Environment and Ecology 38 (4): 933—949, October—December 2020 ISSN 0970-0420

Determination of Heavy Metal Concentration in Fish Muscle Tissue (*Labeo bata, Mastacembelus armatus*) and Water from Konar River and Barakar River and Tenughat Reservoir

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Received 30 September 2020, Accepted 10 November 2020, Published on 9 December 2020

# ABSTRACT

In the present study an attempt has been made to measure amount of heavy metals absorbed in the muscle tissue of Labeo bata and Mastacembelus armatus. Metal content of water of the fish collection sites also have been studied, to determine the bio-accumulation of metals. The study was conducted during the period May 2015-December 2019 at Konar River, Barakar River and Tenughat Reservoir. The result of this study indicates that, Zn is the highest accumulated metal in three rivers water and fish muscle tissue of both the fishes. Co-concentration was found in minimum level in water and fish tissue. In both Mastacembelus armatus and Labeo bata metal content in muscle tissue was in order of (Zn>Pb>Cu>Ni>Cd>Co). All the metals were in excess to the permissible limit as prescribed by WHO. The study determines that fish muscle tissue of both the fishes showed high Zn content. The high R<sup>2</sup> value indicates high absorption level of toxic metals in muscle tissue from water.

**Keywords:** *Mastacembelus armatus, Labeo bata,* Bioaccumulation, Heavy metals.

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#### **INTRODUCTION**

Anthropogenic activities like industrialization, urbanization have drastically changed the natural composition of aquatic environment causing adverse effects on aquatic biota. Ever increasing pollution load in rivers is of great concern globally. Irrational dumping of wastes in river resulted uncontrolled increase of heavy metals (Gugala and Turner 2018, Gupta et al. 2009) causing in damage to aquatic organisms and also human being (Malik et al. 2010, Giguere et al. 2004). Yamuna River water at Okhla Barrage was highly contaminated with Zinc and Nickel that may be the cause of health hazard there (Ambedkar and Munian 2012, Usmani 2013). When the aquatic habitat gets contaminated with toxic metals, fishes simultaneously accumulate them and chances of infestations increases accordingly. Such bioaccumulation leads to biomagnification (Adeniyi and Yusuf 2007, Alhashemi et al. 2012, accumulation of Huang et al. 2019). According and Maiti 2018) also the Chinakuri industrial area showed a higher range of metal contamiation (Banerjee and Gupta 2012, 2016). Macrognathus puncalus and Cirrhina reba from Paful eeding Damodar River to Shivakumar and Lei (2018) the metals in fish depends largely on habit of the fish species and type of the metal and the tissue where the metals get absorbed. Those highly persisting non biodegradable metals gets accumulated in fish tissue through mouth, gill surface, kidney, liver, gut tract, from the aquatic environment (Farcus 2000, Zhang et al. 2007) According to Quratuln et al. (2015), Javed and Usmani (2011) lower exposure to metal contami-

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Fig. 1. Map showing the Study sites of River Konar, River Barakar and Tenughat Reservoir

nated water may affect fishes. Their study also reveals that, fish muscle has poor accumulating property for Copper and Cobalt. Toxicological study on Damodar River water indicated high risk of Cd, Cr and Co contamination were detected contaminated with toxic tissue (muscle) of *Labeo bata* and Mastacembelus armatus fish from Konar River, Barakar River and Tenughat Reservoir and metals (Sarkar and Banerjee 2012). The present study aimed to determine the highly toxic heavy metal (Copper, Lead, Nickel, Zinc, Cobalt and Cadmium) absorption limit in the edible part of fish also determine the bioaccumulation level by studying the metal absorption in river water and aware the consumers about the possible health risk.

#### MATERIALS AND METHODS

### Study area

Konar River, Barakar River and Tenughat Reservoir were main areas of study. Konar River and the Barakar River are two main tributaries of Damodar River. Tenughat Reservoir is a mud built reservoir on Damodar River. Konar River originates at Padma Hazaribagh hills, Hazaribagh Jharkhand. Barakar River originates from Sultana village on Hazaribagh –Chatra Road.

# **Sampling stations**

Estimation of metals was carried out at seven selected stations which are: Fig. 1.

Three study sites at Konar River:

S1.Konar Dam,(23-59-41-64-N,85-46-39-00-E).

S2.Gobindpur, (23.938°N,85.717E). S3.Sangam Ghat-Konar Damodar confluence, (26–23909N, 78–16156E).

Three study sites at Barakar River:

S4. Tilayia Dam, (23–59–41–64N,85–46–39–00–E). S5. Fatehpur, (24.1135–N,86.999E).

