
	Zn	10.05	12.00	11.55	14.40	13.20	16.22	20.06	18.25	8.85	8.02	10.26	8.25

Table 6 Seasonal variation of copper, chromium, cadmium, lead and zinc in fish

Fish	Metals	Concentration of heavy metals (in ppm)		
		Winter (Nov. 2005–Feb. 2006)	Summer (Mar. 2006–Jun. 2006)	Monsoon (July 2006–Oct. 2006)
C. marulius	Cu	0.38	0.74	0.47
	Cr	0.06	0.07	0.05
	Cd	0.04	0.04	0.03
	Pb	3.09	3.15	3.31
	Zn	11.71	17.19	9.41
A. seengala	Cu	0.88	1.20	0.78
	Cr	0.07	0.09	0.06
	Cd	0.04	0.05	0.04
	Pb	3.71	3.48	3.18
	Zn	11.25	16.93	9.04

Tidal effect is one of the prime factors, predominantly controlling the solubility of trace metals in surface water along with water pH (Osmond et al. 1995), water temperature (Iwashita and Shimamura 2003), the river flow (Neal et al. 2000; Iwashita and Shimamura 2003; Miller et al. 2003; Olías et al. 2004) and the redox environment of the river system (Osmond et al. 1995; Iwashita and Shimamura 2003). The composition of the river water suggested there was an abundance of chloride, sulphate and phosphate ions but the solubility rule indicated probably chloride and sulphate (or its reduced form sulfide or hydrogen sulfide) constituted the counter anionic part of the cations of all metals in the solution phase, including those investigated in our present study. In warm season, there was a rise in water temperature owing to increase rate of evaporation. In addition, temperature impacts the rates of metabolism and growth of aquatic organisms, rate of plant's photosynthesis, solubility of oxygen in river water and organism sensitivity to disease, parasites and toxic materials. At a higher temperature, plants grow and die faster, leaving behind organic matter that requires oxygen for decomposition. In 1992, Kabata-Pendias and Pendias suggested that trace elements accumulated to phytoplankton may become soluble during the decay of plants (Kabata-Pendias and Pendias 1992). But the low DO status of water in summer succumb to a decrease in the solubility of metal chloride salts as a result of change of higher oxidation state of metal to a lower one. The common ion effect of free chloride ions during tides caused re-precipitation of metal chloride salt. The phenomena also discernible for metal sulphate salts as the ion concentration in dry season was raised as a result of increase in sulphur oxidizing bacteria activity with temperature (Olías et al. 2004). The process lowered the pH and an increased solubility of lower valence of certain metal such as copper might be expected, but the effect was suppressed by the neutralizing capacity of river alkalinity. In the rainy season, rivers are heavily flooded and the drainage system is drastically affected which results in mixing of polluted and unpolluted waters and this provides necessary dilution (Collvin 1985) that demises the common ion effect. In winter, a fall in water temperature improves oxidation condition. Thus, one could expect a relatively higher concentration of metal ion in winter and monsoon than in summer. In general, the metals are present at a lower concentration in sediment than in solution phase might be due to a neutral to alkaline pH which effected metals released into the river system to remain associated with solid (suspended or dissolved) and sediments, mostly. Unlikely seasonal changes, physico-chemical parameters had no imperative effect on spatial variation of metal ions and probably due to the nature of discharges the river received at different locations of its stretch before sampling.

Heavy metal concentrations in the tissue of freshwater fish vary considerably among different studies (Hayat et al. 2007; Chattopadhyay et al. 2002; Papagiannis et al. 2004), possibly due to differences in metal concentrations and chemical characteristics of water from which fish were sampled, ecological needs, metabolism and feeding patterns of fish and also the season in which studies were carried out (Rauf et al. 2009). Accumulation of bioactive metals like Cu and Zn was actively controlled by the fish through different metabolic processes and the level of accumulations usually independent of ambient concentrations (Chatterjee et al. 2006). On the other hand, environmental concentrations affect the accumulation of non-essential toxic elements like Pb (Pattee and Pain 2003).

Conclusion

The content of protein in fish tissue and its relative affinity towards non-essential toxic elements determine their levels in fish tissue. It has been found that among Pb, Cd and Cr, sulfyhydryl group of metallothionenin protein has the highest affinity for Pb and lowest for Cd. The bottom line principle was soft acid hard base rule. The bioaccumulation was quite evident for Pb among both the fish species. The order of heavy metals accumulation at the impact points as well as middle point was Zn > Cu > Cr > Cd > Pb for water and Cu > Zn > Cd > Cr > Pb for sediment. Cu was maximally accumulated in the riverine sediments whereas least annual average concentration was obtained for lead. The order of heavy metals accumulation in fish muscles was found to be being Zn > Pb > Cu > Cr > Cd for both *C. marulius* and *A. seengala*. The trend of accumulation suggested deposition was maximum for Zn and minimum for Cd in the muscles of both fish species. Seasonal variations were prominent for Cu (minimum concentration in summer and maximum concentration in winter), Cr (minimum concentration in summer and maximum concentration in monsoon) and Zn (minimum concentration in summer and maximum in monsoon). Only Zn has shown some significant seasonal variation in relation to metal deposition in fish muscles (minimum in monsoon and maximum in summer). The main reasons are the sewage water and sludge may wash out heavily by rain and may be deposited in the river and other aquatic bodies. This may also contaminate the aquatic flora and fauna. Moreover, long-term disposal of sewage and sludge in river may result the accumulation of toxic heavy metals in river water, which may adversely affect the growth of various aquatic vertebrates and invertebrates including fishes. Proper care, maintenance, treatment and disposal of sewage water and sludge are most vital. Therefore, an effective management viz. increasing the number of effective sewage treatment plant is required in order to prevent the superfluous leakage of heavy metals in the environment on a priority basis. Therefore, spontaneous involvement of public and private sector with obligatory involvement of local as well as national level regulatory and monitoring authority should be the prime thrust for the nation regarding the effective effluent management of domestic and industrial waste.

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