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Bioaccumulation of Heavy Metals in Two Marine Fishes (*Pristis microdon* and *Scomberomorus guttatus*)

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Abstract: The present study was carried out to evaluate the concentrations of heavy metals from two marine fishes a) *Pristis microdon* and b) *Scomberomorus guttatus* collected from Tuticorin, Tamilanadu, India. The selected metals [Cu^{2+}, Zn^{2+}, Pb^{2+}] were determined in the liver, muscles and gills of the said fishes. All three metals were detected using Atomic Absorption Spectrometry and compared with standard metals. Statistical mean values were calculated then principal component analysis was used to detect the Pearson correlations. Results exhibited that recorded metal concentrations were generally found within the range or below the levels in similar species from global studies. The metals in the present fish organs were accepted by the international legislation limits and are safe for human consumption.

Key words: *Pristis microdon* · *Scomberomorus guttatus* · Atomic absorption spectroscopy

INTRODUCTION

Heavy metals are normal constituents of marine environment that occur as a result of pollution principally due to the discharge of untreated wastes into ocean by many industries. Bioaccumulation of heavy metals in tissues of marine organisms has been identified as an indirect measure of the abundance and availability of metals in the marine environment [1]. Industrialization has spoiled the environment by putting more and more concentrations of several metals. The metal which has a relatively high density and toxic at low quantity is referred as *'heavy metal'*, e.g., arsenic (As), lead (Pb), mercury (Hg), cadmium (Cd), chromium (Cr), thallium (Tl), etc. Some *'trace elements'* are also known as heavy metals, e.g., copper (Cu), selenium (Se) and zinc (Zn). They are essential to maintain the body metabolism, but they are toxic at higher concentrations [2]. Furthermore, heavy metals are said to be most important toxic pollutants for aquatic organisms. The As, Cd, Pb and Hg can be tolerated at very low levels and are highly toxic to human beings [3]. Fish are relatively situated at the top of the aquatic food chain; therefore, they normally can accumulate heavy metals from food, water and sediments. The content of toxic heavy metals in fish can counteract their beneficial effects [4]. The concentrations of heavy metals *viz.,* Cu, Zn, Pb, Cd, Fe and Mn were measured in the liver, gills and muscles of fourteen benthic and pelagic fish species collected from the Egyptian Red Sea. In most studied fish, the liver was the target organ for Cu, Zn and Fe accumulation. Pb and Mn, however, exhibited their highest concentrations in the gills [5]. In many countries, industrial wastes, geochemical structure and mining of metals create a potential source of heavy metals pollution in the aerial, edaphic and aquatic environments, due to their toxicity and accumulation behavior. Under certain environmental conditions, heavy metals might accumulate up to a toxic concentration and cause ecological damage [6]. Heavy metals discharged into the marine environment can damage both biodiversity and ecosystem, due to their toxicity and accumulative tendency in the aquatic biota and pose a risk to fish consumers, such as humans and other wildlife. Though preventive measures have been taken to reduce the input of trace metals into oceans, rivers and estuaries, accumulation in the different aquatic systems have been reported even today [7]. The heavy

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metals, being conservative in nature have the maximum probability of biomagnifications.When they are transferred to the human beings through the various members of different trophic levels in the food chain. Human beings are affected negatively as a result of their accumulation [8]. At present, the pollution has become a serious threat and has brought hazards to the growing population as well as the earth/environment. The speedy urbanization and industrialization has led to increased disposal of pollutants like heavy metals, radio nuclides and various types of organic and inorganic substances into the environment. Thus, the industrial wastes are the main source of metal pollution mainly for aquatic organisms. It has been cited that the heavy metals constitute the major pollutants in the environment [9]. Lead is a toxic element that has no biological role and causes carcinogenic effects in marine biota and humans. ercury (Hg) is a highly toxic metal, which causes severe pollution via industrial waste discharges. Fish acquire Hg through feeding, which can be determined by fish size, diet, ecological parameters and water quality parameters [10].