S6. Maithon Dam, (23–4806N,86–5132E) and S7. Tenughat Reservoir, (23–72719–N,85–84172E).

### Sampling procedure

From each study site nine samples were collected every year. Fish tissue samples and water were collected from seven study sites during the month of December-January, May- June, August- September for five consecutive years 2015, 2016, 2017, 2018, 2019. One liter of water samples were collected from the sampling sites from a depth of below 10 cm in Tarson polyethylene bottle. All the bottles were prior rinsed with 5% Nitric acid first, then with double distilled water. Immediately after collection, water was fixed by adding few drops of 10% Nitric acid. Determination of metals (Cu, Pb, Zn, Cd, Co and Ni) was done from all the collected water samples. Fishes were collected by engaging fishermen. Fish tissues were collected at the collection sites and immediately preserved in the ice box and stored in the refrigerator for metal study.

#### Metal detection procedure of water

Determination of Cu, Pb, Zn, Cd, Co and Ni metal was done in each water samples by Atomic Adsorption Spectrophotometer (Varian AA.575). The actual concentration was calculated on the basis of total amount of the sample taken and expressed in mg/L. A reagent blank determination was done with all batch of sample in each season. The blank values were below detection limits.

# Wet digestion of fish tissue

Tissues of 1 g from 15 samples at each station in every season was taken for metal analysis and made ready for acid digestion, following the procedure of Chernoff (1975). Hydrological parameters of water samples pH of water was estimated by Hanna pH meter. Dissolved oxygen, free carbondioxide and alkalinity was estimated by modified Winkler's method following standard methods of APHA (1999). Temperature of water was measured by the mercury thermometer. Transparency was measured with Secchi disc.

#### Statistical analysis

Some basic statistical analysis like mean and variances of different variables have been done for the study. One way ANOVA was done to compare the metal absorption limit in three seasons and sites in average three years .Seasonal variations (pre-monsoon, monsoon, post-monsoon) of metal absorption was done seasonally with respect to the stations. Cluster analysis was done to find out the relatedness of metal concentration in three study areas considered in the present study. For this analysis software package SPSS1696 was used. The regression analysis was done by XLSTAT 2018 (Adinsoft, France). The regression analysis represents estimation of the relationship between a depended variable and one or more independent variable. The ratio of the concentration of a chemical in an organism to the concentration of the chemical in the surrounding environment was calculated. The greater the regression value (R<sup>2</sup>) more the bioaccumulation of Cu, Pb, Zn, Cd, Co and Ni in muscle of Mastacembelus armatus and Labeo bata with respect to water (Fig. 11 (A-F) and Fig. 12 (A-F)).

Two fishes Macrognathus armatus and *Labeo bata* were considered for the study.

# **RESULTS AND DISCUSSION**

Due to materialistic nature of economic development and consumerism human society exploit natural resources without considering the adverse effects on environment. Smokes, solid wastes and effluents from production units increases pollution load both on land and rivers. Due to irrational use of the river water for various purposes, metals accumulation in aquatic body has increased and reached higher trophic levels through food chain (Ahamed et al. 2019). Fishes are the most special carrier of these toxic elements from habitat environment to human in the form of food source (Usmani 2013). The Konar and Barakar River were contaminated with not only with industrial effluents, but also geogenic sources and natural factors. The riparian zone of Konar River, Barakar River and Tenughat Reservoir have large number of Coal mines, Coal Washeries, Steel Plants and Thermal Power Stations crowed with human habitation. Most of these industries and mines use river water for their production purpose and also to dump their effluents. Moreover, these areas are affected further by morphological alteration, like sand digging and damming.

The physical parameters like Dissolved Oxygen, pH, free carbon dioxide, Temperature, Transparency, Salinity, Alkalinity in the Barakar River, Konar River and Tenughat Reservoir have been depicted in Table 1. The pH of water is a factor that controls all geochemical reactions, that influences metal status in river water. The study reveals that pH value at all



Fig. 2 (A-G:1,2,3). Concentration of Copper in water and fishes (*M. armatus* and *L. bata*) in different sites.

the study sites varied widely and the highest found at Tenughat Reservoir where pH varies from 5.25 10.8 which indicated both acidic and alkaline condition of water. Correspondingly the free carbon dioxide of to this area shows high variation, value ranged from 6.80 to 9.12 and Alkalinity ranged from 17.20 to 19.0 mg/L, low transparency level ranged between 5.40 to 17.50 mg/L which is below normal value and indicate unhealthy condition for aquatic organisms as most of the freshwater fishes require minimum 0.5 mg/L DO in water. This study area has intense network of various industries, such as mining related industries, thermal power station, housing complexes, which directly or indirectly affect Reservoir water. Average pH value at Sangam Ghat was also high (9.50) with low Dissolve oxygen level (4.30-5.80 mg/l), this area is also contaminated with domestic sewage, mine water and industrial effluent. The pH value of Konar Dam, Gobindpur, Tilayia Dam, Fatehpur and Maithon Dam were within normal range and dissolved oxygen was also moderately suitable for the aquatic organisms.

