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Heavy Metal Concentration in Largehead Hairtail (*Trichiurus lepturus* Linneaus, 1758) and Savalai Hairtail (*Lepturacanthus savala* (Cuvier, 1829)) Obtained from Karachi Fish Harbour, Pakistan

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Abstract

In this study, muscle samples gathered from Largehead hairtail (*Trichiurus lepturus* Linneaus, 1758) and Savali hairtail [*Lepturacanthus savala* (Cuvier, 1829)] from the Karachi Fish Harbour, Pakistan were analyzed to determine heavy metal concentrations (iron [Fe], zinc [Zn], copper [Cu], manganese [Mn], lead [Pb] and cadmium [Cd]) between January and December 2016. All samples were analyzed using the AAnalyst 700 Flame Atomic Absorption Spectrophotometer. It was observed that the average measured level of Fe, Zn, Cu, Mn, Pb and Cd in muscle were 77.72 ± 47.84 µg/g, 20.34 ± 8.49 µg/g, 2.23 ± 1.16 µg/g, 0.57 ± 0.36 µg/g, 0.20 ± 0.16 µg/g and 0.42 ± 0.19 µg/g for *T. lepturus*, respectively. Besides, the average level of the same metal concentrations in muscle for *L. savala* were 85.11 ± 57.64 µg/g, 16.63 ± 9.25 µg/g, 2.53 ± 1.90 µg/g, 0.47 ± 0.27 µg/g, 0.23 ± 0.18 µg/g and 0.47 ± 0.20 µg/g, respectively. The correlation between size groups and metal accumulation in muscle tissues were investigated for both fish. In terms of public risk assessment, the provisional tolerable weekly intake's of various heavy metals were compared with the consumption of both fish. As a result of the analysis, Fe, Zn, Cu, Mn, Pb and Cd accumulations in muscle tissues of *T. lepturus* and *L. savala* collected from Karachi Fish Harbour Pakistan did not exceed limit values.

Keywords Heavy metal accumulation · Muscles, fishes · *Trichiurus lepturus* · *Lepturacanthus savala* · Karachi Fish Harbour · Pakistan

As the level of contamination increases and the outcomes on human health become more explicit to be recognized, heavy metal pollution has transformed into a multinational problem. The polluters which are found in seafood can be very poisonous and these materials can pose a threat to human health and make humans vulnerable when they consume seafood (Achary et al. 2017). Consuming food including toxic components may be extremely unhealthy in the long term, even if they are consumed in fairly small amounts. Aquatic living organisms and animals are being exposed to heavy metal pollution due to farming run offs, transport, human and animal excretion, fossil fuel usage, geological destruction and human-made and industrial wastes (Olowu et al. 2010).

The accumulation of metals can increase and become extremely toxic which can invisibly effect the aquatic life without a hint. The conditions have intensified with the migration to cities, practices in agriculture, population growth and industrial growth (Giguere et al. 2004). Metabolism is vital in the increase of metal levels for sea organisms (Langston 1990; Roesijadi and Robinson 1994). It is imperative to state that the distribution in the level of heavy metals among distinct species is due to nutrition, habits, age, size and extent of fish and their living place (Amundsen et al. 1997). Contamination with heavy metals of animal-based food is a great menace to human health owing to their toxicity, long persistence, bioincrease and bio-magnification (Kannan et al. 2007; Chary et al. 2008). In recent years, much caution has been concentrated on the human health hazard assessment of heavy metals in nutrition perfection (Kannan et al. 2007; Chary et al. 2008; Durán et al. 2012).

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Karachi is the biggest city of Pakistan and lies within the coordinates of 23°19′N and 24°07′N latitudes and 67°08′E and 68°54′E longitudes. Growing pollution level of the Karachi coastline, which is tied to the increase of the shipping industry through the Karachi port and the industries producing large amount of industrial waste pose a severe contamination threat for the mangrove forests and marine life (World Bank Report 1991).

The objective of this study is to determine the concentrations of heavy metals such as Fe, Zn, Cu, Mn, Pb and Cd in *Trichiurus lepturus* and *Lepturacanthus savala* obtained from the Karachi Fish Harbour, Pakistan between January and December 2016 regarding the length groups. *T. lepturus* and *L. savala* are important for the study of heavy metal accumulation, which is carnivorous, abundant hunting and commercially important. To detect public hazard, the provisional tolerable weekly intake (PTWI) of varied heavy metals were checked with their consumption for both fish.

