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Advances in Applied Science Research, 2011, 2 (2): 161-166

ISSN: 0976-8610
CODEN (USA): AASRFC

Study for Determination of Heavy Metals in Fish Species of the River Yamuna (Delhi) by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

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ABSTRACT

The presence of heavy metals in our environment has been of great concern because of their toxicity when their concentration is more than the permissible level. These metals enter in the environment by different ways like industrial activities etc. The fish samples Rahu (Labeo rohita), Tilapia (Tilapia zilli) and Catfish (Chrysichthys nigrodigatatus) were collected from Yamuna River in Delhi. In this study we have used Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) technique for determination of Al (Aluminum), B (Boron), Ba (Barium), Cd (Cadmium), Co (Cobalt), Cr (Chromium), Cu (Copper), Fe (Iron), K (Potassium), Mg (Magnesium), Mn (Manganese), Na (Sodium), Ni (Nickel), Pb (Lead), Sb (Antimony), Sn (Tin), Si (Silicon), P (Phosphorus) and Zn (Zinc) in different species of fish like Rahu, Tilapia and Catfish. The concentrations of Ca, K, Mg, Na and P are too high as compared with other metals as these metals were not in the maximum permissible level set by World Health Organization (WHO)

INTRODUCTION

The pollution of the aquatic environment with heavy metals has become a worldwide problem during recent years, because they are indestructible and most of them have toxic effects on organisms. Among environmental pollutants, metals are of particular concern, due to their potential toxic effect and ability to bioaccumulate in aquatic ecosystems [1, 2].

There is increasing concern about the quality of foods in several parts of world. The determination of toxic elements in food has prompted studies on toxicological effects of them in food. Heavy metals are considered the most important form of pollution of the aquatic environment because of their toxicity and accumulation by marine organisms [3, 4].

Recent studies have shown for instance that human activities have created ecological pressure on the natural habitat of fish and other marine organism over time. There is an upsurge of interest in water pollution as a result of this deleterious effect. Furthermore, factors such as high population growth accompanied by intensive urbanization, increase in industrial activities and higher exploitation of natural resources including cultivable land have caused pollution increase. There has been a steady increase in discharges that reaches the aquatic environment from industries. Large amount of organic material are released into the water body although some industrial process such as pump mill and sugar processing plant also produce much finely divided organic material as waste product, which is broken down easily by bacteria activities resulting in the reduction of oxygen level or even anaerobic condition in the vicinity of an effluent. In addition to direct depletion of oxygen, the decomposition of large quantities of organic material in the water produces inorganic nutrients such as ammonia, nitrate and phosphorus. These enrich the water considerably and give rise to dense algae growth or bloom which can cause the wide daily fluctuations in oxygen described for fish pound and in extreme condition, fish –kill can result. This increased productivity caused by excessive organics load can cause a decline in water quality and this symptom of over production is known as eutrophication [5-7].

Aquatic foods have essential amino acids, fatty acids, protein, carbohydrates, vitamins and minerals. Among sea foods, fish are commonly consumed and, hence, are a connecting link for the transfer of toxic heavy metals in human beings. Heavy metals have the tendency to accumulate in various organs of marine organisms, especially fish, which in turn may enter into the human metabolism through consumption causing serious health hazards.

Fishes are major part of the human diet and it is therefore not surprising that numerous studies have been carried out on metal pollution in different species of edible fish. Predominantly, fish toxicological and environmental studies have prompted interest in the determination of toxic elements in seafood [8-10].

The aim of the present study is to determine the concentrations of Al (Aluminum), B (Boron), Ba (Barium), Cd (Cadmium), Co (Cobalt), Cr (Chromium), Cu (Copper), Fe (Iron), K (Potassium), Mg (Magnesium), Mn (Manganese), Na (Sodium), Ni (Nickel), Pb (Lead), Sb (Antimony), Sn (Tin), Si (Silicon), P (Phosphorus) and Zn (Zinc) in different species of fish like Rahu, Tilapia and Catfish by using ICP-OES from different location of Yamuna River. It is expected that the results of this research will assist in acquiring information about the level of toxic metals in this region.

MATERIALS AND METHODS

2.1 Sampling:

There are three fish samples from each kind of fish species were collected from Yamuna river in Delhi region (Lat: 28° 36' 0" North; Lon: 77° 12' 0" East). Samples selected for analysis were

Rahu, Tilapia and Catfish. These are commercially important and nutrient fish species. The samples were collected in sterile polythene bags and kept in the laboratory deep freezer (-20ºC) to prevent deterioration till further analysis.

2.2 Chemicals and Reagents:
Standards solution 1000 µg/ml of Al, B, Ba, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Sn, Si, P and Zn (traceable to NIST) were procured from Scharlau Chemie, Spain. Nitric acid and Hydrochloric acid AR grade were procured from Merck Specialist Chemical limited. All glassware used were “A” grade and calibrated. Calibrated micropipette with range 100µl to 1000µl was used. Whatman filter paper no. 41 was used for filtration.

