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BIOACCUMULATION OF HEAVY METALS IN COMMERCIALLY IMPORTANT EDIBLE MARINE FISHES

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Abstract

Heavy metal disposed through anthropogenic activities finds their way into the oceans and seas through the rivers or through direct fallout from factory effluents. These heavy metals re-suspend back into water column along with the sediments and are known to affect the marine animals. The objective of this study was to determine chromium, nickel, cadmium and zinc concentration levels in edible marine fishes collected from the coastal area of Tuticorin, India. Measurement of heavy metal content of the selected fish was carried out by using atomic absorption spectrophotometer. The metal content, expressed in $\mu g\ g^{-1}$ wet weight for chromium, nickel, cadmium and zinc varied from 4.706-9.020, 3.307-16.760, 9.053-9.480 and 9.878-12.126 respectively. The values were comparable and in the range of the literature values. The results of this study indicate that the selected fish have concentrations well below the standards of FAO/WHO levels of these toxic metals except chromium.

Key words: Heavy metal, atomic absorption spectrophotometer, bioaccumulation

Introduction

The pollution of aquatic environment with heavy metals has become a worldwide problem during recent years because they are destructible and most of them have toxic effect on organisms. Heavy metals are non biodegradable which cause cytotoxic and carcinogenic effect in animals. Being at the top of aquatic food chain fish constitute a major source of heavy metals in food (Ambedkar and Muniyan, 2011). The heavy metals can destroy life when they concentrate in the body above acceptable level and they have the tendency to accumulate in various organs and muscle tissue of fish. These metals cannot excrete by the animals rather they accumulate mostly in the organs as well as skin, hair and bones. Fish accumulate metals from the water where the live as well as from organism they eat. Bottom feeders are particularly susceptible to metals bioaccumulation as they can ingest

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sediments laced wood metals (Martin and Grisswold, 2009). The natural aquatic system may extensively be contaminated with heavy metals released from domestic, industrial and other man made activities. Heavy metal contamination may have divesting effect on the ecological balance of the recipient environment and a diversity of aquatic organisms. Fishes are the inhabitants that cannot escape from detrimental effect of pollutants (Vinodini and Narayana 2008).

The growing human population has increased the need for food supply. Being a good protein source, the demand for fish and shellfish products has increased. Worldwide people obtain about 25 per cent of their animal protein from fish and shellfish. It has been predicted that fish consumption in developing countries will increase by 57 per cent, from 62.7 million tons in 1997 to 98.6 million in 2020 ([illegible]). Heavy metals may enter aquatic systems from different natural and anthropogenic (human activities) sources, including industrial or domestic wastewater, application of pesticides and inorganic fertilizers, storm runoff, leaching from landfills, shipping and harbor activities, geological weathering of the earth crust and atmospheric deposition.

Marine animals like fish, prawn, crab and mussel were collected along the east coast (off Pulicat lake to Chennai Harbour) to evaluate trace metal concentrations in various tissues and organs of these selected species accumulated higher concentration of heavy metals such as Zn, Pb, Cu, Co, Cr, Ni and Cd in low levels by Kumar and Achyuthan (2007). Agarwal *et al.*, (2007) reported mercury and lead content in fish species from the river Cromati, India. Differential accumulation of heavy metals in muscles and liver of marine fish king mackerel, *Scomberomorus cavalla* (Cuvier) was reported by Ploet *et al.*, (2007).

Ghosh, *et al.*, (2007) analysed assessment of toxic interactions of heavy metals and their effects on accumulation in tissues of fresh water fish. Vinodhini and Narayanan, (2008) studied bioaccumulation of heavy metals in organs of freshwater fish *Cyprinus carpio*. Rauf *et al.*, (2009) investigated heavy metal level in three major carps *Catla catla, Labeo rohita* and *Cirrhinus mrigala* from the river Ravi Pakistan. Lakshmanan *et al.*, (2009) studied the heavy metal accumulation in five commercially important fishes of Parangepettai, south east coast of India. Three fish species samples were collected from Cuddalore along Tamil Nadu coast, Bay of Bengal, Indian ocean and analyzed for the levels of heavy metals to elucidate the status of the contamination in fish meat for human consumption. Concentrations of Cu, Cr, Cd, Co, Ni and Zn were determined for the above species using Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) by Vijayakumar *et al.* (2011).

