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Accumulation of Heavy Metals (Fe, Cu, Mn, Zn, Cd, Co and Pb) in *Hemiramphus archipelagicus* Collette & Parin, 1978 and *Hemiramphus far* (Forsskål, 1775) from Ibrahim Hyderi Fish Harbor, Karachi, Pakistan

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ABSTRACT

In this study, the presence of heavy metals (Fe, Cu, Mn, Zn, Cd, Co and Pb) in the muscle tissue of *Hemiramphus archipelagicus* Collette & Parin, 1978 and Hemiramphus far (Forsskål, 1775) caught in the Ibrahim Hyderi Fish Harbor, Karachi, Pakistan was investigated. The concentration ranges of trace elements in muscles tissue of *Hemiramphus archipelagicus* and *Hemiramphus far* were found as follows, respectively: Fe: 19.570 - 62.140 µg g^{-1}; Cu: 0.120 - 1.770 µg g^{-1}; Mn: 0.001 -0.080 µg g^{-1}; Zn: 7.230 - 36.450 µg g^{-1}; Cd: 0.001 - 0.008 µg g^{-1}; Co: 0.001 - 0.008 µg g^{-1}; Pb: 0.002 - 0.080 µg g^{-1}; Fe: 16.320 - 63.250 µg g^{-1}; Cu: 0.130 - 1.220 µg g^{-1}; Mn: 0.010 -0.080 µg g^{-1}; Zn: 7.260 - 20.160 µg g^{-1}; Cd: 0.000 - 0.008 µg g^{-1}; Co: 0.000 - 0.001 µg g^{-1}; Pb: 0.010 - 0.080 µg g^{-1}. Metal concentrations in muscle tissues of *Hemiramphus archipelagicus* and *Hemiramphus far* were decreased as follows, Fe>Zn>Cu>Mn>Pb>Cd>Co. All metal accumulations in muscle tissues of *Hemiramphus archipelagicus* and *Hemiramphus far* samples collected from Ibrahim Hyderi Fish Harbor were not to be exceeding the limit and all values are under the permissible range. Therefore, it is important to continue to protect the Ibrahim Hyderi Fish Harbor against possible dangers that may increase heavy metal pollution, to ensure that the measures taken are maintained in the same way and carried out regular controls.

Keywords: *Hemiramphus archipelagicus*, *Hemiramphus far*, Bioaccumulation, Ibrahim Hyderi Fish Harbor, Pakistan

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1. INTRODUCTION

Heavy metal pollution has become a serious problem worldwide due to increasing pollution levels and its effects on human health. In parallel with environmental pollution, food sources are also polluted and can create important health problems for people. The rapid development of industry and agriculture; it has caused the pollution of rivers, lakes and seas with heavy metals and this pollution has caused significant damage to the ecological environment, invertebrates, fish and people. Biologically, heavy metal accumulation in foods is an important place for human health and the continuation of the ecosystem (Djedjibegovic *et al*., 2012).

There are many toxic heavy metals in the environment that cause pollution of seas and rivers. The main sources of heavy metals that disrupt the ecological balance are; agricultural drainage, factory wastes, sewage flows, mixing of chemical flows into the waters, oil flows from sea vehicles, some organic materials, oils, agricultural fertilizers, fossil fuels, pesticides and various chemicals (Subotic *et al*., 2013; Velusamy *et al*., 2014). The creatures living in the marine ecosystem are accepted as important bioindicators in terms of heavy metals and toxic substances in the water. The reason for this is that heavy metals in water directly affect the biology and metabolism of sea creatures, and these creatures constantly store heavy metals in their digestive system, skin, shells, livers and, albeit in small amounts, in their muscles (Morgano *et al*., 2011; Subotic *et al*., 2013; Velusamy *et al*., 2014).

Heavy metals negatively affect the health of fish by creating toxic effects on the metabolism of fish as well as humans (Yousuf *et al*., 2021). Water, fat, protein and toxin/heavy metal ratio in the body of creatures living in the sea and consumed by humans are important indicators for the health and physiological status of fish (Özan and Kir, 2008). Heavy metals accumulating in rivers, seas and lakes can reach people through the food chain (Alhas *et al*., 2009). In this case, routine monitoring of heavy metal levels in both waters and sea creatures has become mandatory in order to determine whether seafood is suitable for health (Soliman *et al*., 2015).

