E-ISSN: 2347-5129
P-ISSN: 2394-0506
(ICV-Poland) Impact Value: 76.37
(GIF) Impact Factor: 0.549
IJFAS 2023; 11(1): 127-132

www.fisheriesjournal.com
Received: 17-11-2022
Accepted: 19-12-2022

Ikponmwen Efe Gideon
Department of Fisheries and Aquaculture, Federal University Wukari, Nigeria

Asuelimen Steve Osagie
Department of Biochemistry, Federal University Wukari, Nigeria

Corresponding Author:
Ikponmwen Efe Gideon
Department of Fisheries and Aquaculture, Federal University Wukari, Nigeria

Evaluation of physico-chemical parameters and heavy metal concentrations in muscles of *Synodontis courteti* and *Mormyrus macrophthalmus* from lower River Benue, Ibi, Taraba, Nigeria

Ikponmwen Efe Gideon and Asuelimen Steve Osagie

DOI: https://doi.org/10.22271/fish.2023.v11.i1b.2775

Abstract
Heavy metals concentrations in muscles of *Synodontis courteti* and *Mormyrus macrophthalmus* from lower River Benue, Ibi, Taraba state was examined. The heavy metals concentration in the species under consideration was studied with atomic absorption spectrophotometer (AAS). Bulk Model 210VGP scientific equipment. Results obtained confirmed the occurrence and levels of the following heavy metals (lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), zinc (Zn) in muscles of the two commercially important species investigated. Recorded values of heavy metals in muscles of *S. courteti and M. macrophthalmus* overtime showed the metal concentrations ranking profile Pb >Cd >Cr >Cu >Zn > Mn were higher for *S. courteti* than *M. macrophthalmus*. Cadmium (Cd) and Chromium (Cr) showed variation (p>0.05) in concentrations for both species November and December, exception of October. Heavy metal concentration of *M. macrophthalmus* showed less variation with location (p<0.05) but showed some variation with time. Between the metals considered Zn recorded the highest value compare to other metals. The ranking profile Zn>, Mn>, Pb>, Cu>, Cd>, Cr. Between location upstream and downstream. However all values recorded for the metals were within safe limit The levels of Pb, Cr, Cd, Cu, Mn, Zn in the Muscles of the species studied were below WHO/FAO and FEPA recommended limits in fish and fishery products. Lead (Pb) values was low throughout the study period in both species except for the month of October which was higher downstream. Though Pb, Cd and Cr Values was within the permissible limits recommended by FAO and FEPA for fish/fisheries products. This study also reported on some physico-chemical parameter of importance (temperature, pH, D.O., Electrical conductivity (EC) and TDS,) and they were found to be within acceptable levels for sustainable fish survival and growth. The need for continuous monitoring and conservation of the fish and fisheries resources of lower River Benue waters and the heavy metals content therein cannot be overemphasize.

Keywords: Heavy metals, water, fish muscles, lower River Benue, Ibi

Introduction

Research on heavy metals and aquatic environment monitoring have become important due to concerns of bioaccumulation and toxic effects of trace metals on aquatic organisms and to humans through the food chain (Otchere, 2013) [29]. Over the years contaminations of rivers by heavy metal have been a major environmental issue in developing countries including Nigeria (Wangboje *et al*., 2018) [37]. Estuaries and rivers which are source of drinking water in Nigeria, are often contaminated by the urban populations and industrial establishments (Ikponmwen *et al*., 2020) [18]. Increase in population, industrialization, agricultural and domestic pollution and subsequently increase of the problem of waste disposals has adversely affected man and the environment (Ndimele *et al*., 2011) [23]. Untreated waste and effluents discharge into natural aquatic media are also main source of contamination threatening biological life particularly in third world countries, like Nigeria (Ugokwe and Adelowo, 2015) [33]. Furthermore, rivers have been recognized as a major pathway for the transportation of heavy metals (Ikhuoriah and Oronsaye, 2016) [17]. A lot of pollutants can persist for many years in sediments where they hold possibility of affecting the river, the environment, fish and human health, (Mackevičiene *et al*., 2012) [20].