	Water Temp (C°)		Air Te	emp (C°)	(C°) Salini		р	Н
Station	Min	Max	Min	Max	Min	Max	Min	Max
S1. Konar-Dam	20	40	12.4	32.4	2.05	2.15	6.05	7.25
S2. Gobindpur	20	32.45	18.5	32	16.5	18.5	5.35	7.85
S3. Sangam-Ghat	15	45	12.5	36.5	5.0	5.25	7.85	9.50
S4. Tilayia-Dam	10	40	10.5	40.85	2.5	2.85	5.75	7.02
S5. Fatchpur	25	45.5	10.5	49.5	1.5	3.95	6.5	6.53
S6. Maithon-Dam	10.5	18.5	11.5	22.5	1.0	1.25	7.05	8.45
S7. Tenughat-	25	40.05	24.5	38.5	2.95	3.25	5.25	10.8

 Table 1. Physico-chemical parameters measured in the sampling sites.

Reservoir

Table 1. Continued.

					Alkali	nity	Transparency	
	Free Co2		Do (mg/1)		(mg	/1)	Cm	
Station	Min	Max	Min	Max	Min	Max	Min	Max
S1. Konar-Dam	25.00	26.25	8.260	8.90	14.00	12.00	15.80	42.0
S2. Gobindpur	12.30	18.00	2.30	5.20	12.20	17.5	18.35	1.27
S3. Sangam-Ghat	19.5	16.50	4.30	5.80	12.32	15.02	6.58	34.10
S4. Tilayia-Dam	4.85	28.05	2.830	4.90	90.0	90.2	12.86	55.0
S5. Fatehpur	21.30	28.25	2.70	5.32	28.45	32.0	9.05	16.0
S6. Maithon-Dam	45.0	16.30	7.25	8.52	70.50	12.25	24.5	34.50
S7. Tenughat-								
Reservoir	6.80	9.12	120	4.12	17.20	19.0	5.40	17.50

The average mean concentrations of metals, Cu, Pb, Ni, Zn, Co, Cd and standard deviation was determined in water and two fishes. The average mean concentration with Standard deviation of metals in water is shown in Table 2 and Mastacembelus armatus and *Labeo bata* in Table 3 and Table 4 respectively. The graphical representation of metal concentration during pre-monsoon, Monsoon and post-monsoon seasons in water, Mastacembelus armatus and Labeo bata is shown in Fig. 2 (A-G(1,2,3), Fig. 3 (A-G(1,2,3), Fig. 4 (A-G(1,2,3), 5(A-G(1,2,3), 6(A-G(1,2,3), 7(A-G(1,2,3) for Six metals (Cu, Pb, Ni, Zn, Co, Cd) and seven study sites.

The magnitude of Cu contamination is in aquatic body is generally high as this metal is essential for all the usable commodities of mankind. In this study area most of the sites are contaminated with industrial, mining and domestic wastes which are highly contaminated with Cu. The highest mean concentration level of Copper studied in river water was  $67.54 \pm 1.5$ µg/g determined at Tenughat and lowest concentration level 23.54 ± 5.3 µg/L at Maithon, correspondingly in muscle of Labeo bata Cu concentration determined ranged from  $4.84 \pm 0.6 \,\mu g/g$  determined at Tenughat and lowest value 2.13  $\pm$  0.09  $\mu g/g$  determined at Gobindpur. The range of Cu accumulation in Mastacembelus armatus was determined highest 5.64± 0.33  $\mu g/g$  at Tenughat and lowest concentration in this fish was studied at Gobindpur  $2.19 \pm 0.18 \ \mu g/g$ . The average Cu concentration at Govindpur, Maithon Dam and Tilayia Dam are below. This study results shows that Copper concentration in fishes Labeo bata and Mastacembelus armatus exceeds maximum limit prescribed by WHO i.e. 3.0 mg/kg in inland freshwater fish. The Copper concentration in food fish muscle tissue is also threat for human health (Wang 2002, Heyth 1991). Though Copper is essential element for human but when limit exceeds it acts adversely. Ambedkar and Muniyan (2011, 2012) identified the source of Copper pollution in water as domestic waste disposed irrationally in water which is the cause of rise in Cu in food fish tissue.