Fish of the family Hemiramphidae are generally known as half-beaks, with the exception of a few freshwater members of the genus Hyporhamphus, mostly marine, because the lower jaw is as long as a beak (Behera *et al*., 2020). Spines are absent in fins. Represented in Indian waters by 17 species in 7 genera (Nair *et al*., 2018). Several studies on heavy metal accumulation have been carried out in other parts of the world on various fish species (Asmysari *et al*., 2013; Nursanti *et al*., 2017; Sadeghi *et al*., 2020; Shiry *et al*., 2021; Köker *et al*., 2021).

In this study, the presence of heavy metals (Fe, Cu, Mn, Zn, Cd, Co and Pb) in the muscle tissue of *H. archipelagicus* Collette & Parin, 1978 and *H. far* (Forsskal, 1775) caught in the Ibrahim Hyderi Fish Harbor, Karachi, Pakistan was investigated. It is aimed to reveal whether they are suitable for human consumption or not.

2. MATERIAL AND METHOD

Ibrahim Hyderi is a fishing village in the Korangi District of Karachi, Pakistan. The most distinctive component of the area is contiguous to Koranghi Creek. The popular Koranghi Road encompasses the industrial area; the zone has a wharf stretching out to Korangi Creek. The break wateris generally known as Ibrahim Hyderi Fish Harbor which has critical economic significance for the local fisherman of the area (Shahzad, 2020).

H. archipelagicus and *H. far* were collected during the period (Pre Monsoon (Feb-Mar), Monsoon (Aug-Sep) and Post Monsoon (Oct-Nov)) from October 2018 to September 2019 from Ibrahim Hyderi Fish Harbor, Karachi, Pakistan. Pakistan has a subtropical monsoon climate characterized by wide seasonal variations in rainfall, moderately warm temperatures, and high humidity. Generally, Pre-monsoon months are hot and humid; monsoon months are humid and rainy, post-monsoon months are quiet hot and dry but the winter months are cool and dry. These periods were chosen in order to see the effect of monsoon periods. The fish samples were collected from the Ibrahim Hyderi Fish Harbor were washed using deionized water and place in separated labeled polyethylene bags and kept in ice box. The samples were kept in freezer (-20 C˚) until ready for analyses.

The concentration of the heavy metals i.e., iron (Fe), copper (Cu), manganese (Mn), zinc (Zn), cadmium (Cd), cobalt (Co), lead (Pb), and measured in mg/L of both pond water samples and fry stages of *H. archipelagicus* and *H. far* collected from the Ibrahim Hyderi Fish Harbor of district Kohat were also determined by using Atomic Absorption Spectrophotometer (AAS), model Analyat 700 USA with methods followed by Kaur *et al*. (2018) as per standards methods of American Public Health Association (APHA, 2005). The absorption wave lengths (λ) used for the determination of various metals are as follows: Fe, 248.30 nm; Cu, 324.70 nm; Mn, 279.50 nm; Zn, 213.90 nm; Cd, 228.80 nm; Co 240.73 nm and Pb 217.00 nm. Due to the lack of a reference standard material, accuracy of the analysis and the effect of the matrices in the media were controlled with the standard addition method. All studied elements were tested with standard addition method for 3 randomly selected samples. Approximately 20 ml filtered water and fish sample solution was taken for heavy metal analysis.

One-way Analysis of Variance (ANOVA) was used to determine significant differences ($p \leq 0.05$) while post hoc Tukey's (HSD) test was used to separate means where there were significant differences.

3. RESULTS

The lengths (cm) and weights (g) of *H. archipelagicus* and *H. far* 36 samples obtained for element analyses are given in Table 1. Metal concentrations in muscle tissues of *H. archipelagicus* and *H. far* are presented in Tables 2-3, respectively which include mean concentrations with associated standard deviations, minimum and maximum values, and the international limit values.

Table 1. Lenght and weight of fishes.

Season	n	*Hemiramphus archipelagicus*		*Hemiramphus far*	
		Length Min-Max (cm)	Weight Min-Max (gr)	Length Min-Max (cm)	Weight Min-Max (gr)
Pre-Monsoon	12	14.00-19.20	33-66	16.00-19.30	41-65
Monsoon	12	17.80-22.00	49-78	14.30-20.50	36-74
Post Monsoon	12	15.50-19.50	40-63	13.70-22.80	31-78
All Seasons	36	14.00-22.00	33-78	13.70-22.80	31-78

n, number of fish.