2.2 Instrumentation:
Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) equipped with argon saturation assembly, CCD detector and 21 CFR 11 version 4.1.0 software for data acquisition and processing was used

2.3 Preparation of Calibration Standard solution
10 ml each of standard reference solutions (1000µg/ml) was pipette into a 100 ml volumetric flask separately and diluted to volume with HPLC grade water. This gave working standard solution with concentration of 100 µg/ml (solution A). Calibration standards for of Al, B, Ba, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Sn, Si, P and Zn were prepared by adding appropriate volumes of standard working solution A with HPLC grade water at 6 levels in the ranged between 0.5 mg/l, 1.0 mg/l, 2.0 mg/l, 5.0 mg/l, 10.0 mg/l and 20.0 mg/l.

2.4 Sample preparation
About 20.0 ±0.01 g dried homogenized fish samples were weighed accurately in a iodine flask separately, 25 ml of concentrated HNO_3 was added into each flask. The iodine flasks were refluxed for 1 hr. at 95°C ± 5°C. The sample solutions were cooled and 10 ml of Concentrated HNO_3 was added into each flask. The flasks were again were refluxed for about 1 hr. at 95°C ± 5°C. Repeated the process until the digestion was completed. Evaporated the solution to 5 ml. Solutions were cooled and 10 ml of Concentrated HCl was added into each flasks. Kept the solutions for refluxed for about 15 min. to removed the nitrous fumes. Cooled the digested sample solutions, 20 ml of HPLC grade water was added into each flask. Filtered the digested solution through Whatman filter paper no. 41 into 50 ml volumetric flask and made upto the volume using HPLC grade water. Recovery study was carried out by fortifying known concentration of standards into preanalysed sample.

2.5 ICP-OES conditions
Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) with radial torch equipped with argon saturation assembly was used for the determination of lead and cadmium. High purity (99.99%) argon was used as plasma, auxiliary and nebulizer gas. The gas flows were kept at 15.0 l/min for plasma, 1.50 l/min for auxiliary and 0.56 l/min for nebulizer. Radio frequency (R.F) power of the plasma generator was 1.35 kW. Vertical height of the plasma was fixed at 7 mm. Sample uptake time of 30.0 sec, delay time of 5 sec, rinse time of 10 sec, initial

stabilization time of 10 sec and time between replicate analysis of 5 sec was maintained throughout the studies for ICP-OES. All the observation of emission were recorded at 396.152 nm, 249.772 nm, 233.527 nm, 214.439 nm, 238.892 nm, 267.716 nm, 327.395 nm, 259.940 nm, 766.491 nm, 285.213 nm, 260.568 nm, 589.592 nm, 231.604 nm, 220.353 nm, 206.834 nm, 189.927 nm, 251.611 nm, 213.618 nm and 213.857 nm, which corresponds to the most sensitive emission wave length of Al, B, Ba, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Sn, Si, P and Zn respectively. The instrument was calibrated for various parameters before the studies.

RESULT AND DISCUSSION

The concentration of metals in three different fish sample from different location of Yamuna river in Delhi shown in Table 1. The high concentration of heavy metals in fish indicates that the water of Yamuna is highly polluted. The concentration of Ca, K, Mg, Na and P is too high as compared with other metals. The concentration of P ranged between 3828 mg/kg to 6794 mg/kg in Rahu, 5516 mg/kg to 9476 mg/kg in Tilapia and in Catfish its ranged between 7398 mg/kg to 9988 mg/kg. The concentration of K in Rahu ranged between 2214 to 2501, in Tilapia ranged 2045mg/kg to 2405 and in Catfish ranged between 1950 mg/kg to 2045mg/kg. Mg is Second highest in the level of metals concentration and ranged from 3274 mg/kg to 3747 mg/kg for Rahe, 3312 mg/kg to 4833 mg/kg for Tilapia and 3443 mg/kg to 4868 mg/kg for catfish.

Table 1: Detection of Heavy metals in Fish samples collected from Yamuna River (Delhi)

