Trace Metal Contaminants in Tissues of the Orinoco Sailfin Catfish *Pterygoplichthy smultiradiatus*, (Hancock, 1828); Sri Lanka

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Abstract: The objective of this study was to identify the presence of trace metals in Orinoco Sailfin Catfish *Pterygoplichthys multiradiatus* from the freshwater reservoir of the Eastern Province, Sri Lanka. A total of 48 fish samples was analysed for cadmium (Cd), arsenic (As), lead (Pb), copper (Cu), iron (Fe), zinc (Zn) and mercury (Hg) using atomic absorption spectrophotometer (AAS) during the period of Aug.-Nov. 2013. The mean values of all trace metals in muscles of *P. multiradiatus* were within the international safety limits and pooled mean concentration of trace elements were in following order; Fe>Zn>Cu>Hg>Pb>Cd>As.
[B.K.K.K. Jinadasa, D.S. Ariyarathne and S.B.N. Ahmad. **Trace Metal Contaminants in Tissues of the Orinoco Sailfin Catfish *Pterygoplichthy smultiradiatus*, (Hancock, 1828); Sri Lanka.** *Nat Sci* 2014;12(6):1-4]. (ISSN: 1545-0740). http://www.sciencepub.net/nature. 1

Key Words: Orinoco sailfin catfish, trace metals, freshwater fish, Sri Lanka, AAS

1. Introduction:

The inland fish production makes a significant contribution to animal protein supplies in many rural areas of Sri Lanka. The freshwater fishery segment is experiencing some problem at present. Fish type called as “scavenger or janitor fish” has been increased widely within a short period of time. The rapid increase of this species has been affected the livelihood and fishing operation of the fisherfolk which led to a decrease in marketable catch of endemic and commercial fish species due to its predominance in gill net catch. They could possibly displace native fish species. In addition to that their large pectoral and dorsal spines are a choking hazard to predaciousbirds.These scavenger fish have invaded the natural freshwater ecosystems due to the negligence of breeders. This fish basically feed on algae. However, with the age fish gets bigger in size. With time there is a clear change in their food regimen. This can be seen even in a domestic fish tank. The growth process of these fish which occurs along with the change of the body as well as their food regimen creates a threat to the survival of the fish (CEC, 2009, Karunarathne *et al.*, 2010).

Scavenger fish belong to the Loricariidae family and is considered as a type of catfish. Scientifically it is known as *Pterygoplichthys multiradiatus* (Hancock, 1828). It is an indigenous fish of South America. *P. multiradiatus* browses on a substrate, mainly feeding on benthic algae and aquatic weeds, but will also take worms, insect larvae and other bottom-dwelling invertebrates as food. Many who breed fish and maintain aquariums show love to this fish not because of any beauty it adds to the tank, but for the sole purpose of cleaning the tank. Those who maintain aquariums introduce this fish to tanks to help clean up the algae and other forms of debris in the tanks (USFWS, 2012).

Heavy metal pollution in aquatic ecosystem has been recognized as a serious environmental problem. In many cases, heavy metal occur in natural water bodies at the levels below their toxic thresholds. Their non degradable nature, such low concentration may still pose risk of damage via uptake and subsequent bioaccumulation by organisms. Metal bioaccumulation can be importance in two points of view; human consume accumulators and environmental quality (Bhalchandra and Ram, 2013). *P. multiradiatus*is new experience to Sri Lankans that they are not aware of consuming scavenger fish. However these fish are consumed in Brazil, Colombia and other countries. But, fish has attracted much attention in the biomonitoring ofwater pollution due to its special biological characters such asrelatively big body size, long life cycle, easy to raise etc. (Qunfang *et al.*, 2008). In this respect *P. multiradiatus* are particularly suited to bioaccumulation studies. Bottom feeders are readily exposed to metals that accumulate in sediment, while predators accumulate metals from surrounding water or from feeding on other fish. *P. multiradiatus* are bottom-dwelling omnivores, but also actively feed on a wide variety of prey including small fish (Crafford and Oldewage, 2010).

In the current study the concentrations of seven metals cadmium (Cd), arsenic (As), lead (Pb), copper (Cu), ferrous (Fe), zinc (Zn) and mercury (Hg) were determined inmuscle tissues of Orinoco sailfincatfish (*P. multiradiatus*) and provide baseline data on the biomonitoring and food safety studies.

2. Material and Methods:

Fish samples were obtained from commercial fishing efforts of local fisherman along two reservoirs in Sri Lanka from Aug-Nov. 2013 (Fig. 1). The two sampling sites were Eastern Province (Rambakenwewa and Mahaoya) of Sri Lanka. Samples (48 fish) were collected and frozen and brought to the laboratory on ice. Total body length and weight of the samples were measured tothe nearest millimeter and gram prior to dissection.Individuals were sexed during dissection by the examination of the gonads. A portion of edible muscle tissues was removed from the dorsal part of the each fish, homogenized, packed in polyethylene bags and stored at -18 °C until chemical analysis.