Ambedkar and Muniyan (2011) reported bioaccumulation of some heavy metals in the selected five fresh water fish, from Kollidam River, Tamil Nadu. Bhuvaneshwari *et al.*, (2012) analysed the bioaccumulation of metals in muscle, liver and gills of six commercial fish species (*Channa melenosome, Silurus, Mughil cephalus, Oreochromis mossambicus, Parastromaleus niger* and *Scardinius erythropthalamus*) at Anaikari dam of river Kaveri south India. The common edible fishes such as *Mugil cephalus, Arius arius, Lutjanus ehrenbergii, Etroplus suratensis* were collected from Cochin backwaters, south west India and analysed for mercury and other heavy metals (zinc, cadmium, lead and copper) in various body parts by Mohan *et al.*, (2012). Dhamodar *et al.*, (2012) evaluated the concentrations of heavy metals Cu, Zn, Mn, Fe, Cd, Hg and As in edible muscle tissues of commercially valuable fishes from Uppanar river at Cuddalore, Tamil Nadu, India. The present work has been carried out to study the bioaccumulation of heavy metals (Cr, Cd, Ni and Zn) in the muscle tissues of commercially important marine fishes sampled from Tuticorin coast, Tamil Nadu so as to evaluate their safety for human consumption.

Materials and Methods

Sample collection

Five species of marine fishes (*Stolephorus indicus, Sardinella longiceps, Rastrelliger kanagurta, Sphyraena barracuda and Silago sihama*) were purchased from the fishermen from Thrashpuram, Tuticorin, south east coast of India. The collected samples were brought to the laboratory in an ice box in cold conditions and then washed with distilled water. Fish samples were weighed using digital weighing balance and values were recorded to the nearest grams. The weighed samples were dissected to separate the muscles from head/viscera and bones as described by Nanji et al. (2007).

Metal extraction

All the glassware used for the analysis was cleaned by soaking over night in 50 per cent (Vn) concentration nitric acid solution. A known weight of muscle samples were dried at a hot air oven at 100°c until reaching constant weight. One gram of powdered tissue samples were taken in 100 ml beaker then treated with 10 ml nitric acid (HNO_3) and 5ml hydro chloric acid (HCL) and let it over night. Next day they were dried at 150°C in a hot air oven for 30 minutes. Cool the digestible and make it into 100 ml and filtered through Whatman filter paper. The heavy metals were analyzed by flame atomic absorption spectrophotometer (AAS). Metal concentrations were calculated in micro grams per gram dry weight (µg metal g-1 d. w.) in the prepared sample, bioaccumulation of metals such as Ni, Cr, Cd and Zn were estimated.

Flame atomic absorption spectro--photometer (AA-6300, Rome version 1.03) with multi element hollow cathode lamp was used for analysis of heavy metals (Ni, Cr, Cd and Zn) present in muscle tissue of selected fishes. Air acetylene was used as fuel for flame. The wavelength (nm) and slit band width (mm) for the analysis of metals in flame atomic absorption spectro--photometer were as follows 357.9 nm and 0.7 nm for Cr 232.0 nm and 0.2 mm for Ni and 213.9 nm and 0.7 mm for Zn respectively.