Sediments are important sink of a variety of pollutants, particularly heavy metals and may serve as enriched source of contaminants for benthic organisms and fish (Wang *et al*., 2019) [35]. The occurrence of higher levels of heavy metals in sediments found at the bottom of the water column can be a good indicator of man-induced pollution rather than natural enrichment by physical weathering (Davies *et al*., 2011, Chang *et al*., 2018) [6, 5]. The absorption of heavy metals by fish through food and water may affects not only the yield capabilities of such fish, but eventually the health of man that depends on it as a major source of protein (Fonge *et al*., 2011; Wangboje and Ikhuabe, 2015) [15, 36]. Heavy metals are classified as metallic elements belonging to most important category of pollutant (Tabari *et al*., 2010) [31]. Heavy metal are metallic elements which have moderately high atomic weight and lethal at low concentration (Butu and Igiusi, 2013) [4]. All metals are possibly harmful to fish and most organisms at some level of contact and absorption (Adedeji and Okocha, 2011) [1]. Concentrations of essential elements in organisms are normally homoestatically-controlled, with uptake from the environment regulated according to nutritional demand, effects on the organisms are manifest when this regulation mechanism breaks down as a result of either insufficient (deficiency) or excess (toxicity) metal (Duffus, 2012) [8].Hence, information of the change in concentration and dispersal of heavy metals in various components of the environment is a priority for good environmental control plans all over the world (Defew *et al*., 2014) [7]. The use of fish as a bio-indicator metal contamination in water and its suitability for man's use from toxicological view has been documented (Oguzie and Okhagbuzo, 2010; Wangboje and Ekundayo, 2016; Orowe and Ikponmwen, 2020a) [25, 34, 27].

Materials and Methods

Study Area

This study was carried out at Lower river Benue at Ibi, Taraba State, Nigeria. Ibi is located at latitude 8° 38' North and longitude 10° 46' East. The flora in the area is mostly secondary forest, shrubs re-growth and swamp. There are two seasons, April- October, raining season. The month of November-March are much drier than the other months. The annual rainfall ranges from 130 cm to 266.30 cm/yr with temperature between 32 °C and 36 °C. The area has a inhabitants of over 244,749 scattered over small to large villages all over the area and is largely drained by the Tela Rivers. The people are majorly farmers and fishermen.

Collection of Samples

Fish samples were caught using various fishing gears and nets from two locations (Upstream and Downstream) monthly, for three (3) months, between October and December, 2021. Fish caught were identified using keys and monograph in the laboratory using methods described by (Olaosebikhan and Raji, 2013) [26]. Routine body measurements such as standard length will be taken and recorded respectively. Fish weight were determine by means of top loader (mettle balance) and 0.1g fish samples will be placed in clean polyethylene bags and stored. Fish muscles was obtained by dissection using a dissection kit. Muscles were milled separately and placed in a polythene bag. Fish was allowed to thaw at room temperature prior to the dissection at (27 °C) and stored at -10^{0}C prior to digestion and analysis.

Surface water was collected in triplicates from each sampling location using container well corked, monthly from October to December, 2021 and stored in ice chest. Immediately physico-chemical parameter like dissolved oxygen was however measures in-situ, other were taken to the laboratory and analyzed within the next 24hours. The containers were washed with distilled water to remove any form of contaminant prior to sample collection.

Laboratory procedures

Digestion of Fish Samples

Fish parts were treated separately. Organic Extraction method was used to digest each fish part using methods as described by Sreedivi *et al*., (1992) [30]. 1g of each milled sample was placed in Kjeldhal (50ml) flask. The following were added to the samples in the flask, nitric acid (10ml), perchloric acid (2ml) and sulfuric acid (2ml) in ratio (5:1:1). The contents were treated with moderate heat under a hood. Digestion was completed with the formation of white fume. An aliquot of the digest was diluted with purified water (10ml), further boiled for a some minutes before allowing to cool, and subsequently filtered into volumetric flask (50ml) and made up to mark. Blanks were prepared with the same quantities of mixed acids.

Determination of Physicochemical Parameters

The following physico-chemical parameters were analyzed: The dissolved oxygen (mg/l) (DO) was determined in-situ using Extech instrument- DO meter (407510A model), while other parameters: pH, temperature, total dissolved solids (TDS) and electrical conductivity (EC), were determined with Hanna (HI 9813-6 model) digital combo meter at the Federal University Wukari biological laboratory, Taraba state, Nigeria.

Analysis of Heavy Metals

The following heavy metals were analyzed in the fish muscles zinc (Zn), lead (Pb), copper (Cu), nickel (Ni), chromium (Cr) at Central Laboratory Federal University Wukari, Taraba state, Nigeria. Heavy metals analyses was carried out using an Atomic Absorption Spectrophotometer (AAS) model 210 VGP Buck scientific equipment. Blanks, standards and specimen digests was aspirated into the AAS using air-acetylene flame as oxidant.

Statistical Analysis

The data were presented as means and standard deviations. Mean generated were subjected to one-way analysis of variance (ANOVA) using statistical package for scientists and engineers (SPSS) 9.0 Edition (2012) for windows to determine the significant difference between physico chemical parameters, heavy metals and the locations at 5% level of probability. New Duncan Multiple Range Test (DMRT) was used to separate the means (Duncan, 1955) [9].