Lead is a non-essential metal, but causes harm to the human being by damaging the nervous system,



Fig. 3 (A-G:1,2,3). Concentration of Metals Pb in Water and fishes Mastacembelus armatus and Labeo bata in different.

affects mental and physical growth, metabolism, life span, infant neural disorder and natality also Garcia-Leston et al. (2010), Unlu et al. (1994). Rashed (2000, 2001) revealed that Lead contamination in river water was caused by agricultural, industrial and textile runoff which is common in the entire studied area. The highest concentration level of Lead in water was observed at Tenughat 94.35 ± 1.22 µg/L to 22.2 ± 0.41 µg/L at Tilayia, where as in *Labeo bata* the range of this metal was,  $5.95 \pm 0.02$  µg/g to  $1.23 \pm$  0.102  $\mu$ g/g at Tenughat and Maithon respectively. The metal accumulated in Mastacembelus armatus muscle tissue 5.72±0.25  $\mu$ g/g at Tenughat and 1.608±0.2  $\mu$ g/g, the lowest value was at Tilayia. In these findings, Lead level did not exceed the WHO and FEPA standards limit of 2.0 mg/kg for food fish. The Tenughat area, Sangam Ghat, Fatehpur area is densely surrounded with various industries, effluents from various industries, agriculture fields and coal mines contaminates water which may be the source of Lead



Fig. 4 (A-G:1,2,3). Seasonal Ni Concentration in water, Mastacembelus armatus and Labeo bata in seven study sites.

pollution. Shivakumar and Lei (2018) while working on bioaccumulation of heavy metals in different fish tissue at Meiliang Bay, Taihu Lake China, observed that bottom feeders gets directly affected because Lead get absorbed in the sediment of water body immediately and permanently. Gupta et al. (2016) indicated that, Pb may interact with other metals in aquatic environment. The permissible limit of intake of Lead in food stuff is 0.3  $\mu$ g/g as recommended by WHO (2011). Sand mining is one of the sources of Ni contamination in river water which comes from the machine for sand mining and mine waste has worsened the situation in this study area. The present study determined Ni concentration in river water as well as fish muscle tissue is much higher than permissible limit of 0.5–0.6 mg/kg prescribed by WHO (1985). The average highest concentration level  $57.48 \pm 2.05$ µg/L of Ni in water was observed at Tenughat and the lowest value  $16.37 \pm 0.25$  µg/L was determined at



Fig. 5 (A-G:1,2,3). Concentration of Zinc in Water and Mastacembelus armatus and Labeo bata.

Tilayia. Accumulation of Ni in muscle tissue of *Labeo bata* and *Mastacembelus armatus* was  $5.8 \pm 0.08 \ \mu g/g$  and  $5.49 \pm 0.165 \ \mu g/g$  respectively at Sangam Ghat which was much higher than permissible limit. The least value of Ni accumulation  $(2.52 \pm 0.04 \ \mu g/g$  and  $2.11 \pm 0.06 \ \mu g/g)$  of *Labeo bata* and *Mastacembelus armatus* was determined at Tilayia. Ni contamination decreases fertility rate in fish and also retards growth (Montazer and Ali 2018). A high Ni contamination

in fish tissue affects its nuclear structure and genetic instability in fish Sahar et al. (2014) and may cause carcinogenic effect in the consumers Krastyna et al. (2009).

Zinc metal is the easy source from mine water, rocks and mineral rich soil. All these are common source recorded in the riparian zone of Barakar River, Konar River, as well as whole valley of Damodar



Fig. 6 (A-G:1,2,3). Concentration of Co in water and Mastacembelus armatus and Labeo bata.

River. The study indicated that, Zn accumulation in river water as well muscle tissue of both the fishes was highest compared to all other metals. High concentration of Zn 141.74 $\pm$  8.3 µg/L in water was observed at Sangam Ghat and at Tenughat average value of Zn was determined 135.11 $\pm$  2.31 in river water which was higher than the permissible limit 10-40 µg/L in natural ground water or 100 mg/kg (WHO 1985). Lowest value 34.07  $\pm$  1.4 was determined at Tilayia in river water. Maurya et al. (2019) also indicated that Zinc was the highest adsorbed metals compared to Copper, Cadmium and Lead in the Ganga River water and fish tissue. But this study revealed that, highest metal accumulation value in *Labeo bata* determined at Tenughat  $9.9 \pm 0.03 \ \mu g/g$  and in *Mastacembelus armatus*  $9.8 \pm 0.05 \ \mu g/g$  in the same site. According to Damodharan and Reddy (2013) high Zinc content in river water leads excess accumulation of other metal such as Cadmium and Lead.

