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Impact of heavy metals on water, fish (*Cyprinus carpio*) and sediments from a water tank at Tumkur, India

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Abstract

This study was carried out to assess the concentrations of various heavy metals and their distribution in a hyper-eutrophic urban Tumkur tank system, which is being polluted from industrial, domestic and sewage effluents. Samples of water, fish and soil sediment were analyzed for the concentration of seven heavy metals (iron, zinc, copper, nickel, chromium, lead and cadmium) using atomic absorption spectrophotometry. The water-soluble (bioavailable) fractions of heavy metals correlated positively with their total concentration, exhibiting the following sequence of bioavailability: Zn > Cd > Ni > Pb > Cu > Cr > Fe. *Cyprinus carpio* exhibited a maximum bioaccumulation factor for copper (5500). The mean values of all types of collected samples were correlated with the corresponding mean values in a control tank (Teetha tank). The sequence of the order of the concentration of the metals in water, fish and sediment samples exhibiting higher values than those observed in the control tank was as follows: Cr > Pb > Cu ≈ Ni > Fe > Cd > Zn, Cr > Cd > Cu ≈ Zn > Pb > Fe ≈ Ni and Fe > Pb > Cr > Cu > Ni > Zn > Cd, respectively. The geoaccumulation indices of the heavy metals revealed that the tank is moderately to strongly contaminated. As *Cyprinus carpio* is extensively used for human consumption, there is a growing health risk that these metals could find their way into the human food chain.

INTRODUCTION

The bioaccumulation of trace elements in living organisms and biomagnification in them describes the processes and pathways of these (possible) pollutants from one trophic level to another, exhibiting the higher bioaccumulation ability in the organisms concerned. Increasing concentration through the food chain caused higher retention time of toxic substances than that of the other normal food components. Therefore, various fish species are widely used as bio-indicators of metal contamination (Svobodova et al. 2004).

Under acidic conditions, the free divalent ions of many metals may be absorbed by fish gills directly from the water (Merlini and Pozzi 1977, Part et al. 1985). Hence, concentrations of heavy metals in organs of fish determined primarily the level of pollution in the water and food (Farkas et al. 2000).

The concentration of pollutants in water samples only indicate the situation at the time of sampling, while concentrations in the organism are the result of past as well as current pollution levels in the environment in which the organism lives (Ravera et al. 2003). A previous study indicated that potential sources of elevated levels of heavy metals were sewage wastes, wastes from metal processing industries and other household refuse (Lokhande and Kelkar 1999).

The present study was undertaken to assess the extent of heavy metal (Fe, Zn, Cu, Ni, Cr, Pb and Cd) contamination in Tumkur Tank, which is located in an area that is both residential and industrial. Analysis of the enrichment of these heavy metals in water, fish and sediment samples was used to evaluate the magnitude, impacts and possible sources of heavy metal contamination on tank systems. *Cyprinus carpio* (common carp) is a valuable, cheap food item and a source of protein in the human diet. Thus, it is important to identify the extent of heavy metal concentration in fish samples and consider its potential impacts on the food chain and its human health risks.

METHODS

Study Area

Tumkur Tank, the study area, is located in Tumkur town, 70 km west of Bangalore, the capital city of Karnataka, India. The tank is heavily polluted from effluent discharges from industry and sewage from a local residential area. An extensive growth of a range of weeds were seen, with *A. philoxeroides* as the dominant species, especially near the overflow region. Teetha tank was used as a control site for this study. It is located in Goravanahalli village, Tumkur District, 60 km northwest of Bangalore. Analysis of water, fish and sediment samples from these tanks were used for comparison of heavy metal contamination.

Sampling

Sampling was carried out over a period of 2 years (Jan. 2006 to Jan. 2008). Twenty-four grab water samples were collected at monthly intervals from each tank in cleaned 2 liter polythene bottles. The fish were sampled with gill nets from the tanks. Adult individuals of similar size were selected from both the tanks. Eight fish samples and eight sediment samples were collected at 3 months intervals from both the study and control tanks. All the samples were brought to the laboratory and stored at 4°C for 1 day.

