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HEAVY METALS ACCUMULATION IN SOME FRESHWATER FISH SPECIES OF AGRA REGION, INDIA

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ABSTRACT
Fish are a valuable source of high-grade protein and nutritious component of the human diet and occupy an important position in the socio-economic conditions of south Asian countries. Fish constitutes a major source of heavy metals in food. Five most commercially important fresh water fish species were collected from different fish markets of Agra city and analyzed for the metals (Pb, Cd and Hg). The metal concentration was evaluated using a Perkin Elmer AA analyst 100 atomic absorption spectrophotometer. Wet digestion method was used for analysis of metals with nitric acid and sulfuric acid. The metal concentrations ranges of Pb, Cd and Hg detected were 0.02-18.0, 0.05- 21.0 and 0.01-26.0 µg kg^{-1}respectively. The highest concentrations were detected for all metals in summer followed by winter and rainy seasons. The present study showed that the levels of metals are different in different fish species but within the maximum residue levels recommended at National and International standards.

KEYWORDS: Metals, Accumulation, Fish species, Wet digestion method.

INTRODUCTION
Fish are a valuable source of high-grade protein and nutritious component of the human diet and occupy an important position in the socio-economic conditions of South Asian countries. India is the third largest producer of fish and second in inland fish production with annual production of 7.75 million tones. Metals from natural and anthropogenic sources like atmospheric precipitation, wastewater, industrial discharge are released into aquatic ecosystems, where they pose a serious threat because of toxicity, long persistence, bioaccumulation and biomagnifications in the food chain (Kucykbay and Orun 2003; Pourang et al. 2005). Sources of metals are highly variable and regionally specific; the environmental contamination level of metals even for small territories is highly variable (Biksham et al. 1991; Allen-Gil and Martynov 1995). In aquatic food webs, metals can accumulate and reach high concentrations in mollusks, macrophytes, predatory fish, and benthic feeding fishes (Chen et al. 2000). Considering the importance of fish in the human diet, consumption of contaminated fish could pose a significant threat to human health (Schmitt et al. 2006). A lot of studies have been published on the heavy metal levels in the aquatic environment (Rashed 2001; Canli and Atli 2003; Canpolat and Çalta 2003; Demirak et al. 2006; Farkas et al. 2003; Karadede et al. 2004; Tekin-Özan and Kır 2006; Velcheva 2006; Yılmaz, 2006).

Toxic metals are also bio accumulative and relatively stable, as well as carcinogenic. Most metals are released into the environment then find their way into the aquatic phase as a result of direct input, atmospheric deposition, and erosion caused by rains. Therefore, aquatic animals may be exposed elevated levels of metals. Mercury and lead are globally well-distributed environmental heavy metal pollutants, once they are released into the environment, they circulate between air, water, soil, and biota in various forms. When deposited in the biota, mercury undergoes biotransformation, in which inorganic mercury may convert to organic mercury (methyl mercury). Environmental pollution by metals as a result of rapid industrialization has been reported by researchers in different part of India and the globe as the whole (Chakraborty R, 2003). Consumption of significant amounts of contaminated fish could pose a significant threat to human health. Hence, the present study was proposed to monitor some metals level in edible fresh water fish species of Agra region, keeping in view of public health significance of metal residues, safety of consumers and legal restrictions on export.

MATERIAL AND METHOD
Agra, the city of Taj (latitude 27^0 10′ N and longitude 78^0 5′ E) is located in the North central part of India. Information available from different fish dealers indicates that fresh water fishes available in Agra

markets are brought from river Yamuna and its tributaries.

Wet digestion method was used for the analysis. All reagents like Sulfuric Acid (H_2SO_4), Nitric acid (HNO_3) and Hydrogen peroxide used were of analytical grade purchased from E. Merck (India) Ltd, India. Certified reference material of mercury, cadmium and lead procured from the National Physical Laboratory, New Delhi. Fresh samples were purchased from commercial fishery market of Agra. After identifying the species, samples were immediately kept in pre cleaned polythene bags, which were sealed and kept in an ice box until further analysis in the laboratory. The soft tissue was removed and oven dried to remove moisture and was crushed with a mortar and pestle to fine powdery form. To estimate the metal content 5g.±0.1 of samples were digested with conc. HNO_3 and conc. H_2SO_4 (1:1). The completely digested sample were allow to cool to room temperature, filtered with a Whatman filter paper (No.-1) and made up to 50 ml with double distilled water. The elemental analysis was carried out in a Perkin Elmer AA analyst 100 atomic absorption spectrophotometer as per standard conditions (Table-1).

Table 1: Working conditions for the analysis of trace elements by atomic absorption spectrophotometer.

Heavy Metals	Wavelength (nm)	Slit (nm)	Detection Limit (mg/1)	Sensitivity (mg/1)	Linear Range	Gas	Support	Mode
Pb	283.3	0.7	0.05	0.45	20.0	Acetylene	Air	Absorption
Cd	228.8	0.7	0.002	0.028	2.0	Acetylene	Air	Absorption
Hg	253.7	0.7	0.001	0.077	5.0	Acetylene	Air	Absorption

Homogenized samples (5.0 ± 0.5 g) were spiked with three different concentrations (Table 2) of metals for determination of recovery, each run in triplicate and blanks were carried through the whole procedure described above. Recoveries were 94% to 103% for mercury, 97% to 101% for cadmium and 98% to 102% for lead.

Table 2: Recovery (%) of Pb, Cd and Hg residues obtained in fresh water fishes.