According to Tripathi and Mittal (2010) predator fishes accumulate low level of Cobalt than in

	Cu	Pb	Ni	Zn	Со	Cd
S1. Konar-Dam S2. Gobindpur	$37.29 \pm 2.68$ $28.59 \pm 0.8$	$37.8 \pm 4.02$ $26.64 \pm 3.4$ $71.16 \pm 1.4$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$55.47 \pm 2.02 \\ 52.8 \pm 5.14 \\ 141.74 \pm 8.2 \\ $	$1.2 \pm 0.21$ $1.07 \pm 0.2$ $2.11 \pm 0.5$	$1.31 \pm 0.14$ $1.53 \pm 0.014$ $2.42 \pm 0.06$
S3. Sangam-Gnat S4. Tilayia-Dam S5. Fatehpur	$\begin{array}{r} 44.4 & \pm & 1.9 \\ 25.37 & \pm & 3.3 \\ 48.313 \pm & 1.26 \end{array}$	$71.16 \pm 1.4$ 22.2 ± 0.41 54.16 ± 3.25	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$
S6. Maithon-Dam S7. Tenughat-	23.54 ± 5.3	22.59 ± 0.09	20.44 ± 0.15	36.32 ± 0.57	0.98 ± 0.39	0.24 ± 0.24
Reservoir	67.54 ± 1.57	94.35 ± 1.22	57.48 ± 2.05	$135.11 \pm 2.31$	$4.75 \pm 0.35$	$5.02 \pm 0.89$

 Table 2. Average metal concentrations in river water.

omnivore fishes. Prasad and Simhachalam (2018), noted that, Labeo bata is herbivorus but feeds sand and mud in large quantity which may be the main source of metals contamination, already absorbed in the river sediment. Paul and Maity (2018) studied that Labeo bata showed higher accumulation of toxic metals than Labeo rohita. The present study reveals that the highest concentration level of Co 4.75  $\pm$  $0.35 \,\mu g/L$  in water was determined at Tenughat and the least value  $0.98 \pm 0.39 \ \mu g/L$  was determined at Maithon. Andeniyi and Ysuf (2007) recorded that, Cobalt usually accumulates in very low amount in fish tissue. Mastacembelus armatus accumulated less amount of Co than other fishes in spite its carnivorus nature Gupta and Banerjee (2016). The present study determined highest accumulation of Co in Labeo bata  $(1.74 \pm 1.3 \mu g/g)$  at Konar Dam which was higher than permissible limit of WHO. But at Maithon the average value accumulated was  $0.01 \pm 0.01 \ \mu g/g$  is below the permissible limit of WHO. Mastacembelus armatus highest concentration level of accumulated Co is  $0.86 \pm 0.03 \,\mu\text{g/g}$  at Tenughat and the least value was  $0.05 \pm 0.05 \ \mu g/g$  at Maithon.

Cadmium contamination may induce carcino-

genesis in human Andeniyi and Yusuf (2007). Mine discharge and road runoff may be the source of Cd. According to Chunhabundit Rodjana (2016), a very low Cd in food can harm human. Cd concentration in aquatic environment may be less if the pH of the aquatic body becomes slightly acidic. The highest concentration of Cd in water was observed at Tenughat  $5.02 \pm 0.89 \ \mu g/L$ , and the least value was  $0.24 \pm 0.24 \ \mu g/L$  at Maithon, where the average pH level was alkaline and alkalinity is also high. Andreji et al. (2005) reported that fish muscle tissue usually accumulates Cd, Ni, in low amount. In the present study it was revealed that, the fish muscle tissue in this area showed raised Cd environment may be less if the pH of the aquatic body becomes slightly acidic. The highest concentration of Cd in water was observed at Tenughat  $5.02 \pm 0.89 \ \mu g/L$ , and the least value was 0.24  $\pm$  0.24  $\mu g/L$  at Maithon, where the average pH level was alkaline and alkalinity is also high. Andreji et al. (2005) reported that fish muscle tissue usually accumulates Cd, Ni, in low amount. In the present study it was revealed that, the fish muscle tissue in this area showed raised Cd environment may be less if the pH of the aquatic body becomes slightly acidic. The highest concentration of Cd in water was

Table 3. Concentration of metals in muscle tissue of Mastacembelus armatus (µg/g).