Heavy Metals	Heavy Metal Concentration (mg/kg)								
	Rahu			Tilapia			Catfish		
	1	2	3	1	2	3	1	2	3
Al	5.0	5.0	9.0	9.0	4.5	33.8	36.1	8.2	25.4
B	0.4	0.4	2.0	2.0	0.04	ND	ND	ND	ND
Ba	0.4	0.4	6.1	6.1	3	10.5	13.3	4.57	6.99
Cd	ND	ND	ND	ND	ND	0.03	0.04	0.02	0.02
Co	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cr	0.2	0.3	1.0	1.0	0.25	0.89	1.07	0.57	0.8
Cu	0.9	0.9	1.5	1.5	1.39	2.86	1.69	3.68	1.43
Fe	13.0	13.0	20.0	20.0	10.5	41.13	54.52	20.0	34.10
K	2428.0	2501.0	2214.4	2405.2	2063.9	2045.24	1950.9	2040.9	1857.4
Mg	3275.0	3584.7	3746.9	4204.7	3311.6	4833.36	4867.7	3442.8	4421.3
Mn	0.3	0.08	0.91	1.09	0.78	1.00	5.14	1.19	1.25
Na	869	917.2	1184.7	1004.7	1173.5	1259.9	1243.7	1036.3	1174.9
Ni	0.05	0.04	0.64	0.02	0.04	0.29	0.50	0.3	0.3
Pb	4.0	3.8	ND	0.75	0.22		0.47	24.0	0.87
Sb	0.5	0.3	ND	ND	ND	0.10	0.10	0.22	ND
Sn	0.4	0.1	ND	0.13	ND	0.27	0.3	ND	0.32
Si	9.0	9.0	6.0	9.8	5.0	5.36	6.88	5.05	0.67
P	3828.4	5166.5	6794.4	7092.5	5516.3	9476.4	9988.1	7397.7	8554.8
Zn	4.0	4.0	6.4	6.5	5.8	6.85	7.67	6.49	4.91

Na concentration in Rahu 868 to 1185 mg/kg, in Tilapia 1004 mg/kg to 1260 mg/kg and in Catfish 1036 mg/kg to 1260 mg/kg. Table 1 shows concentrations of heavy metals in fish samples in the ranged Not detected (ND) to 36 mg/kg for Al, Not detected (ND) to 2 mg/kg for B, ND to 13.3 mg/kg for Ba, ND to 0.04 mg/kg for Cd, ND for Co, 0.2 mg/kg to 1.1 mg/kg for Cr, 0.9 mg/kg to 3.7 mg/kg for Cu, 11 mg/kg to 55 mg/kg for Fe, 0.08 mg/kg to 5 mg/kg for Mn, 0.04 mg/kg to 0.6 mg/kg for Ni, ND to 24 mg/kg for Pb, ND to 0.5 mg/kg for Sb, ND to 0.4 mg/kg Sn, 4 mg/kg to 8 mg/kg Zn and 0.7 mg/kg to 9 mg/kg for Si. From the above results we have seen that K, Mg, Na and P are very high in concentration which are not in the ranged of acceptable limits. This pollution may be come through industries or from drainage lines which are connected with the river Yamuna. Si, Pb and Fe also shows high values in fish samples.

The calibration curve prepared using the pure standards of Al, B, Ba, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Sn, Si, P and Zn were found to be linear with correlation coefficient (r) of more than 0.999. The recovery studies were carried out at three different concentrations and results are given in Table 2. The percent recoveries in all the case was within the acceptable limits of 70% to 120% as per regulatory guidelines.

Table 2. Percent recovery of Heavy metals from three species of fish sample

Heavy metals	**Percent Recovery Concentration (mg/kg)**					
	Rahu		**Tilapia**		**Catfish**	
	% Recovery	%RSD	% Recovery	%RSD	% Recovery	%RSD
Al	89.2	2.1	90.4	2.9	92.9	1.9
B	94.9	2.5	92.5	2.2	93.7	2.4
Ba	86.5	3.1	88.3	2.4	89.4	2.1
Cd	79.9	1.9	81.6	2.6	88.9	3.5
Co	85.8	2.0	87.6	2.1	86.7	3.8
Cr	88.4	3.4	90.6	2.9	84.6	2.6
Cu	94.2	1.1	91.8	3.6	92.7	2.0
Fe	82.0	1.9	84.9	1.5	89.4	2.1
K	80.1	1.7	81.2	3.7	79.6	2.9
Mg	77.0	1.1	76.8	3.1	80.7	3.7
Mn	89.0	1.0	79.9	2.5	84.8	2.4
Na	85.6	2.9	82.6	2.4	88.2	2.7
Ni	90.7	2.4	92.5	1.9	91.7	3.5
Pb	96.8	3.8	92.4	3.2	93.8	1.7
Sb	99.1	2.1	97.3	2.4	96.7	1.5
Sn	95.3	2.8	92.4	3.1	94.9	\2.2
Si	82.5	3.4	86.1	2.7	84.1	3.0
P	95.6	1.8	96.4	2.6	95.8	1.7
Zn	90.2	2.3	92.7	3.8	93.3	2.1

CONCLUSION

Present study provides new information on the concentration of heavy metals in the fish from Yamuna River. Based on sample analysis the metal concentration found in the fish samples are not in the ranged of maximum acceptable limits as per WHO. The probable sources of the heavy metals in the river may be caused by various industries outlet which comes to the river and also affected to the human health.

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