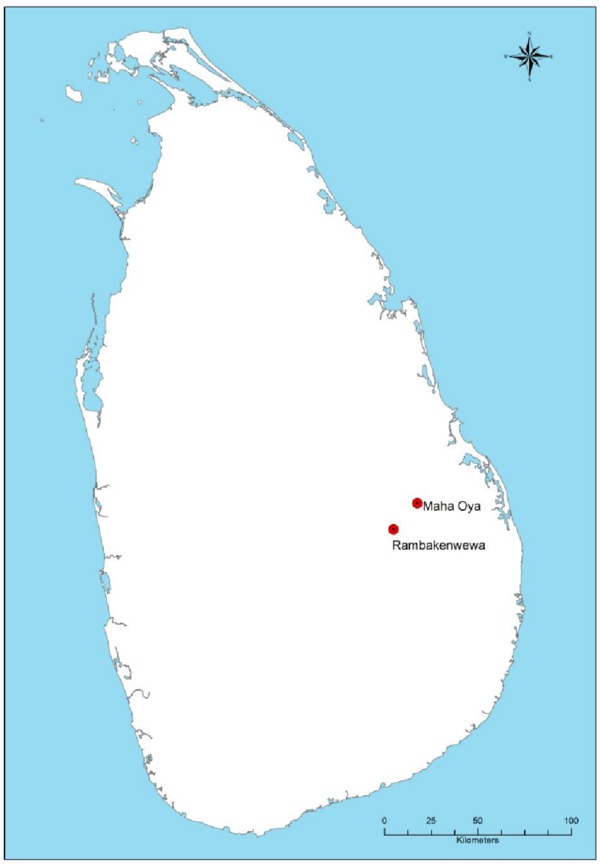

Fig. 1: Location of sampling site

Special care was taken to prevent metal contamination of the sample by the laboratory equipments, therefore all laboratory ware was soaked in detergent for 24 hrs, and rinsed 3 times with distilled water and then again soaked in 10% HNO_3 for 24 hrs, and rinsed 3 times de-ionized water prior to use. All chemicals and trace metal standards were obtained from Sigma Aldrich (Dorset, United Kingdom).

A MARS-CEM-XP-1500+ microwave accelerated system (CEM, Matthews, USA) was used for sample digestion. Aliquots (1 g) of homogenized fish samples were accurately weighted into digestion vessels of the CEM microwave oven, followed by acid digestion using 10 mL of HNO_3 (65% nitric acid, AR). Digestion vessels were capped after 15 min. of pre digestion time and placed into a 12 position turn table in microwave oven. A ramp temperature program applied (up to 200 °C, 800 psi) followed by stable temperature for 15 min. (100% power) and 15 min cooling down. The digestion sequence was controlled by a temperature and pressure probe place in one vessel. After cooling down, microwave vessels were vented and extractions were diluted to a final volume of 50 mL using de-ionized water. Each sample was analyzed in duplicate.

The digested samples were analysed using an atomic absorption spectrophotometer (AAS) Varian model 240 FS (Varian, Springvale, Australia) equipped with Varian vapor generation accessory (VGA 77) and Varian graphite tube atomizer (GTA 120). Cd, As and Pb were analysed using graphite tube atomizer and Hg was analysed using cold vapour techniques while Cu, Fe and Zn were analysed using flame techniques. The reagent blanks and calibration standard solutions were also analysed in a similar manner as the sample.

The accuracy of the method is confirmed by analysing quality control materials (As, Cd, Hg, Cu) from Fapas, UK (T0774, canned fish) and spiked sample recovery values (Pb, Fe, Zn).

The length, weight and metal concentrations were reported using mean values. T-test from IBM-SPSS 22 software used to analyse the difference of mean or comparing the size and metal levels between male and female fish.

3. Results and discussion:

Table 1 shows determined values, certified values recovery % of As, Cd, Hg and Cu (T0774), spiked recovery % of Pb, Fe and Zn and limit of detection of each heavy metal. The recovery levels of all trace metals from this study were within the acceptable range (80-120 %).

The body size distribution shows that thesize differences among the females and males captured, the largest female attaining 48 cm (806 g) and male 46 cm (875 g) of total body size (Table 2).There is a significant difference in length and weight data between male and female fish (p>0.05).