Materials and Methods

A total of 64 *T. lepturus* and 52 *L. savala* were collected from Karachi Fish Harbour from January to December 2016. 116 fish samples were taken from fishing boats in Karachi Harbour. Six size classes (30–40, 41–51, 52–62, 63–73, 74–84, 85–95) were taken as length groups during the study.

Fish samples were immediately transported to freezer in the laboratory after being collected, then thawed and rinsed in distilled water to remove any foreign particles. Length (cm) and weight (g) were measured. Fish were labelled for recognition and then frozen until the time of the analysis. Following the biometric measurements, approximately 2 g of the epaxial muscle situated on the dorsal surface of each sample were dissected, washed with distilled water, dried in filter paper, weighed, packed in polyethylene bags and kept at −20°C until the analysis. AAnalyst 700 Atomic Absorption Spectrophotometer was used to perform the analysis in Centralized Science laboratory of the University of Karachi. The absorption wavelengths (λ) used for the determination of the analyzed metals are as follows: Fe: 248.30 nm; Zn: 213.90 nm; Cu: 324.70 nm; Mn: 279.50 nm; Pb: 217.00 nm; Cd: 228.80 nm. Due to the absence of a standard reference of the material, the accuracy of the analysis and the effect of the matrices in the media were controlled with the standard addition method using three randomly selected samples for each analyzed element and cut into as small pieces as possible. Typical detection limit were 0.1, 0.018, 0.035, 0.01, 0.012 and 0.025 µg/mL for iron, zinc, copper, manganese, lead and cadmium respectively, were calculated by regression analysis as suggested by the US Environmental Protection Agency. A 1–2 g aliquat of each dry sample was placed in cylindrical Teflon vessel and digested with 3 mL of a 1:2 v/v mixture of H_2O_2 and HNO_3 at 250°C. The organic part was discarded, and the remaining part was diluted with demineralized water to 50 mL in a graduated flask (Bernhard 1976).

All heavy concentrations of the metals in *T. lepturus* and *L. savala* within muscle tissues among length groups were determined by carrying out analyses of variance (ANOVA) using Tukey's HDS post-hoc comparison method. The results were assessed on the basic of homogenous groups with a significant level of ($p < 0.05$). The elements which were common in the muscle tissue of both fish were assessed by means of Pearson's correlation coefficients. Then, the correlation between length groups and metal accumulation were investigated. Finally, the data collection and statistical calculations were performed using SPSS software (Ver.24).

Results and Discussion

Length and weight (min–max) of *T. lepturus* and *L. savala* found in our samples were 30.00–95.00 cm and 41.00–456 g (Table 1). The length range and average dispersions of metal (Fe, Zn, Cu, Mn, Pb and Cd) concentrations were given in Table 2.

While the observed accumulation of metals in muscles has an order of Fe > Zn > Cu > Mn > Cd > Pb for *T. lepturus*, that of in muscles of *L. savala* was as Fe > Zn > Cu > Mn = Cd > Pb.

It was observed that the amount of Fe, Zn and Cu in muscle tissues of *T. lepturus* and *L. savala* decreases gradually in the VI, V, IV, III, II and I length groups, respectively. The amount of Cd in muscle tissues of *T. lepturus* and the

Table 1 Length ranges, weight ranges and frequency

Fish name	Frequency	Length ranges (cm)	Weight ranges (g)
Trichiurus lepturus	9	30–40	46–106
	14	41–51	110–188
	11	52–62	190–263
	13	63–73	267–321
	11	74–84	328–392
	6	85–95	397–456
Total	64		
Lepturacanthus savala	7	30–40	41–93
	11	41–51	97–146
	9	52–62	149–218
	8	63–73	223–304
	13	74–84	311–380
	4	85–95	384–433
Total	52		