Marine organisms found in Ennore Creek at the north east of Chennai are Fishes like (*Oreochromis mossambica*, *Mugil cephalus, Clarias batrachus* and *Channos channos*), shrimps (*Penaeus monodon* and *Penaeus indicus*), crab (*Portunus pelagicus*) and mussels (*Perna viridis, Mytilus gravincia provincialis* and *Crassostrea madrasensis*) showed the presence of Cu, Cr, Zn, Ni, Pb and Cd. The bivalve mollusc, *Crassostrea madrasensis* have been identified to accumulate higher concentrations of non-essential Cu (22.3 to 26.3), Ni (7.36 to 10.4), Cr (2.73 to 4.63), Cd (2.3 to 3.90) and Pb (5.2 to 6.40mg kg^{-1}) levels [11]. Bio-accumulation means an increase in the concentration of a chemical or substance in a biological organism over time, compared to its concentration in the environment. Thus, understanding the dynamic process of bioaccumulation is very important in protecting human beings and other organisms from the adverse effects of chemical exposure and has become a critical consideration in the regulation of chemical [12]. Pollution of aquatic ecosystem due to heavy metals is an important environmental problem, as heavy metals constitute some of the most dangerous toxicants that can bioaccumulate. Aquatic organisms have been reported to accumulate heavy metals in their tissues several times above ambient levels [13]. The objective of the present study is to analyze the levels of metals *viz.,* copper (Cu^{2+}) zinc (Zn^{2+}) and lead (Pb^{2+}) from the selected two marine fishes a) *Pristis microdon* and b) *Scomberomorus guttatus* collected from Tuticorin. These metals are detected in the liver, muscles and Gills of the fishes.

MATERIALS AND METHODS

Collection of Fish Samples: Two marine fishes like *Pristis microdon* and *Scomberomorus guttatus* were collected from Tuticorin. It is called the Gulf of Mannar region. The Gulf of Mannar Biosphere Reserve covers an area of 10,500 km^2 of ocean, islands and the adjoining coastline. Fish samples obtained were immediately kept in pre-cleaned polythene bags, which were sealed and kept in an ice box until further analysis.

Samples Preparation: In the present study accumulation of metals such as Cu^{2+}, Zn^{2+} and Pb^{2+} were estimated in the liver, muscles and Gills of two fishes i.e., *Pristis microdon* and *Scomberomorus guttatus*. The fishes were dissected and the organs were removed and oven dried at 60°C. The dried tissues were then reduced into fine powder in a pestle and mortar. The samples were digested in concentrated nitric acid and concentrated sulphuric acid (4:1) till all the material gets dissolved. It was then filtered through whatman filter paper No.1 and washed with distilled water and collected in a 50 ml volumetric flask. Sample preparation and analysis were carried out according to the procedure described by UNEP Reference Methods.

Determination of Heavy Metals: The digested samples of liver, muscles and gills from the fishes of *Pristis microdon* and *Scomberomorus guttatus* were then poured into auto analyzer cups and concentration of heavy metals (Cu^{2+}, Zn^{2+} and Pb^{2+}) in each sample was determined using Atomic Absorption Spectrophotometer (AAS). The values of the heavy metal concentrations in the tissues were calculated based on dry weights as this discounts the variability due to inner parts differences in the moisture content of organisms.

Statistical Analysis: The mean and standard deviations was calculated in the present study and was used to compare metals differences between two fish species. The principal component analysis was also used to detect Pearson correlations.

RESULTS

The concentrations of trace elements in the liver, muscles and gills in the fish of *Pristis microdon* were measured and presented in Table 1. Significant differences in metal accumulation were observed in different body parts of the fishes. Accumulation patterns of all metals were significantly different between the different species and organs. The present study revealed that the presence of Cu was detected at 324.8nm, Zn at 213.9 nm and Pb at 283.3nm.

The concentrations of trace elements in the liver, muscles and gills in the fish of *Scomberomorus guttatus* were also measured and presented in Table 2. The highest concentration of copper was found in the muscles and Zinc was found in the gills of *Scomberomorus guttatus*. The highest level of lead was found in the gills of *Pristis microdon.* The accumulation of metals in a single species showed significant inter-specific variations in all metals. The present study showed that the presence of metals like Cu, Zn and Pb could be due to anthropogenic sources. The highest recorded values of metals like Cu, Pb and Zn was recorded in *Scomberomorus guttatus*. The metals were compared with the standards. The statistical results show significant values were observed from mean and standard deviation and differences were determined by means of principal component analysis (Table 3 & 4). Comparatative analysis was analyzed using Pearson correlations (Table 5). It indicates linear correlation. According to the present result of these metals accumulation, level did not exceed the permissible international limits.