	Cu		Pb	Ni		Zn		Со	Cd
S1. Konar-Dam	3.65	+ 0.44	$2.41 \pm 0.26$	3.81	+ 0.12	4.64	+ 0.07	$0.48 \pm 0.05$	$0.455 \pm 0.03$
S2. Gobindpur	2.19	$\pm 0.18$	$1.8 \pm 0.21$	2.69	$\pm 0.39$	5.3	$\pm 0.75$	$0.37 \pm 0.07$	$0.44 \pm 0.015$
S3. Sangam-Ghat	3.4	± 0.3	$5.02 \pm 0.25$	5.49	± 0.165	9.29	± 0.28	$0.7 \pm 0.08$	$0.66 \pm 0.035$
S4. Tilayia-Dam	2.47	$\pm 0.5$	$1.608 \pm 0.2$	2.11	$\pm 0.06$	2.82	$\pm 0.13$	$0.41~\pm~0.16$	0
S5. Fatehpur	4.44	$\pm 0.46$	$3.96 \pm 0.22$	5.08	$\pm 0.404$	5.4	$\pm 0.3$	$0.7$ $\pm$ $0.05$	$0.73 \hspace{0.2cm} \pm \hspace{0.2cm} 0.018$
S6. Maithon-Dam	2.24	$\pm 0.63$	$1.8 \pm 0.02$	2.15	$\pm 0.08$	3.68	$\pm 0.14$	$0.05~\pm~0.05$	0
S7. Tenughat-									
Reservoir	5.64	$\pm \ 0.33$	$5.72 \hspace{0.2cm} \pm \hspace{0.2cm} 0.25$	4.9	$\pm 0.67$	9.8	$\pm \ 0.05$	$0.86~\pm~0.03$	$0.93 \ \pm \ 0.11$



Fig. 7(A-G:1,2,3). Concentration of Cadmium in water and Mastacembelus armatus and Labeo bata.

Table 4. Concentration of metals in muscle tissue of Labeo bata ( $\mu g/g$ ).

	Cu		Pb	Ni		Zn		Co	Cd
S1. Konar-Dam	3.07	± 0.21	2.49 ± 0.81	3.37	± 0.28	4.7	± 0.36	$1.74 \pm 1.3$	$0.546\pm\ 0.03$
S2. Gobindpur	2.13	$\pm 0.09$	$2.13 \hspace{0.2cm} \pm \hspace{0.2cm} 0.08 \hspace{0.2cm}$	3.14	$\pm 0.37$	5.02	$\pm 0.7$	$0.41~\pm~0.23$	$0.45 \hspace{0.2cm} \pm \hspace{0.2cm} 0.03$
S3. Sangam-Ghat	3.58	$\pm 0.29$	$4.81 \hspace{0.2cm} \pm \hspace{0.2cm} 0.35$	5.8	$\pm 0.08$	9.3	$\pm 0.3$	$0.63~\pm~0.08$	$0.65 \pm 0.06$
S4. Tilayia-Dam	2.17	$\pm 0.6$	$1.82 \hspace{0.2cm} \pm \hspace{0.2cm} 0.55$	2.52	$\pm 0.04$	3.03	$\pm 0.07$	$0.34~\pm~0.016$	0
S5. Fatehpur	4.43	± 0.7	$4.18 \pm 0.4$	5.1	$\pm 0.22$	5.79	$\pm 0.35$	$0.53 \pm 0.12$	$0.7 \pm 0.003$
S6. Maithon-Dam S7. Tenughat-	2.35	$\pm 0.04$	$1.23 \pm 0.102$	2.64	$\pm 0.18$	3.95	$\pm 0.03$	$0.01~\pm~0.01$	0
Reservoir	4.84	$\pm 0.6$	$5.95  \pm 0.02 $	5.08	$\pm \ 0.65$	9.9	$\pm \ 0.03$	$0.68~\pm~0.09$	$0.03 \hspace{0.2cm} \pm \hspace{0.2cm} 0.18$



Fig. 8. Coefficient of Variance of met.

observed at Tenughat  $5.02 \pm 0.89 \ \mu g/L$ , and the least value was  $0.24 \pm 0.24 \mu g/L$  at Maithon, where the average pH level was alkaline and alkalinity is also high. Andreji et al. (2005) reported that fish muscle tissue usually accumulates Cd, Ni, in low amount. In the present study it was revealed that, the fish muscle tissue in this area showed raised Cd environment may be less if the pH of the aquatic body becomes slightly acidic. The highest concentration of Cd in water was observed at Tenughat  $5.02 \pm 0.89 \,\mu\text{g/L}$ , and the least value was  $0.24 \pm 0.24 \mu g/L$  at Maithon, where the average pH level was alkaline and alkalinity is also high. Andreji et al. (2005) reported that fish muscle tissue usually accumulates Cd, Ni, in low amount. In the present study it was revealed that, the fish muscle tissue in this area showed raised Cd environment may be less if the pH of the aquatic body becomes slightly acidic. The highest concentration of Cd in water was observed at Tenughat  $5.02 \pm 0.89 \ \mu g/L$ , and the least value was  $0.24 \pm 0.24 \mu g/L$  at Maithon, where the average pH level was alkaline and alkalinity is also high. Andreji et al. (2005) reported that fish muscle tissue usually accumulates Cd, Ni, in low amount. In the present study it was revealed that, the fish muscle tissue in this area showed raised Cd accumulation, the highest mean concentration level of Cd in Labeo bata at Tenughat is  $1.03 \pm 0.18 \,\mu\text{g/g}$  where as in Mastacembelus armatus highest concentration level of Cd  $0.93 \pm 0.11 \ \mu g/g$ . These indicates that, Cd level was above maximum permissible limit as dietary intake is concerned as, recommended by WHO.