Table 2 Metal concentrations of *T. lepturus* and *L. savala*

Fish name	Length range	Metal concentration (µg/g)					
		Fe	Zn	Cu	Mn	Pb	Cd
		Median + SD (Min–max)	Median + SD (Min–max)	Median + SD (Min–max)	Median + SD (Min–max)	Median + SD (Min–max)	Median + SD (Min–max)
Trichiurus lepturus	I	26.78 + 4.90 (16.73–33.06)	13.17 + 2.40 (9.34–16.21)	1.12 + 0.33 (0.29–1.40)	0.47 + 0.15 0.24–0.71	0.15 + 0.09 0.01–0.28	0.27 + 0.10 0.12–0.46
	II	39.56 + 9.52 23.16–53.03	14.95 + 3.81 7.53–24.12	1.20 + 0.47 0.36–1.72	0.50 + 0.12 0.23–0.66	0.13 + 0.11 0.01–0.36	0.38 + 0.16 0.18–0.76
	III	58.05 + 8.89 46.56–76.88	19.10 + 4.81 11.14–28.46	2.44 + 0.69 0.85–3.34	0.27 + 0.12 0.16–0.52	0.20 + 0.27 0.01–0.79	0.47 + 0.22 0.15–0.69
	IV	83.17 + 13.19 64.16–111.46	19.87 + 4.06 14.28–28.16	2.53 + 1.09 0.62–4.24	0.47 + 0.26 0.02–0.89	0.24 + 0.16 0.04–0.66	0.42 + 0.16 0.12–0.72
	V	131.08 + 20.34 88.71–154.22	26.72 + 8.42 10.84–39.63	3.46 + 1.08 1.16–4.64	0.91 + 0.55 0.34–2.04	0.25 + 0.14 0.09–0.56	0.44 + 0.17 0.13–0.78
	VI	169.58 + 33.14 141.48–234.75	35.30 + 11.37 17.34–52.64	3.03 + 0.59 2.52–4.06	0.99 + 0.27 0.49–1.24	0.25 + 0.11 0.14–0.46	0.60 + 0.23 0.23–0.83
	Mean	77.72 + 47.84 16.73–234.75	20.34 + 8.49 7.53–52.64	2.23 + 1.16 0.29–4.61	0.57 + 0.36 0.02–2.04	0.20 + 0.16 0.01–0.79	0.42 + 0.19 0.12–0.83
Lepturacanthus savala	I	31.06 + 7.39 22.36–40.87	7.26 + 1.32 5.22–9.32	1.08 + 0.50 0.39–1.88	0.28 + 0.08 0.16–0.37	0.09 + 0.09 0.01–0.21	0.55 + 0.16 0.36–0.87
	II	51.75 + 10.70 34.23–67.26	11.11 + 3.78 6.21–17.88	1.63 + 0.57 0.89–2.95	0.27 + 0.12 0.11–0.58	0.19 + 0.17 0.01–0.54	0.36 + 0.19 0.12–0.66
	III	60.95 + 7.87 51.32–76.52	14.64 + 5.03 9.23–26.63	1.66 + 0.48 1.21–2.54	0.42 + 0.14 0.21–0.65	0.25 + 0.19 0.01–0.58	0.41 + 0.10 0.24–0.52
	IV	77.27 + 13.96 56.23–103.67	19.90 + 8.24 7.03–34.88	1.93 + 0.77 0.93–3.34	0.58 + 0.16 0.35–0.78	0.17 + 0.10 0.02–0.32	0.45 + 0.21 0.20–0.89
	V	117.26 + 35.43 63.52–175.66	22.25 + 9.12 11.56–44.56	3.67 + 1.71 1.33–6.66	0.56 + 0.25 0.10–0.87	0.31 + 0.16 0.12–0.68	0.48 + 0.17 0.23–0.69
	VI	238.29 + 41.05 190.96–281.39	27.82 + 13.54 14.18–46.48	7.03 + 1.46 5.16–8.66	0.94 + 0.39 0.43–1.32	0.44 + 0.25 0.22–0.78	0.86 + 0.12 0.68–0.95
	Mean	85.11 + 57.64 22.36–281.39	16.63 + 9.25 5.22–46.48	2.53 + 1.90 0.39–8.66	0.47 + 0.27 0.10–1.32	0.23 + 0.18 0.01–0.78	0.47 + 0.20 0.12–0.95

amount of Pb in muscle tissues of *L. savala* were found to be decreasing gradually in VI, V, IV, III, II and I length groups. It was determined that the accumulation of Pb in the muscle tissues of both fish is the least regarding all length groups. Concerning all length groups for both fish, the highest amount of metal found in the muscles was Fe. On the other hand, the least amount of metal was Pb.