Sample Preparation

Water samples (500 ml) were filtered through Whatman filter paper No. 41 (0.45 µm pore size). The filtrate (500 ml) and unfiltered (~1.5 ml) water samples were preserved in 2 ml concentrated nitric acid (HNO_3) to prevent precipitation of metals and growth of algae. Both samples were concentrated 10 times (from 500 to 50 ml) in a water bath and subjected to nitric acid digestion with a microwave-assisted technique (pressure 30 bar; power at 700 W) as per standard methods outlined by the American Public Health Association (2000).

Fish, *Cyprinus carpio,* were dissected to extract a 10 g sample of the fish muscle which was oven dried at 100±1°C for 3 h. 2 g of the dried samples were put in a 250 ml conical flask and then subjected to acid digestion with nitric acid and perchloric acid (4:1) 15 ml. The flasks were then cooled to room temperature and the residues were dissolved in 10 ml of dilute nitric acid and filtered. The filtrate was diluted to 50 ml with distilled water (Frank 1984).

Sediment samples were air-dried and ground to a fine powder with a pestle and mortar and then sifted on a 1 mm sieve. Two grams of the fine powder samples in 50 ml distilled water were put in 250 ml conical flasks and subjected to acid digestion with 8 ml aqua regia for 2 h on a hot plate using a sand bath. The samples were then evaporated to near dryness. The flask was cooled and the residue dissolved in 10 ml of dilute nitric acid and filtered. The filtrate volume was made to 50 ml with distilled water (Kaviraj and Das 1990).

Sample Analysis

Analysis of the heavy metal content of the samples was performed with a flame atomic absorption spectrophotometer (GBC Avanta version 1.31), using acetylene gas as fuel and air as an oxidizer. Calibration curves were prepared separately for all the metals analyzed using different concentrations of standard solutions. The instrument was set to zero concentration for all types of samples, using a reagent blank. Digested samples were aspirated into the fuel-rich air-acetylene flame and the metal concentrations were determined from the calibration curves. Each determination was based on the average values of three replicate samples. The detection limits for iron (Fe), zinc (Zn), copper (Cu), nickel (Ni), chromium (Cr), lead (Pb) and cadmium (Cd) were 0.05, 0.008, 0.025, 0.04, 0.05, 0.06 and 0.009 $\mu g\ ml^{-1}$, respectively (Athanasopoulos 2002). The precision of the analytical procedures, expressed as relative standard deviation, ranged from 5 to 10%.

Statistical analysis for the parameters (maximum, minimum, mean & standard deviation) were calculated for the data obtained from seven selected heavy metals in water, fish and sediment samples. Correlation analyses were performed with Pearson's product moment correlation. For samples with heavy metal concentrations below the analytical detection limit, half of the respective limit of quantification was substituted to perform statistical analysis (Watanabe et al. 2005). The value of probability level $P<0.05$ was considered statistically significant.

Bioavailability

The term "bioavailability" is meant to denote heavy metals in a water-soluble form that plant and animal communities can readily uptake and assimilate (Kaviraj and Das 1999). The bioavailability of metals (expressed in percent) with respect to total metal content can be calculated as follows:

$$\%\ \text{Bioavailability} = \frac{\text{Dissolved metal concentration } (\mu g\ l^{-1})}{\text{Total metal concentration } (\mu g\ l^{-1})} \times 100$$

where the dissolved metal concentration is determined via analysis of filtered water samples and the total metal concentration of unfiltered water samples.