Table 1: Concentration of heavy metals in the tissues of Fish (*Pristis microdon*).

Organs	Cu^{2+} (324.8nm)	Zn^{2+} (213.9nm)	Pb^{2+} (283.3nm)
Liver	0.0122 ppm	0.6429 ppm	0.0786 ppm
Muscles	0.2234 ppm	6.4616 ppm	0.1310 ppm
Gills	0.0855 ppm	4.8216 ppm	0.0419 ppm

Table 2: Concentration of the heavy metals in the tissues of Fish (*Scomberomorus guttatus*).

Organs	Cu^{2+} (324.8nm)	Zn^{2+} (213.9nm)	Pb^{2+} (283.3nm)
Liver	0.2780 ppm	3.3587 ppm	0.0052 ppm
Muscles	0.3111 ppm	2.5518 ppm	0.0210 ppm
Gills	0.2004 ppm	12.4574 ppm	0.0105 ppm

Table 3: Principal component analysis and mean of *Pristis microdon.*

Variable	PC1	PC2	Mean ±SD
Copper (Cu^{2+})	-0.204	0.978	0.24±0.11
Zinc (Zn^{2+})	-0.722	-0.185	4.41±0.36
Lead (Pb^{2+})	-0.661	-0.100	2.45±0.16
Eigenvalues	2.890	0.010	
%Variation	99.70	0.30	
Cum.%Variation	99.70	100.00	

Table 4: Pricipal component analysis and mean of *Scomberomorus guttatus*.

Variable	PC1	PC2	Mean ±SD
Copper (Cu^{2+})	0.409	-0.595	0.30±0.10
Zinc (Zn^{2+})	0.334	-0.608	6.20±0.25
Lead (Pb^{2+})	0.849	0.526	3.45±0.12
Eigenvalues	4.93	0.03	
%Variation	99.40	0.60	
Cum.%Variation	99.40	100.00	

Table 5: Pearson correlation between fishes.

Variables	*Pristis microdon*	*Scomberomorus guttatus*	*Pristis microdon*	*Scomberomorus guttatus*	*Pristis microdon*	*Scomberomorus guttatus*
Copper (Cu^{2+})	1.000	1.000				
Zinc (Zn^{2+})	0.912	-0.975	1.000	1.000		
Lead (Pb^{2+})	0.717	0.465	0.369	-0.258	1.000	1.000

a) *Pristis microdon*

b) *Scomberomorus guttatus*

Fig 1: Two marine fish species used for bioaccumulation of heavy metals a) *Pristis microdon* and b) *Scomberomorus guttatus*

DISCUSSION

The present study showed that the comparative analysis of metals like Copper, lead and Zinc from the liver, muscles and gills of the selected fishes *viz., Pristis microdon* and *Scomberomorus guttatus* were generally found to be species specific and may be related to their feeding habits and the bio-concentration capacity of each species Zn^{2+} and Cu^{2+} are essential elements and play important roles in growth, cell metabolism and survival of most animals including blue-blooded. Hence, the relatively high levels of these metals can be blue-blooded to their essentiality. In case of cadmium, the reverse case can be observed. Hence in the present study the metals of Cu^{2+}, Zn^{2+} and Pb^{2+} were analyzed in *Pristis microdon* and *Scomberomorus guttatus* [14]. In general, accumulation of the heavy metals (total mean) analysed in the sampled fishes was of the following trend: *H. forskahlii* > *H. bebe occidentalis* > *C. gariepinus* and the pattern of distribution is Ni > Cr > Co > Cd > Pb for all the fish species. This showed that the accumulation of the heavy metals was species-related as *H. forskahlii* is a predatory and carnivorous fish which might favor its higher tendency for metal bioaccumulation than others [15]. Differences in metal concentrations related to diet and feeding habits of benthic and pelagic fish species. It was identified that benthic fish generally accumulate higher concentrations of heavy metals than pelagic fish. Plankton feeding fish contain much higher concentrations of some heavy metals than bottom feeding fish. This is agreed with the present study of *Pristis microdon* and *Scomberomorus guttatus* [16].