The coefficient of variation (CV) is a measure of relative variability. It is used to compare results



Fig. 9. Coefficient of Variance of metals in *Mastacembelus armatus* in all study sites.

from different survey data or tests that have different measures or values. The coefficient of variance of river water is reflected in the Figs. 8 and 9 shows coefficient of variance of *Mastacembelus armatus* and Fig. 10 is the graphical representation of coefficient of variance of *Labeo bata*. In river water Pb, showed highest coefficient of variance value whereas in *Mastacembelus armatus* Cd was highest and in *Labeo bata* the most varied metal is Cu.

The high accumulative rate of metal in fish tissue is alarming in this study area. Fig. 11 (A to F) and Fig. 12 (A to F) illustrate the regression value of metals (Cu, Pb, Ni, Zn, Co, Cd) in muscle tissues of two fishes *Mastacembelus armatus* and *Labeo bata* with respected to water metal content. Fig. 11 A and B represented the regression value of Cu in *Mastacembelus armatus* and *Labeo bata* respectively.



Fig. 10. Coefficient of Variance of metals in *Labeo bata* in all study sites.



Fig. 11 (A-F). Regression of Water, M. armatus and L. bata.

In both the fishes  $R^2$  value satisfies regression model and it is positive. The regression is significant because p <0.05.  $R^2$  value for *Mastacembelus armatus* was 0.0863 and *Labeo bata* was 0.1290. The lager  $R^2$  value indicates high bioaccumulation of Cu in fish tissue. Fig. 11 C and D similarly represented the regression value of Pb in *Mastacembelus armatus* and *Labeo bata* respectively where  $R^2$  value satisfies regression model. The regression is significant because p is<0.05. R value for Pb with respect to muscle tissue *Mastacembelus armatus* was 0.06380 and *Labeo bata* 0.0668. The lager  $R^2$  value indicates high bioaccumulation of Pb in fish tissue and the regression model was positive. The R<sup>2</sup> value of Fig. 11 E and F represented the regression value of Ni in *Mastacembelus armatus* and *Labeo bata* respectively. Similarly R value satisfies regression model. The regression is significant because p<0.05. R value for *Mastacembelus armatus* was 0.06380 and *Labeo bata* was 0.0668. The lager R value indicates high bioaccumulation of Cu in fish tissue. Regression value for Ni in *Mastacembelus armatus* 0.2488 where as in *Labeo bata* R<sup>2</sup> was 0.0085 which signifies high bioaccumulation and it also positive regression



Fig. 12 (A-F). Regression of Water, M. armatus and L. bata.

model as it satisfies p value <0.05. In the Fig. 12. A, B the R<sup>2</sup> value of Zn was 0.0586 for *Mastacembelus armatus* and in *Labeo bata* the value was 0.2441, that indicates high accumulation of metals in fish tissue, also represents as positive regression model which satisfies the level of significance positive and below <0.05. The metal Co shows positive regression. R<sup>2</sup> value 0.1336, 0.0517 for *Mastacembelus armatus* and *Labeo bata* respectively. The values are positively significant and <0.05. AS the R<sup>2</sup> value of Cd in *Mastacembelus armatus* and *Labeo bata* was 0.1577, 0.3355 respectively. The values are positively significant *Mastacembelus armatus* was 0.06380 and *Labeo bata* was 0.0668. The lager R value indicates high bioaccumulation of Cu in fish tissue. Regression value for Ni in *Mastacembelus armatus* 0.2488 where as in *Labeo bata* R<sup>2</sup> was 0.0085 which signifies high bioaccumulation and it also positive regression model as it satisfies p value <0.05. In the Fig. 12. A, B the R<sup>2</sup> value of Zn was 0.0586 for *Mastacembelus armatus* and in *Labeo bata* the value was 0.2441, that indicates high accumulation of metals in fish tissue, also represents as positive regression model which satisfies the level of significance positive and below



Fig. 13. Dendogram of cluster analysis of the accumulated metals in fish tissue.