Bioaccumulation Factor

The bioaccumulation of all seven heavy metals (HM) in different samples of the same tank was quantified with a bio-accumulation factor (BAF), defined as the ratio of the concentration of a specific heavy metal in the organism to the concentration of the metal in the tank water (Hassan et al. 2003). The BAF was calculated as follows:

$$\text{BAF} = \frac{\text{Concentration of HM in dry fish muscle } (\mu\text{g kg}^{-1})}{\text{Concentration of HM in tank water } (\mu\text{g l}^{-1})}$$

Geoaccumulation Index

A geoaccumulation indexing (I_{geo}) approach was used to quantify the degree of anthropogenic contamination and to compare the different metals in lake sediments (Muller and Suess 1979, Forstner et al. 1993). This quantitative check of metal pollution in aquatic sediments was proposed in the form of an equation defined as the index of geoaccumulation, which is as follows:

$$I_{geo} = In\left(\frac{C_n}{1.5} \times B_n\right)$$

where C_n = measured concentration of heavy metal in sediment (μg g^{-1} dry mass); B_n = background value of heavy metal (μg g^{-1} dry mass) and 1.5 = background matrix correction factor.

The background matrix correction factor of 1.5 is used to account for possible variations in the background data as a result of such lithogenic effects as the chemical leaching of bedrock, water drainage basins and run-off from banks (Upadhyay et al. 2006). For this study, the average values of sediments from Teetha Tank are considered the local background values. The index of geoaccumulation consists of seven grades, for which the highest grade (6) reflects 100-fold enrichment above background values. Forstner et al. (1993) identified geoaccumulation classes and the corresponding contamination intensity for different indices, as illustrated in Table 1 (Gulfem and Balkas 1999).

Table 1

Geoaccumulation index classification (Forstner et al. 1993).

Sediment geoaccumulation index, I_{geo}	I_{geo} class	Intensity of contamination
< 0	0	Practically uncontaminated
> 0-1	1	Uncontaminated to moderate
> 1-2	2	Moderately contaminated
> 2-3	3	Moderately to strongly contaminated
> 3-4	4	Strongly contaminated
> 4-5	5	Strongly to very strong contamination
> 5	6	Very strong contamination

RESULTS

Heavy metal concentration in water

Data on heavy metal concentrations in water from the tanks investigated are presented in Table 2. Based on comparison of the results from Tumkur Tank with that of Teetha Tank (control), the average total concentrations (μg l^{-1}) of Fe, Zn, Cu, Cr, Pb, Cd and Ni in the samples were found to be 5, 2.08, 8.66, 100, 9.5, 4.5 and 8.66 fold higher, respectively. The Cr concentration in the sample was highest, while Zn concentration was the lowest. The average total and dissolved concentration of Fe in the water samples exceeded the permissible limits prescribed by the Bureau of Indian Standards (Table 2). The mean concentration of the remaining 6 heavy metals did not exceed these limits. The maximum concentrations of Cu, Cr and Pb in the water samples, however, did exceed the limit.

The bioavailability of the heavy metals depends in part on the concentration of anions and chelating ligands present in the water, pH and Redox status and the presence of absorptive sediments (Mido and Satake 2003). The percentage bioavailability of the metals exhibited a maximum and minimum value for Zn (50%) and Fe (21%) respectively, while Cd, Ni, Pb, Cu and Cr exhibited 33, 32, 26, 23 and 22 respectively.

Table 2

Maximum, mean and standard deviation of total and dissolved metals in tank water samples (μg l^{-1}).

Concentration	Metal						
	Fe	Zn	Cu	Cr	Pb	Cd	Ni
Maximum : Total	10810	285	128	71	105	2	65
Maximum : Dissolved	980	230	24	17	25	0.4	20
Mean : Total	1500	125	26	10	9.5	0.09	13
Mean : Dissolved	318	62	6	2.2	2.5	0.03	4.1
Standard deviation: Total	2873	57	31.95	18.91	29.4	0.4	16.19
Standard deviation: Dissolved	244	53	5.89	4.58	6.9	0.08	5.33
Mean of local control	300	60	3	0.2	1.0	0.02	1.5
Indian Standards (μg l^{-1})	300	5000	50	50	100	10	--

Minimum values are half of the detection limit of the metal; Indian standards for drinking water (Awasthi 2000).