Atomic absorption spectrophotometric (AAS) determination of metals

Aqueous stock solutions were prepared for nickel, chromium, zinc and cadmium using appropriate salts. Four working standards were prepared in triplicate for each metal by serial dilution of stock solution. Working standard and blank solution were aspirated into the model AA-6300 (Rome version 1.03) atomic absorption spectrophotometer to obtain the absorbance of each sample and standard solution for each of the metals. A calibration curve for absorbance versus concentration of standard metal concentration was prepared. For each metal from calibration graph for each of the metals in the sample was described by Nanji et al., (2007). The metal concentrations of the samples were determined from the graphs.

Results and Discussion

There are numerous heavy metals some of which are highly toxic like Cd, Cr, Zn and Ni. Fish accumulate toxic materials at various levels depending on species, age, season, feeding habits and so on. This study summarizes the result obtained in September 2012 for the monitoring of various heavy metals in the edible part of fish used as meal for human consumption (Table 1). None of the metals are biodegradable and though they can change forms from solid to liquid, to dust and gas they never completely disappear. The ones that are toxic in even in some minute amounts create instant cellular destruction in any of their forms. Marine animals such as fish are able to really absorb metals and their bodies regulate to accommodate their presence. They are easily stored in fatty tissue and will accumulate if the fish is exposed to further contamination.

Chromium is an essential element and play important role in insulin function. It is used in metal alloys, paints, electroplating, cement, paper and rubber. Chromium compounds are toxins and known human carcinogens. It will cause breathing problems, asthma and skin ulcer. Long term exposure can cause damage to liver, circulatory system, nerve tissue and kidney (Martin and Grisworld, 2009). *Rastrelliger kanagurta* accumulated high amount of Cr (9.020$\mu gg^{-1)}$ in their muscle than the other fishes. The estimated value of Cr in *Sardinella longiceps* (4.706 μgg^{-1}), *Sphyraena barracuda* (6.078 μgg^{-1}), *Stolephorus indicus* (8.235 μgg^{-1}) and *Silago sihama* (8.43μgg^{-1}) exceed the permissible limit recommended by World Health Organization (WHO)/ Food and Agricultural Organization (FAO) (1 μgg^{-1}). The muscle tissue of *Silago sihama* has shown higher concentration of Ni (16.76 μgg^{-1}) than the permissible limit (10.00 μgg^{-1}) set by FAO.

Except the concentration of Ni the muscle tissue of *Silago sihama* the concentration observed in all the fishes

(*Stolephorus indicus, Sardinella longiceps, Rastrelliger kanagurta, Sphyraena barracuda,*) were below the permissible limit (10 μgg^{-1}). The present result was also supported by Bhuvaneshwari *et al.*, (2012) who observed exceeding limit of chromium (4.3 μgg^{-1}) and lower limit of Ni content (4.5 μgg^{-1}) in the muscle tissues of *Oreochromis mossambiscus* than the permissible limit. Vijayakumar *et al.*, (2011) collected three fish species samples (*Rastrilliger kanagurta, Kathala axillaris* and *Sardinella longiceps*) from Cuddalore along Tamil Nadu coast, Bay of Bengal, India and find out the levels of heavy metals concentration of Cu, Cr, Cd, Co, Ni and Zn were below the maximum residual level recommended by various organizations and they reported the fish muscles of the samples analyzed were fit for human consumption in this region.

The high concentration of Cd (9.480 μgg^{-1}) is detected in the *Rastrelliger kanagurta* may be due to industrial operation. Cadmium is highly toxic, non essential heavy metal and it does not have a role in boiological process in living organism. Thus even in low concentration Cd could be harmful to living organisms (Ambedkar and Muniyan, 2011). Cadmium is highly toxic element that would deposit and biomagnified in the human body which may dangerous to human health. It also has many uses including batteries, plastics and they are known human carcinogens. High level of Cd irritates stomach leading diarrhea, lung damage fragile bones (Martin and Griswold 2009). The level of Cd in all the fishes (*Sardinella longiceps* 9.362 μgg^{-1}, *Sphyraena barracuda* 9.053 μgg^{-1} , *Silago sihama* 9.219 μgg^{-1}, *Stolephorus indicus* 9.190 μgg^{-1} and *Rastrelliger kanagurta* 9.480 μgg^{-1}) were below the level set by FAO (20 μgg^{-1}). The values of cadmium were comparable with earlier reports on heavy metals in fishes from north east coast of India and lower than south west coast of India (Dural *et al.*, 2010).