Table 2. Heavy metal concentrations in muscle of *H. archipelagicus*

Season	Mean± SD Min-Max						
	Fe	Cu	Mn	Zn	Cd	Co	Pb
PM	30.965±9.57	0.783±0.310	0.043±0.02	12.061±3.95	0.003±0.002	0.000±0.000	0.026±0.028
	19.570-46.800	0.240-1.210	0.020-0.080	7.230-19.360	0.001-0.007	0.000-0.0001	0.002-0.080
M	37.395±11.371	0.685±0.465	0.033±0.028	18.522±4.397	0.003±0.002	0.000±0.000	0.033±0.017
	21.500-56.300	0.210-1.770	0.004-0.080	12.540-26.320	0.001-0.008	0.000-0.001	0.010-0.060
PoM	43.918±13.8	0.410±0.382	0.030±0.025	22.513±7.576	0.003±0.002	0.000±0.000	0.033±0.023
	26.450-62.140	0.120-1.110	0.001-0.080	14.420-36.450	0.001-0.008	0.000-0.001	0.010-0.080
AS	37.426±12.334	0.626±0.411	0.035±0.025	17.699±6.935	0.003±0.002	0.000±0.000	0.030±0.023
	19.570-62.140	0.120-1.770	0.001-0.080	7.230-36.450	0.001-0.008	0.000-0.001	0.002-0.080

PM: Pre-Monsoon; M: Monsoon; PoM: Post Monsoon; AS: All Season

Table 3. Heavy metal concentrations in muscle of *H. far*

Season	Mean± SD Min-Max						
	Fe	Cu	Mn	Zn	Cd	Co	Pb
PM	41.303±15.014	0.795±0.330	0.045±0.021	14.152±3.454	0.001±0.001	0.000±0.000	0.021±0.024
	18.240-63.250	0.330-1.220	0.020-0.080	8.560-19.630	0.000-0.003	0.000-0.000	0.010-0.080
M	24.478±10.885	0.563±0.138	0.023±0.015	13.592±3.792	0.003±0.002	0.000±0.000	0.026±0.020
	16.360-50.740	0.360-0.780	0.010-0.060	8.210-.20.160	0.001-0.006	0.000-0.001	0.010-0.080
PoM	24.359±8.349	0.243±0.168	0.028±0.020	11.473±3.213	0.004±0.003	0.000±0.000	0.024±0.019
	16.320-44.190	0.130-0.740	0.010-0.080	7.260-17.460	0.001-0.008	0.000-0.001	0.010-0.060
AS	30.047±13.970	0.533±0.319	0.032±0.021	13.072±3.589	0.002±0.002	0.000±0.000	0.025±0.019
	16.320-63.250	0.130-1.220	0.010-0.080	7.260-20.160	0.000-0.008	0.000-0.001	0.010-0.080

PM: Pre-Monsoon; M: Monsoon; PoM: Post Monsoon; AS: All Season

4. DISCUSSIONS

Table 2 and Table 3 show that mean metal concentrations in the tissues of *H. archipelagicus* and *H. far* and international limits. Fish muscle tissue has been considered in the study of heavy metal concentration, since fish tissues are exposed to metal contamination in the aquatic system (Carla *et al*., 2004; Al-Kahtani, 2009). In this study, it was found that Fe (37.426±12.334 µg/g) for *H. archipelagicus* and Fe (30.047±13.970 µg/g) for *H. far* show higher concentration than other metals. Due to the absence of heavy metal (Fe, Cu, Mn, Zn, Cd, Co and Pb) studies in *H. archipelagicus* and *H. far*, some studies were examined for comparison.

Table 4. Comparison of concentrations in fish tissues reported in the literature

Location	Fish	Metal concentration (µg g−1 dry wt.)							Reference
		Fe	Cu	Mn	Zn	Cd	Co	Pb	
Marmara Sea (3rd station)	*T. mediterraneus*	83	1.0	-	21	0.3	-	0.8	Köker *et al*., 2021
	M. merlangus	63.1	0.6	-	19.6	0.2	-	0.9	
Gulf of Guinea	*S.aurita*	2.66	0.25	-	0.41	<0.2	-	<0.5	Botwe, 2021
	P.bellottii	1.23	0.04	-	0.17	<0.2	-	<0.5	
Liusha Bay	*S.albella*	-	1.50	-	14.2	0.03	-	0.55	Yang *et al*., 2020
Southeastern India	*H. archipelagicus*	-	-	-	-	-	-	6.34	Rajaram *et al*., 2018
	H.far	-	-	-	-	1.4	-	8.6	
Ibrahim Hyderi Fish Harbor	*H.archipelagicus*	37.426	0.626	0.035	17.699	0.03	0.000	0.030	This study
	H.far	30.047	0.533	0.032	13.072	0.02	0.000	0.025	
International limits		100	30	1.0	50	1.0	-	0.50	WHO, 1989
		-	10-100	-	40	0.5	-	0.50	FAO, 1983
		410	54	-	410	1.4	-	-	EPA, 1989