Heavy metal concentration in Cyprinus carpio

The average total concentration of Fe, Zn, Cu, Cr, Pb, Cd and Ni in common carp exhibited an increase of 1.5, 2, 2.25, 1.6, 2.3 and 1.5 fold respectively. The average concentration mean and maximum values of Zn and Cu in the fish samples exceeded the permissible limits prescribed by the Bureau of Indian Standards (Table 3). The mean concentration of the remaining 5 metals did not exceed these limits, while Ni with its maximum value exceeded the permissible limit.

Table 3

Maximum, minimum, mean and standard deviation of metals in fish muscle samples (μg g^{-1} dry weight).

Concentration	Metal						
	Fe	Zn	Cu	Cr	Pb	Cd	Ni
Maximum	1080	91	42	5	2	0.3	7
Minimum	220	12	6	1	0.004	0.003	0.05
Mean	600	55	33	2.0	0.8	0.07	3
Standard deviation	292	28	10.5	1.2	0.78	0.095	2.59
Mean of local control	400	27	16.0	0.8	0.5	0.03	2
Indian standards (mg kg^{-1})	--	50	30	20	2.5	1.5	1-5

Indian Standards for Food (Awasthi 2000).

Heavy metal concentrations in sediments

Comparison of the average concentrations of heavy metals in sediments of both the Tumkur Tank and Teetha control tank, exhibited 1.6, 3.5, 2.5, 2 and 1.5 fold increases with regard to Zn, Cu, Ni, Pb and Cd, respectively. The average Zn, Cu, Ni, Pb and Cd concentrations remained below the Bureau of Indian Standards limits (Table 4).

A comparison of the average total concentration of the heavy metals in the water, fish and sediment samples from the Tumkur and Teetha tanks is presented graphically in Fig 2.

Bioaccumulation factor

The bioaccumulation factor (BAF) for different heavy metals from water to fish was Cu (5500), Cd (2383), Fe (1887), Cr (909), Zn (887), Pb (320) and Ni (732). While Cu exhibited a maximum (5500) BAF in common carp followed by Cd, Fe, Cr, Zn and Ni with Pb exhibiting the lowest (320) BAF.

Table 4

Maximum, minimum, mean and standard deviation of metals in sediment samples ($\mu g\ g^{-1}$ dry weight).

Concentration	Metal						
	Fe	Zn	Cu	Ni	Cr	Pb	Cd
Maximum	29250	91	115	68	165	62	0.3
Minimum	475	20	14	8	35	8	0.0035
Mean	5552	75	66	45	105	32	0.03
Standard deviation	7908	20.4	30.4	19.8	43.3	15.6	0.83
Mean of local control	410	45	19	14	18	05	0.02
Indian Standard	--	300 – 600	135 – 270	75 – 150	--	250 – 500	3 – 6

Indian Standard for Soil (Awasthi 2000)

The BAFs for metals from sediment to fish were Fe (0.1), Zn (0.73), Cu (0.5), Cr (0.01), Pb (0.02), Cd (2.3) and Ni (0.06), indicating Cd with a maximum BAF (2.3) in common carp followed by Zn, Cu, Fe, Ni, Pb and Cr.

Geoaccumulation index

The calculated index of the heavy metals in Tumkur Tank and their corresponding contamination intensity are summarized in Table 5. The I_{geo} value for Cd exhibited a zero class, indicating unpolluted sediment quality. However, the index value for Fe showed that the samples were moderately to strongly contaminated, whereas, index values for Zn, Cu, Ni, Cr and Pb exhibited a low to moderate enrichment in sediments.

Table 5

Geoaccumulation indices of Tumkur Tank sediments.