<0.05. The metal Co shows positive regression. R2 value 0.1336, 0.0517 for *Mastacembelus armatus* and *Labeo bata* respectively. The values are positively significant and <0.05. AS the R<sup>2</sup> value of Cd in *Mastacembelus armatus* and *Labeo bata* was 0.1577, 0.3355 respectively. The values are positively significant and indicate high bioaccumulation in both the fish.

In comparison of metal absorption limit in fish muscle tissue both the fishes are found to absorb more or less same amount Zn in highest quantity Javed and Usmani 2011. This study also revealed that Zinc was the metal which showed maximum absorption. Usmani and Kumar (2017) indicated high bioaccumulation of metals in Puntius sarana and Labeo rohita in a case study at Damodar River. The present study found that Labeo bata and Mastacembelus armatus also showed metal absorption higher than permissible limit. Statistical analysis for Kruskal Wallis test was done to compare the metal absorption limit in three seasons and sites. The Kruskal Wallis Test for seasonal metals variation with respect to sites reveals that Copper value does not vary significantly in pre-monsoon and post-monsoon season. Lead value varied significantly in pre-monsoon season (0.014); monsoon season (0.017) and in post-monsoon season (0.030) Nickel value did not show any significant variation among seasons according to sites. Zinc value varied significantly in pre-monsoon season (0.021); monsoon season (0.003) and in post-monsoon season (0.041) Cobalt value varies significantly in pre-monsoon season (0.001) and in post-monsoon season (0.030) but the monsoon Cobalt does not vary significantly. Cadmium value varied significantly in pre-monsoon season (0.000); monsoon season (0.000) and in post-monsoon season (0.000).

The result of cluster analysis (done by SPSS1696) has been illustrated by the dendrogram in Fig. 13. Cluster I demonstrated that Ni and Cd were more similar in absorption pattern in river water and fish tissue than to Cd. Cluster II showed the association between Pb and Zn than other metals. The hierarchical cluster analysis is a technique often used in combination with to study the structure of a data set. A dendrogram is two-dimensional tree, a graphical format of the hierarchical clustering. This is the most significant and strongest method to express the graphical summery of clustering, that allows one to map the multidimensional space of variables. The individual metal samples were represented by the vertical lines and the branches of the dendrogram did not cross similar clusters which are separated by horizontal cluster lines. The horizontal axis represents the distance between the clusters when they are joined. The dendogram constructed on the basis of similarity (or distance) between samples. Two distinct cluster emerged from the grouping of heavy metals (Fig. 13). Cluster I consists of Nickel (Ni) - Cadmium (Cd) - Cobalt (Co) and Cluster II Lead (Pb) - Zinc (Zn)-Copper (Cu). The metals, Ni-Cd-Co showed strong similarity in absorption limit. Andreji et al. (2005) also found Ni and Co are positively correlated in relation to bioaccumulation. These metals strongly showed similarity in the absorbent rate in fish tissue. Waste water from mining, coalwashery, agricultural runoff in the river valley could be the main sources of these elements. According to Loska and Wiechula (2003) combustion of fossil fuels (particularly coal) releases Cd into environment. Parent rock and weathering condition also may be the source of these metals. The analysis indicated Pb and Zn are found to be absorbed similarly in fish tissue. Metals Pb-Zn-Cu showed close relationship and indicates similar absorption limit in fish tissue. These metals in fish tissue indicate contamination of the aquatic body by industrial effluents in the study area. Cu is substantially different, does no indicate similar trend of absorption as other metals does.

# CONCLUSION

Fishes are most easy available animal protein source, highly nutritious for the fish eating people. According to the annual per person fish consumption by the fish eating population of India is 5-6 kg in average. But polluted aquatic environment is the root cause of metal contamination. Even very low exposure and low metal absorption in the edible part of fish may harm human. The studied river vallies are rich in mineral source and extensive network of mining and mine related industries are there creating large employment. It is alarming for the consumers that these two food fishes are contaminated with heavy metals which are higher than permissible limit. This study reveals that Konar River, Barakar River, Tenughat Reservoir, water and two fishes studied from the seven stations highly are contaminated by heavy metals. The metal concentrations were above the maximum permissible limit recommended by WHO and consuming muscles of these food fishes will definitely bring health hazard among the consumers. Responsibility to save river and its biota to ensure safe life is of utmost important, so that hazardous metals may not affect those who consume them.

### ACKNOWLEDGEMENT

The author is highly grateful to the Principal of the college as well as to the Research and development cell of the college for their continuous cooperation and encouragement for the research work. Author contributions: Collection of water and fishes from individual sites. Preparation of the fish tissue and water for metal analysis. Statistical Funding: The funding was by Research and Development Cell Shree Chaitanya College. Conflicts of Interest: The authors declare no conflict of interest.

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