The amount of Fe found in the muscles was higher than that of the literature (Yousuf et al. 2013; Jithesh and Radhakrishnan 2017) but lower than the amount provided by another study in the literature (Velusamy et al. 2014). Fe is concentrated to a considerable degree by some fish organism, and fish accumulate high levels of Fe. Because of the low toxicity of Fe to human, Fe in seafoods and freshwater fishes does not constitute a hazard to human consumers (Glenn and Rosemarie 1978). The obtained Zn accumulation values in the muscle were lower than those of all previous studies regarding the same region (Sharif et al. 1993; Velusamy et al. 2014; Agrahari et al. 2006) except for Yousuf et al. (2013) and Jithesh and Radhakrishnan (2017). The accumulation of Zn in the muscles of fish could be attributed to the increasing number of fishing vessels and trawlers which use galvanized metal coatings to prevent from rusting that ultimately find its way into the ambient medium by leaching (Lakshmanan et al. 2009). The detected Cu accumulation values in the muscles were higher than the values in the literature (Sharif et al. 1993; Velusamy et al. 2014; Mok et al. 2009), while Cu values were lower than the reported values in the literature (Jithesh and Radhakrishnan 2017; Agrahari et al. 2006; Yousuf et al. 2013). Finally, Mn values were lower than the values stated in the literature (Velusamy et al. 2014; Jithesh and Radhakrishnan 2017; Yousuf et al. 2013).

Mn values, it was higher than the values in the literature (Mok et al. 2009). Pb values are higher than the values in reported data provided by some studies of the literature (Mok et al. 2009; Velusamy et al. 2014). On the other hand, Pb values were lower than the values in the literature

(Agrahari et al. 2006; Ngumbu et al. 2016; Jithesh and Radhakrishnan 2017). Cd values were lower than the values in the reported data from literature (Agrahari et al. 2006). However, Cd values were higher than the values provided by some studies in the literature (Velusamy et al. 2014; Ngumbu et al. 2016; Mok et al. 2009) (Table 3).

Zn, Cu, Mn and Cd metal accumulations in muscle tissues of *T. lepturus* and *L. savala* fish were found to be lower than the limits of WHO (1989) and FAO (1983).

Considering metal accumulation in the muscle of *T. lepturus*; in all elements except Pb element, significant differences were detected between the groups in terms of length. In general, the difference in metal accumulation is more significant between small size groups and large size groups ($p < 0.05$).

The accumulation of Fe, Zn, Cu, Mn, Pb and Cd in muscle tissues of *L. savala* was found to be significantly different between small and big fish ($p < 0.05$).

There is a high correlation between the elements of Fe, Zn, Cu, Cd and length groups for *T. lepturus*, while a high correlation was found between the elements of Fe, Zn, Cu, Mn, Pb and the length groups for *L. savala*. Table 4 indicates that there is a high correlation between Fe, Zn, Cu and L.R for *T. lepturus* and Fe, Cu and L.R for *L. savala*.

The metal increase in fish is related to the location, dispersion, features of the habitat, heat level, nutrition habits, age, size, time of exposure to metals and homeostatic regulation activity (Sankar et al. 2006). Concentrations of Fe, Zn, Cu, Mn, Pb and Cd found in per capita daily fish consumption was calculated to evaluate potential health risk to Pakistani people. Average daily fish consumption in Pakistan is 33 g per capita (Chughtai and Mahmood 2012). PTWI values (PTWI for 60 kg adult person (µg/week/60 kg body weight)) of Fe, Zn, Cu, Mn, Pb and Cd was calculated as 5600, 7000, 3500, 980, 25 and 7, respectively in µg/week/60 kg body weight. (FAO/WHO 2004).

The EWI intake value was calculated based on Eq. 1. Here, EWI refers to the ratio of weekly consumed fish. Average concentrations (C_{metal}; µg/g) and average weekly consumed fish (WCF; g) were used in the calculation. If EWI intake value is divided by seven, EDI intake value is obtained.

$$EWI = C_{metal} \times ACF \tag{1}$$

The heavy metal accumulation in muscles of *T. lepturus* and *L. savala* was found to be below nationally and internationally stipulated values and do not pose a serious health threat (Table 5).

The amount of accumulation of Fe, Zn and Cu elements in muscle tissues of *T. lepturus* and *L. savala*, the amount of Cd accumulation in muscular tissues of *T. lepturus* and the amount of Pb accumulation in muscle tissues of *L. savala* were found to increase from the lowest to the highest length groups.