Metal	Mean ($\mu g\ g^{-1}$)		Index of geo-accumulation (I_{geo})	Level of sediment contamination
	Cn[a]	Bn[b]		
Fe	5552	410	2.2	Moderate to strongly contaminated
Zn	75	45	0.1	Uncontaminated to moderate
Cu	66	19	0.83	Uncontaminated to moderate
Cr	105	18	1.35	Moderately contaminated
Pb	32	5	1.45	Moderately contaminated
Cd	0.03	0.02	0	Practically uncontaminated
Ni	45	14	0.76	Uncontaminated to moderate

[a] Average sediment values of Tumkur Tank;
[b] Average sediment values of local control;
Sediment contaminations were interpreted by comparing I_{geo} values with Table 1.

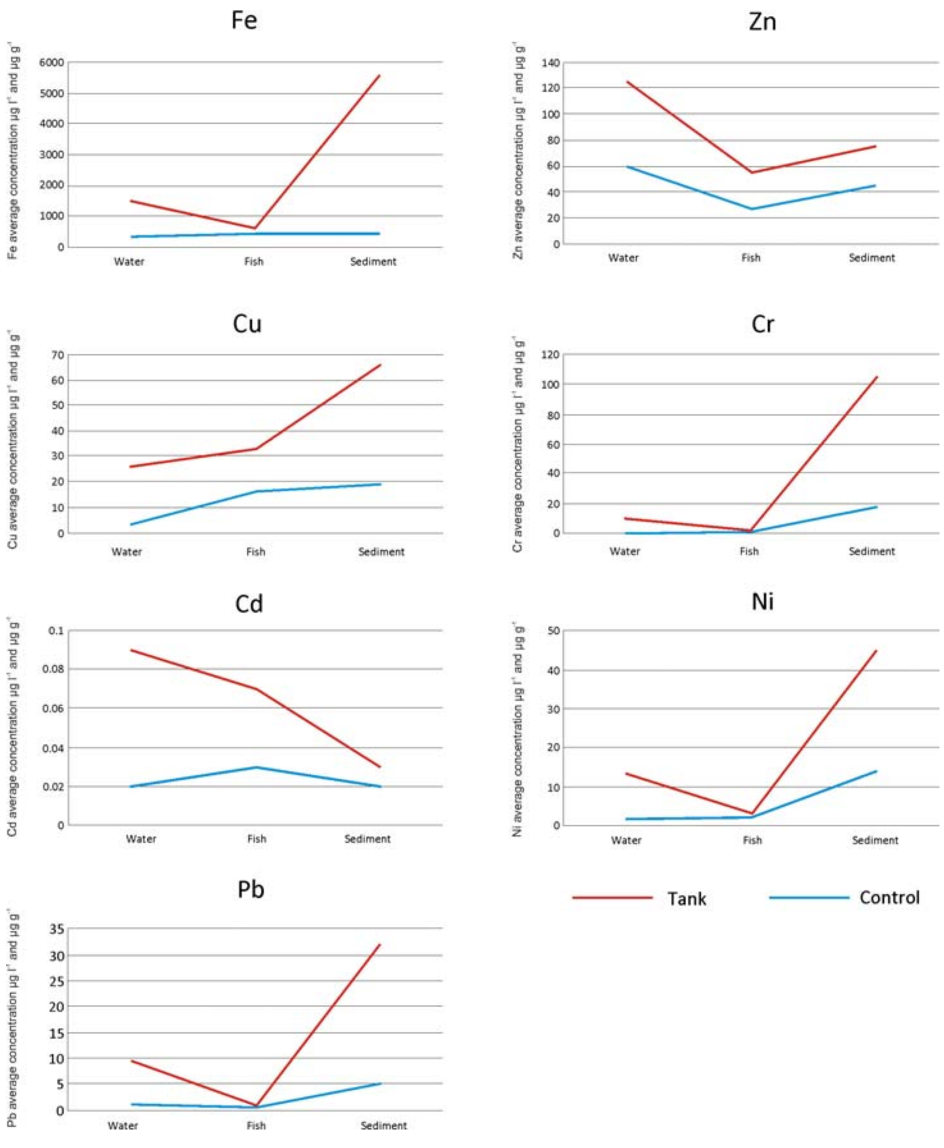

Fig. 2. Comparison of average total concentration of heavy metals in water, fish and sediment samples from Tumkur and Teetha Tanks: a) Fe, b) Zn, c) Cu, d) Cr, e) Cd, f) Ni and g) Pb.

DISCUSSION

Heavy metal concentrations in water, fish and sediment samples

The contamination of soils, sediments, water resources and biota by heavy metals is of major concern, especially in many industrialized countries, because of the toxicity, persistence and bioaccumulative nature of these metals (Ikem et al. 2003).

Results of our study exhibited the highest increase in chromium concentration (factor of 100) in the water samples from the Tumkur tank, compared to the control (Teetha Tank), mainly because of the discharge of effluents from chemical and metal industries that subsequently drain to the tank. In the present study, however, it was interesting to note that although Cr is less bioavailable in water (22%) its accumulation in the fish muscles placed highest.

Copper exhibited a 3.5-fold increase in concentration in the sediment samples, compared to Teetha Tank, also because of effluent discharges from industry. Efforts to recover the heavy metals from the waste water prior to discharge are strongly suggested to alleviate further water quality degradation.

As far as the availability of total and dissolved metals to fish is concerned, it is about 30%. Among the samples of water, common carp and sediment, the metal concentrations were generally highest in the sediments. In the case of Zn, however, the concentration was slightly higher in the water samples, which could be because of its weak absorption by soil sediments (Mido and Satake 2003). The presence of the metals in common carp is likely to cause health risks for both animals and humans. Further studies are needed to fully assess the present health risks associated with the discharges to the tanks.