Sprat is zooplanctonivorous fish and has high metabolic rate. According to their ecology and food habits, sprat seems suitable as tools for descriptions of environmental conditions of coastal waters. It is also known that metal concentrations in fish tissues are related to the pollution status of the regions. Sprat is migrating between the open sea and inshore areas. It was observed that concentrations of heavy metals were higher in fish skin than in muscles tissues [17]. The reason for high Cd^{2+} concentrations in sprat could be due to the metal complexion in skin with the mucus that is impossible to be removed completely from sprat the tissue before the analysis. However, in the present study it is found that the concentrations of metals Cu^{2+}, Zn^{2+} and Pb^{2+} in muscle, gills and liver were lower than reported by [18]. The Gills of fishes *Pristis microdon* and *Scomberomorus guttatus* were found to contain maximum levels of metals viz Cu^{2+}, Pb^{2+} and Zn^{2+}. Similarly higher concentrations of metals also found in gill tissue of fish species. Since gills are the uptake site of waterborne ions where the concentrations increase especially at the beginning of exposure, before the metal enters other parts of organism. Knowledge of heavy metal concentrations in aquatic organisms is important due to the nature of management and human consumption of these species. Bioaccumulation of metals in periwinkles can be considered an index of metal pollution in aquatic bodies [19].

Hydrocarbons take longer time to sink to the riverbed and that marine organisms accumulate hydrocarbons due to their sedentary and bottom feeding habit. It is useful to express results in terms of bio-concentration factor (BCF) when comparing the order of uptake of metals. In this study, bio-concentration potentials were very low and varied with the mean concentration of heavy metals and total hydrocarbon (THC) [20]. The highest levels of Zn^{2+} in the present study were observed in the gills of *Districhodus rostratus*. Other workers also reported the highest concentration of Zn^{2+} in the gills of *Labeo dyocheilus, Wallago attu* and in liver of *C. punctatus*. Fish can accumulate zinc from both the surrounding water and from their diet. Although zinc is an essential element, at high concentrations, it can be toxic to fish, cause mortality, growth retardation and reproductive impairment. Zinc is capable of interacting with other elements and producing antagonistic, additive or synergistic effects [21]. The permissible limits for Zn^{2+} set by WHO, is 40 ppm which is less than the values observed during this study. Copper toxicity in fish is taken up directly from the water via gills. The permissible limit for Cu set by WHO is 30 ppm, which exceeds the accumulation levels obtained in the present study. Lead is highly toxics to aquatic organisms, especially fish [22]. The levels of Zn, Cu and Pb were determined in the muscle in each species because of its importance for human consumption and also the gill and stomach were analyzed since these organs tend to accumulate metals [23]. These organs are also good indicators of chronic exposure to heavy metals because they are the site of metal metabolism. It is well known that heavy metals accumulate in the tissues of aquatic animals and therefore heavy metals measured in the tissues of aquatic animals can reflect the past exposure. The stomach is often considered a good monitor of water pollution with heavy metals since their concentrations are proportional to those present in the environment. The gills are the uptake site of waterborne ions, where metal concentrations increase especially at the beginning of exposure, before the metal enters other parts of organism [24]. Gills are the first organs to be exposed to resuspended sediment particles, so they can be significant sites of interaction with metal ions. On the other hand, the stomach has a key role in basic metabolism and is the major site of accumulation, biotransformation and excretion of contaminants in fish. It is well known that a large amount of metallothionein induction, caused by contamination, occurs in stomach tissues of fish [25].

CONCLUSIONS

Health risk analysis of heavy metals in the edible parts of the fish indicated safe levels for human consumption and concentrations in the muscles are generally accepted by the international legislation limits. The excess levels of heavy metals cause severe toxicity. Though some heavy metals are essential for animals, plants and several other organisms, all heavy metals exhibit their toxic effects via metabolic interference and mutagenesis. The accumulation of heavy metals (Cu^{2+}, Zn^{2+} and Pb^{2+} in Fishes *Pristis microdon* and *Scomberomorus guttatus* is to a considerable extent and it is relatively more than that reported from other regions in the literature. The high bioaccumulation of these metals is believed to be occurring due to the rigorous anthropogenic input of bioaccumulative contaminants into the aquatic environment.

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