Results and Discussion

Results on heavy metals in muscles of two commercially important fish species *Synodontis courteti* and *Mormyrus macrophthalmus* Upstream and Downstream of Lower River Benue are presented in Tables 1-4. Variation of physico-chemical parameter measured during the study are also presented in Table 1. The values for water temperature were within the optimum range (23-32mg/l) for fresh water fish survival and growth during the study period as recommended by Federal Ministry for Environment (FMENV) (2001) [11]. Values obtained for water pH was also within optimum range for fresh water fish survival FMENV (2001) [11]. Fish can live in waters with a pH range of between 5 to 10 which is the desirable pH range for fish survival. Availability of carbon dioxide in water bodies has been shown to influence pH levels of water bodies and fresh water fish survival (Aquaculture Information Network Centre (AINC), 2007) [3]. Values obtained for total dissolve solid (180-200mg/l) during the study period was within optimum range (600-1000mg/l) recommended by FMENV (2001) [11] for fresh water fish survival. Higher levels of total dissolved have been seen to affect heavy metal availability which will also affect the level of sedimentation in the river water and will have negative effect on fish survival. High TDS values have been found to also favor high aquatic plant growth, which also result to high turbidity of River water and affect fish. (Mironga *et al*., 2012) [21].

Table 1: Mean variations between location of physico-chemical parameters in Lower River Benue waters

		Month		
physico-chemical parameters	**Sampling Location**	**Oct**	**Nov**	**Dec**
Water temperature (^{0}C)	Downstream	32.10^b±0.85	31.55^b±0.07	32.40^b±1.13
	Upstream	31.50^b±0.14	31.85^b±0.07	33.15^b±1.91
D.O (mg/l)	Downstream	6.50^c±0.42	6.65^d±0.21^a	6.70^c±0.85
	Upstream	6.70^c±0.14	7.90^d±0.00^a	7.10^c±0.99
pH	Downstream	4.56^e±0.07	4.52e±0.042^a	4.81^d±0.05
	Upstream	4.65^e±0.02	4.43e±0.042^a	5.04^d±0.13
Electrical conductivity(μS/m)	Downstream	14.0^d±0.00	15.0^c±0.03^a	8.0e±0.01
	Upstream	13.0^d±0.01	15.0^c±0.00^a	8.0e±0.00
Total dissolved solids (mg/l)	Downstream	190^a±0.00	200^a±0.01	200^a±0.00
	Upstream	200^a±0.00	200^a±0.01	180^a±0.01

Results are expressed as Mean ± Standard deviation (SD). Means with similar alphabets in a row are not significantly different (p>0.05).

Mean variations in physico-chemical parameters between locations of Lower river Benue waters with time as presented in Table 1 showed total dissolve solid recorded the highest value of 200 mg/l, between October and December while the lowest values were recorded for pH (4.43 and 4.52) in November. The values of dissolve oxygen range between 6.50 mg/l to 7.90 mg/l during the study period, which happens to be dry season periods. Studies have showed that warm water does not contain as much oxygen as cold water (Orowe and Ikponmwen, 2020b) [28]. Thus during warm weather months over fertilization and pollution can result in oxygen depletion and fish kills. For successful hatching, oxygen concentration of the water should be at least 6mg/l. However report showed that optimum range of dissolved oxygen for growth and reproduction in fresh water fish may be between 5 mg/l-8mg/l (Tejpal and Sahu, 2015) [32]. Generally, when fish are subjected to chemical, physical, or biological (i.e. pathogen infection) stress, sudden shortage of dissolve oxygen may result in abnormal oxidative reactions in the aerobic metabolic pathways, (Orowe and Ikponmwen, 2020b and may lead to formation of excessive amounts of oxygen and free radicals (Orowe and Ikponmwen,2020b; Tejpal and Sahu, 2015) [28, 32].

Table 2: Mean heavy metal Variations in muscles of two species (mg/kg) with time

		Concentration (mg/kg) Months		
Heavy Metals	**Fish Muscles**	**Oct**	**Nov**	**Dec**
Pb	Synod	0.216^c±0.141	0.057^c±0.020	0.016^e±0.020
	MRR	0.200^b±0.360	0.022^d±0.022	0.015^e±0.012
Cd	Synod	0.023^e±0.014	0.007^f±0.002	0.018^d±0.012
	MRR	0.246^c±0.375	0.014^e±0.012	0.011^e±0.008
Cr	Synod	0.010^f±0.005	0.024^e±0.020	0.009^f±0.003
	MRR	0.013^f±0.008	0.020^f±0.011	0.020^c±0.011
Cu	Synod	0.075^d±0.050	0.025^d±0.050	0.025^c±0.050
	MRR	0.050^d±0.058	0.000^e±0.000	0.000^f±0.000
Zn	Synod	0.625^a±0.126	0.600^a±0.082	0.625^a±0.171
	MRR	0.475^a±0.050	0.450^a±0.058	0.525^a±0.050
Mn	Synod	0.267^b±0.046	0.303^b±0.172	0.290^b±0.137
	MRR	0.123^c±0.076	0.185^b±0.065	0.213^b±0.067