S.No.	Heavy Metals	Sample wt. (g)	Spiked concentration mg/kg	Recovery concentration mg/kg	Recovery (%)
1	Pb	5.0±0.1	0.05	0.049	98
		5.0±0.1	0.1	0.099	99
		5.0±0.1	0.2	0.204	102
2	Cd	5.0±0.1	0.05	0.0485	97
		5.0±0.1	0.1	0.101	101
		5.0±0.1	0.2	0.196	98
3	Hg	5.0±0.1	0.05	0.047	94
		5.0±0.1	0.1	0.097	97
		5.0±0.1	0.2	0.206	103

RESULTS AND DISCUSSION

Knowledge about heavy metal concentration in fish is important both with respect to nature management and human consumption. The mean values and standard deviations of metal concentrations of different metals detected in the edible portion of the selected species of fish are shown in Table 3. A total of 123 samples of various fish were monitored for lead (Pb), cadmium (Cd) and mercury (Hg) residues. Approx 37% samples were detected with metals residues. To study the seasonal variation, sampling was carried out during winter, summer and rainy seasons. In the present study, among the three metals, mercury was observed in major amount in all fish species in summer followed by winter and rainy season. Fishes have a natural tendency to concentrate mercury in their bodies, often in the form of methyl mercury, a highly toxic organic compound of mercury. Lead was highest in summer season in *Labeo rohita* in comparison to other fish species. Lead is known to induce reduced cognitive development and intellectual performance in children and increased blood pressure and cardiovascular disease in adults (Commission of the European Communities 2001). Lead was not detected in any samples of *Labeo rohita* and *Catla catla* in rainy season and in any samples of *C.puntatus, H.fossilis and Clarias batrachus in winter season*. The value of Cadmium was highest in *H.fossilis* in summer. All three metals were higher in summer season followed by winter and rainy season.

Table 3: Concentration of Pb, Cd and Hg residues obtained in fresh water fishes.

S.No.	Fish Species	Winter Season ((µg kg^{-1}))			Summer Season (µg kg^{-1})			Rainy Season (µg kg^{-1})		
		Pb	Cd	Hg	Pb	Cd	Hg	Pb	Cd	Hg
1.	Labeo rohita	6.0 ± 4.3	5.0 ± 3.0	9.0 ± 4.5	8.0 ± 4.2	8.0 ± 5.5	11.0 ± 3.5	ND	5.0 ± 5.1	7.0 ± 3.5
2.	Catla catla	6.0 ± 2.1	6.0 ± 3.4	5.0 ± 3.1	ND	6.0 ± 4.8	11.0 ± 6.3	ND	5.0 ± 3.1	5.0 ± 4.1
3.	Channa punctatus	ND	6.0 ± 4.3	6.0 ± 2.9	6.0 ± 2.7	ND	8.0 ± 4.4	5.0 ± 2.1	ND	6.0 ± 6.3
4.	Heteropneustes fossilis	ND	7.0 ± 3.5	6.0 ± 2.5	ND	9.0 ± 3.5	14.0 ± 2.5	ND	ND	6.0 ± 4.1
5.	Clarias batrachus*	ND	ND	12.0 ± 6.3	ND	6.0 ± 3.5	11.0 ± 5.3	-	-	-

- Data are presented as the mean values ±SD
- ND: Not detected
- * : Clarias batrachus was not available in fish market of Agra in rainy season
- MRL of Pb, Cd and Hg – 5.0 , 1.5 and 0.5 mg kg^{-1} respectively

In India, various workers have determined the presence of toxic metals in Indian rivers. Prebha and Selvapathy (1997) have studied the status and trend of river water pollution due to toxic metals. Kumar and coworkers (1998) have reported cadmium and zinc in the sediment and water of the Kali and Hindon rivers. Priyadarshani (1998) has reported the presence of zinc, copper, nickel, cadmium, lead, manganese, mercury, cobalt and iron in the Safi River. A monitoring study of fish and fish products from Ganga river (CIFT, 2006), showed that Yamuna have also shown comparatively higher metal concentration in the Agra stretch of the river, may be due to heavy discharge of industrial effluents and its different chemical characteristics. In present study levels of metals detected were below the tolerance limits recommended by National and International authorities, the same results has been reported by Batvari et al, (2007). But Sankar et al (2006) found higher lead content above the legal limit of 0.2-0.4 µg g^{-1}. So comparison of various studies reveal that there is not a definite pattern of heavy metal contamination level. The levels of metals in fish also vary with respect to different species depends upon its feeding habit, age, size and length of the fish and their habitats and different aquatic environments. Moreover, the affinity for metal absorption from contaminated water and food may differ in relation to ecological needs, metabolism and the contamination gradients of water, food and sediment, as well as other factors such as salinity, temperature and interacting agents (Kalay et al., 1999).

Seasonal variation in metal has been well- documented in different studies from fresh water marine environment (Foster et al., 2000; Kargin et al., 2001; Eastwood and Couture. 2002). Saesonal variations was reported to be due to varying seasonal growth rate, reproductive cycle, water salinity and temperature. In present study high metal concentration was observed mainly during summer month in comparison to winter and rainy season, similar trend were observed in Mediterranean shrimp and Mediterranean fish (Frenet- Piron, 1990).

CONCLUSION

Present study provides information on the accumulation of metals in fish species from Agra region. The concentration of metals like Pb, Hg and Cd were found to be higher during summer than the winter and rainy. The metals concentration found in edible parts of fishes are not heavily burdened with metals. None of the fish samples exceeded maximum residue levels of metals prescribed by regulatory authorities of India. ***Hence these fresh water fish varieties are safe for human consumption. In view of the fact that fish is a highly nutritious food, which constitutes a major dietary component of the people of the Agra region so its rejection from the regular diet is neither possible nor advisable.***

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