Bioaccumulation factor

Most laboratory research on the bioaccumulation of heavy metals suggests that no single mechanism is responsible for metal uptake in aquatic systems. The accumulation of a particular metal depends to a large degree on the presence of the metal in the water column.

In the present study, however, it was interesting to note that although average total concentration ($\mu g\ l^{-1}$) of Cr (100) in the water sample was highest, its BAF value in common carp placed it in the fourth highest position among the heavy metals. More Cu accumulated (first position) in common carp, even though its bioavailability is less (fifth position) among the metals examined in this study. Thus, the BAFs appear to be largely independent of the bioavailability values. This means that some heavy metal accumulation in fish could depend not only on the concentration of the metal in the water column but also on the abiotic features of the environment (eg., pH, Redox potential, alkalinity and salinity), and the duration of exposure (Protasowicki and Chodyniecki 1988, Cain et al. 2000, Jezierska and Witeska 2001, Martinez et al. 2002, Witeska and Jerierska 2003, Smolders et al. 2003).

The BAFs for different heavy metals from water to fish and soil to fish are a key component of human exposure to the metals via the food chain. The highest BAF value in this study is for Cu. Overall, the BAF values for Cu, Cd, Fe and Cr were all significant, supporting the finding that the accumulation of Pb and Ni is comparatively less, while that of Cu, Cd, Fe, Cr and Zn is more in fish.

The I_{geo} calculations of the sediment samples revealed low to moderate to strong contamination of heavy metals from anthropogenic sources in the Tumkur tank basin. A similar study was carried out for the surface sediments of Dasarahalli Lake, India (Lokeshwari, Chandrappa 2007). Comparing the results of both studies, it was observed that sediments in the Tumkur tank exhibited higher values than the Dasarahalli Lake study.

Based on the results of this study, it is concluded overall that unplanned urban settlements, combined with the proliferation of unorganized small-scale industries and the sewage from Tumkur city lead to the contamination of the Tumkur tank.

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