The results of this study show that Fe, Zn, Cu, Mn, Pb and Cd accumulations of *T. lepturus and L. savala* caught from Karachi Harbour were generally below the international limits. However, these results are attributed to Pakistan, which has a small amount of daily intake. The present study shows that precautions are needed to be taken in order to obviate metal pollution in the future. It is thought that intake values may trigger some health problems in case of excessive

Table 3 Comparison of mean concentrations

Location	Fish	Metal concentration (µg/g)						References
		Fe	Zn	Cu	Mn	Pb	Cd	
Bangladashi Coast	*L. savala*	–	38.02	0.231	–	–	–	Sharif et al. (1993)
Mumbai Harbour	*T. lepturus*	141	42.34	2.11	6.34	0.04	0.12	Velusamy et al. (2014)
Monrovia Markets	*T. lepturus*	–	–	–	–	0.356	0.160	Ngumbu et al. (2016)
Chaliyar River 2014	*T. lepturus summer*	16.18	16.14	14.28	1.50	1.06	–	Jithesh and Radhakrishnan (2017)
	T. lepturus pre monsoon	16.48	15.14	14.75	1.07	1.95	–	
	T. lepturus monsoon	18.26	16.28	16.38	1.68	2.10	–	
	T. lepturus post monsoon	18.50	16.80	16.80	1.45	1.98	–	
Mumbai Coastal	*L. savala 1.St*	–	60.30	63.43	–	38.67	1.99	Agrahari et al. (2006)
	L. savala 2.St	–	37.07	97.24	–	60.79	5.60	
	L. savala 3.St	–	27.92	53.10	–	27.63	1.58	
Korean Coast	*T. lepturus*	–	–	0.325	0.066	0.09	0.008	Mok et al. (2009)
Cost of Karachi	*T. lepturus*	27.9	9.86	3.23	2.04	–	–	Yousuf et al. (2013)
International Limits	General	100	100	30	1	2	0.50	WHO (1989)
		–	30–100	10–100	–	0.5–6	1	FAO (1983)
This study	*T. lepturus*	77.72	20.34	2.23	0.57	0.20	0.42	This study
	L. savala	85.11	16.63	2.53	0.47	0.23	0.47	

Table 4 Pearson correlation coefficients for the relationships between the concentrations of different metals in *T. lepturus* and *L. savala*

	Fe	Zn	Cu	Mn	Pb	Cd	L.R
Trichiurus lepturus							
Fe	1.000	0.684**	0.621**	0.453**	0.205	0.323**	0.923**
Zn	0.684**	1.000	0.510**	0.415**	0.293*	0.476**	0.727**
Cu	0.621**	0.510**	1.000	0.398**	0.307*	0.347**	0.700**
Mn	0.453**	0.415**	0.398**	1.000	0.262*	0.150	0.453**
Pb	0.205	0.293*	0.307*	0.262*	1.000	0.030	0.285*
Cd	0.323**	0.476**	0.347**	0.150	0.030	1.000	0.375**
L.R	0.923**	0.727**	0.700**	0.463**	0.285*	0.375**	1.000
Lepturacanthus savala							
Fe	1.000	0.661**	0.816**	0.644**	0.458**	0.470**	0.807**
Zn	0.661**	1.000	0.468**	0.568**	0.299*	0.134	0.671**
Cu	0.816**	0.468**	1.000	0.606**	0.366**	0.350**	0.716**
Mn	0.644**	0.568**	0.606**	1.000	0.337*	0.296*	0.671**
Pb	0.458**	0.299*	0.366**	0.337*	1.000	0.318*	0.445**
Cd	0.470**	0.134	0.350*	0.296*	0.318*	1.000	0.277*
L.R	0.807**	0.671**	0.716**	0.671**	0.445**	0.277*	1.000

L.R length range

*Correlation is significant at the 0.05 level; **correlation is significant at the 0.01 level

Table 5 Estimated daily and weekly intakes for the economically significant fish species consumed by adults in Pakistan

	PTWI	PTDI[a]	*Trichiurus lepturus* EWI (EDI)	*Lepturacanthus savala* EWI (EDI)
Fe	5600[a]	336,000	2565 (366)	2809 (401)
Zn	7000[a]	420,000	671 (96)	549 (78)
Cu	3500[a]	210,000	74 (11)	84 (12)
Mn	980[a]	58,800	19 (3)	16 (2)
Pb	25[a]	1500	7 (1)	8 (1)
Cd	7[a]	420	14 (2)	16 (2)

PTWI provisional tolerable weekly intake, in µg/week (FAO/WHO 2004), *EWI* estimated weekly intake, in µg/week for a 60 kg adult, *EDI* estimated daily intake, in µg/day for a 60 kg adult

[a]PTDI, provisional tolerable daily intake, in µg/day for a 60 kg adult

consumption because these pollutants can be detrimental for the health of fish population and human consuming them.

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