Next to Cd the zinc concentration was found more in muscle tissue of *Silago sihama* (12.120 μgg^{-1}) compared to other species. The Zn concentration in all the fishes were below the permissible level set by FAO (50 μgg^{-1}). Zn is associated with activities of nearly 100 enzymes involved in lipid, protein, carbohydrate and nucleic acid metabolism in all organisms. Zinc is the least toxic and is in fact an essential element for both animals including humans and plant nutrition. It is an essential element present in fish act as activators of several enzymes. Presence of zinc and its accumulation attributable to the leaching into ambient media from galvanized metal coating used to prevent rusting of fishing boats, trawlers and vessels that are frequently seen on the water for fishing (Damodhar and Reddy, 2012). The present result showed a moderate limit of Zn (12.136 μgg^{-1}) accumulation in fish.

Fishes are able to regulate metal concentration to some extent after which the bioaccumulation occur. Therefore total concentration of metal will control the regulation and bioaccumulation capacity of each tissue. In the present study comparatively low level of metal accumulation in the muscle tissue were observed and the same was reported in the literature also. Muscle does not come into direct contact with the metals as it totally covered externally by the skin that in many ways helps the fish to ward off the penetration of the trace metals and also it is not an active site for detoxification and therefore transport of trace metals from other tissue to muscle does not seem to arise. However though there are relatively lower level of heavy metals in fish a potential risk may occur in future due to the persistence nature of the heavy metals in the environment and rapid industrial development in the area which is major source of heavy metals in this region.

Table 1. Accumulation of heavy metals in the muscle tissues of selected marine fishes

Fish species	Concentration of heavy metals (µg/g)			
	Chromium	Nickel	Cadmium	Zinc
Stolephorus indicus	8.235	5.307	9.196	10.513
Sardinella longiceps	4.706	3.307	9.362	9.878
Rastrelliger kanagurta	9.020	6.425	9.480	10.690
Sphyraena barracuda	6.078	3.073	9.053	11.918
Silago sihama	8.431	16.760	9.219	12.126

Summary and Conclusion

Metals are inherent component of environment that poses a potential hazard to human beings and animals. The consumption of fish from the polluted site may result in bioaccumulation of persistent pollutants in ultimate recipient of the food web. In the present investigation the mean concentration of Cr (4.706-9.020μgg^{-1}) in the muscle tissue of all the fishes were exceeding the permissible limit of FAO which is (1μgg^{-1}). The fish *Silago sihama* shows higher concentration of Ni in the muscle tissue thus it can be used as bioindicator species for Ni pollution in aquatic environment.

The observed highest concentration of heavy metals (Cr and Ni) in the selected fishes compared to maximum permissible limit which is due to the release of partially treated industrial effluents. Though the level of heavy metals (Zn and Cd) did not exceed the acceptable levels in muscle tissues, but keeping in view the persistence nature of heavy metals in the environment and in view of the importance of fish in the diet of human beings particularly of coastal regions. Biological monitoring and assessment of heavy metals in the water as well as in fish meant for consumption should be carried out regularly to ensure the future food safety. Safe disposals of domestic sewage and industrial effluents as well as enforcement of laws enacted to protect our environment are therefore advocate.

Based on the findings of this study it is recommended that considerable attention should be paid to the Cr and Ni level in marine fishes from the study sites by continuous monitoring of heavy metals concentration in the muscle tissues. Measures should be put in place to regulate the indiscriminate discharge of raw effluent into the sea and regular public health checks on the level of heavy metals among the communities that border the area can be employed in order to safeguard public health.

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