Fe concentration in *H. archipelagicus* and *H. far* had much higher values in the literature (Botwe, 2021) except for Köker (2021). Cu concentration in *H. archipelagicus* and *H. far* was lower values in the literature (Köker *et al*., 2013; Yang *et al*., 2020) and higher than Botwe (2021). Cd and Pb concentrations in *H. archipelagicus* and *H. far* were found to be lower than the studies in the literature (Köker *et al*., 2013; Rajaram *et al*., 2018; Botwe, 2021; Yang *et al*., 2020). Zn concentration in *H. archipelagicus* and *H. far* was found to be lower than Köker *et al*. (2018) and higher than Botwe (2021). No comparable study could be found in the literature, while the Mn and Co concentrations of *H. archipelagic* and *H. far* were examined (Table 4).

The variability observed in the metal levels of different species depends on feeding habits (Watanabe *et al*., 2003), ecological needs, metabolism (Canlı *et al*., 1998), age, size and length of the fish (Al-Yousuf *et al*., 2000) and their habitats (Canlı and Atli, 2003). The characteristics of the ecosystem, the quality of the water and the nutritional needs reveal this situation.

In this study, it was determined that the metal concentration for both species decreased towards November and was the highest in February. The increase in the amount of metal in the spring and the increase in agricultural activities (spraying, fertilizing and irrigation) around the lake due to evaporation after the summer months show that there is a decrease in the autumn and winter months. It has been evaluated that the reason for the decrease may be due to low evaporation and precipitation.

The ANOVA results reveal that all heavy metals vary significantly between seasons and heavy metal concentrations in fish tissues. The concentration ranges of trace elements in muscles tissue of *H. archipelagicus* and *H. far* were found as follows, respectively: Fe: 19.57-62.14 μg g^{-1}; Cu: 0.12-1.77 μg g^{-1}; Mn: 0.001-0.08 μg g^{-1}; Zn: 7.23-36.45 μg g^{-1}; Cd: 0.001-0.008 μg g^{-1}; Co: 0.001-0.008 μg g^{-1}; Pb: 0.002- 0.08 μg g^{-1}; Fe: 16.32-63.25 μg g^{-1}; Cu: 0.13- 1.22 μg g^{-1}; Mn: 0.01-0.08 μg g^{-1}; Zn: 7.26-20.16 μg g^{-1}; Cd: 0.000-0.008 μg g^{-1}; Co: 0.000-0.001 μg g^{-1}; Pb: 0.01-0.08 μg g^{-1}. Metal concentrations in muscle tissues of *H. archipelagicus* and *H. far* were decreased as follows, Fe>Zn>Cu>Mn>Pb>Cd>Co.

All metal accumulations in muscle tissues of *H. archipelagicus* and *H. far* samples collected from Ibrahim Hyderi Fish Harbor were not to be exceeding the limit and all values are under the permissible range. Therefore, it is important to continue to protect the Ibrahim Hyderi Fish Harbor against possible dangers that may increase heavy metal pollution, in order to ensure that the measures taken are maintained in the same way and to carry out regular controls.

5. CONCLUSION

As a result, it has been determined that fish *H. archipelagicus* and *H. far* from İbrahim Hyderi Fish Port are not under the threat of contamination. For this reason, it is important to continue to be protected against possible dangers that may increase heavy metal pollution in the same location, to ensure that the measures taken are maintained in the same way and to carry out regular controls.

AUTHORSHIP CONTRIBUTION STATEMENT

Farzana YOUSUF: Conceptualization, Methodology, Validation, Formal Analysis, Resources, Supervision. **Semra BENZER:** Conceptualization, Methodology, Writing - Original Draft, Writing-Review and Editing, Data Curation, Software, Visualization. **Quratulan AHMED:** Methodology, Validation, Formal Analysis, Resources, Writing-Review and Editing.

CONFLICT OF INTERESTS

The author(s) declare that for this article they have no actual, potential or perceived conflict of interests.

ETHICS COMMITTEE PERMISSION

No ethics committee permissions is required for this study

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