Table 1: Determined values, certified values, recovery % of quality control samples (T0774) and spiked recovery values (n=7)

Metals /Description	Determined value	Certified value	% Recovery	Limit of detection (µg/kg)
As (µg/kg)	352	344	102	4.36
Cd (µg/kg)	2.61	2.59	100.73	0.06
Hg (µg/kg)	19.79	19.9	99.4	6.6
Cu (µg/kg)	745	726	102.62	20
Pb (mg/kg)	_	_	89.5	5
Fe (mg/kg)	_	_	96.78	60
Zn (mg/kg)	_	_	103.64	10

Table 2: The variation of weight and length of fish

Description		Avg(±SD)	Max	Min
Male (n=24)	Weight (g)	544 (131)*	875	397
	Length (cm)	38 (4)*	46	30
Female (n=20)	Weight (g)	516 (96)*	806	391
	Length (cm)	37 (4)*	48	32

*are statistically significant, $p>0.05\%$

The concentrations of the seven elements in the muscle of male and female *P. multiradiatus* are shown in table 3. Fe was the highest in both male and female samples analysed in this study, followed by Zn. In muscle tissue other studied metals decreased in the following order Cu>Pb>Hg>Cd>As in female and Cu>Hg>Pb>As in male.

Table 3: Trace metal levels of male and female fish

	Male	Female
Cd (µg/kg)	5.15 (±5.83)*	4.57 (±4.15)*
As (µg/kg)	<4.36	<4.36
Pb (µg/kg)	24.62 (±74.83)*	61.88 (±41.94)*
Cu (mg/kg)	0.07 (±0.13)	0.05 (±0.07)
Fe (mg/kg)	10.84 (±6.68)*	13.83 (±7.90)*
Zn (mg/kg)	7.78 (±2.52)*	9.26 (±3.23)*
Hg (µg/kg)	43.68 (±30.11)*	44.53 (±28.02)*

*are statistically significant, $p>0.05\%$

The mean concentration of trace metals of female *P. multiradiatus* always higher than male *P. multiradiatus* and each metals showed significant diferences between male and female for all metals ($p>0.05$) except Cu.The membrane permeability, the nature of hormones and enzymatic system and the number of available binding sites in male and female fish may account for these differences (Leili *et al.*, 2013).

The Cd level found in muscles of fish in present study ranged from <0.06-10.30 µg/kg for female and <0.06-20.08 µg/kg for male respectively. The As levels of both male and female fish were below the detection limits. The As concentration from the literature of *Pterygoplichthys* sp in Philippines was 0.0159±0.00276 mg/kg (Jacquline and Glenn, 2009). But it has long been considered that total As in marine fish species were much higher than freshwater fish species (Richard *et al.*, 2006). The Pb and Hg levels ranged from <5.0-491.19, 12.27-133.73 in female and <6.6-192.36, <6.6-81.43 µg/kg male fish respectively. The value of Hg in the analysed samples was comparatively below than avialble literature value of *Pterygoplichthys* sp (0.0142±0.02104 mg/kg) (Jacquline and Glenn, 2009). The Cu levels found in the present study ranged from <0.02-0.32 for female and <0.02-0.24 mg/kg for male fish. The Fe levels ranged from 3.60-25.98 for female and 4.43-20.30 mg/kg for male fish. As well as Zn concentrations in the muscles of fish ranged from 4.84-13.69 for female and 5.08-11.76 mg/kg for male. The mean concentration of Cd, Pb and Hg of fish muscles tissues were below the maximum allowable levels of EU/EC legislation 1881/2006 (EU/EC, 2006). Accroding to that legislation the maximum levels of Cd, Pb and Hg of *P. multiradiatus* are 0.10, 0.30 and 0.50 mg/kg in wet weight basis and the studied species was below those limits and that means this fish are suitable for human consumption with regarding to the level of trace metals.

The adverse effects of heavy metals in the aquatic environment has been well-documented in the literature. Bioaccumulation of trace metals in aquatic life, especially fish is of significance, owing to the possible detrimental effects and direct toxic effect on human life and environmental concern. The heavy metals predominantly present fromindustrial activities, domestic households, agriculturaland livestock production empty into the lake in theform that can readily be assimilated by phytoplankton, other aquatic plants and organisms which could result to higher metal uptake. Thus, the metal concentrationin the water is a significant source of increased metal levels in fish (Hannibal *et al.*, 2006). The concentration of heavy metals in janitor fish shows that as an omnivoreand bottom feeder, their heavy metal uptake comesmostly in the food they eat which can easily beabsorbed through water and in the environment theyinhabit. Bernard and Andreae (1984) reported that the largest concentration of heavy metals was found in omnivorous fish, followed by herbivorous and carnivorous.

Conclusion:

The concentrationsof heavy metals in the flesh of *P. multiradiatus* were within the standard limits but these should not be ignored. Heavy metals are acutely toxicin excessive amounts and tend to bioaccumulate atlow concentration. Based from the results of the study, *P. multiradiatus* can be processed into human consumption, fishery products, feed production for fish or fertilizer production.

Acknowledgement:

The authors are grateful to Mr. Ruchitha Perea, Mr. Kapila Jayasena and Mr. Tissa Chandrasekara for their help in the laboratory and the field.

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4/15/2014