Results are expressed as Mean ± Standard deviation (SD). Means with the similar alphabets in a row are not significantly different (p >0.05).
Where; Synod= *Synodontis courteti*; MRR=*Mormyrus macrophthalmus*

The concentration of heavy metals among muscles of the two species studied are presented in Tables 2 above. The results showed that there was no significant difference (p> 0.05) between the species for Zn, Cu, Cr in October and November. However, there was variation (p< 0.05) for values of Cd (0.022 mg/kg) Cadmium (Cd) (0.485mg/kg) and Pb (0.369 mg/kg) for other months in *Mormyrus macrophthalmus* compare to *Synodontis courteti* with time. Results obtained from this study showed that there was significant difference (p< 0.05) of heavy metals concentrations between muscles of *Synodontis courteti and Mormyrus macrophthalmus* with time. Heavy metals concentrations values were higher for all the metals Pb >Cd >Cr >Cu >Zn > Mn for *S. courteti* than *M. macrophthalmus* for November and December except in October were Cd and Cr showed some variation for both species. However all values recorded for both species were within the safe limit for fish and fish products as recommended by WHO/FAO (2004) [19]. and FEPA (2003) [14]. Higher values recorded for Zn (0.625 mg/kg) in this study was recorded in S. courteti was however lower than that reported in flesh of *H. fasciatus, O. niloticus, C. nigrodigitatus, C. gariepinus* by Wangboje and Ikhuabe (2015) [36] in the Niger River at Agenebode, Edo state. It so also lower than values reported by Idodo-umeh (2003) [16] in

Olomoro river of Delta state but higher than those reported by Saeed and Shakar (2008) [30] in O. niloticus in North Delta Lake, Egypt. The lower value report in this study could be due to differences in the species, sizes, ages, and sampling periods (Idodo-umeh, 2003) [16]. The higher concentration of Zinc in this study may occur as a result of anthropogenic activities and vehicle movement taking place around the environment. Anthropological activities such as the use of substances such as Zinc-based fertilizers by farmers and locomotive oil left-over from rice milling equipment and other petrochemicals around the area (Adekola *et al.*, 2002; Edward *et al.*,2013) [1, 12].

Table 3: Heavy metals variation in muscles *Synodontis courteti* with location

Concentrations (mg/kg) Month				
Heavy Metals	**Sampling locations**	**Oct**	**Nov**	**Dec**
Pb	upstream	0.275^{b}±0.031	0.028^{d}±0.026	0.037^{d}±0.013
	downstream	0.158^{b}±0.210	0.056^{c}±0.030	0.025^{d}±0.004
Cd	upstream	0.029^{d}±0.000	0.007^{e}±0.003	0.017^{e}±0.004
	downstream	0.016^{e}±0.021	0.006^{e}±0.001	0.022^{e}±0.005
Cr	upstream	0.009f±0.001	0.022^{e}±0.018	0.010^{f}±0.004
	downstream	0.011^{f}±0.009	0.025^{d}±0.003	0.009^{f}±0.002
Cu	upstream	0.050^{e}±0.070	0.000^{f}±0.000	0.050^{c}±0.071
	downstream	0.100^{c}±0.000	0.050^{c}±0.071	0.000^{g}±0.000
Zn	upstream	0.550^{a}±0.070	0.600^{a}±0.141	0.600^{a}±0.283
	downstream	0.700^{a}±0.140	0.600^{a}±0.000	0.650^{a} ±0.071
Mn	upstream	0.265^{c}±0.078	0.345^{b}±0.219	0.215^{b}±0.177
	downstream	0.270^{b}±0.014	0.260^{b}±0.184	0.365^{g}±0.049

Results are presented as Mean ± Standard deviation (SD). Means having the similar alphabets in a row are not significantly different ($p < 0.05$).

Results from Table 3 shows heavy metals variation in *Synodontis courteti* was higher downstream compared to upstream generally. The highest value (0.700 mg/kg) was recorded for Zn downstream in October while the lowest (0.000 mg/kg) was recorded for Copper (Cu) in November and December. Values (0.275 mg/kg) recorded for Lead (Pb) in both location upstream and downstream was the highest compare to value (0.025 mg.kg) downstream in December. The value of Cu, Cd, and Cr for this study were however within the safe limit recommended by WHO/FAO (2004) [13] and FEPA (2003) [14]. The observed low levels of Cu, Cd, and Cr of S. *courteti* in comparison with fish muscles studied in some other water bodies in other area (Edward *et al.*, 2013) [12] recorded higher metals levels in Niger River. The observed low concentration are consistent with finding of (Obire *et al.*, 2008) [24] in Elechi creek in Port Harcourt.

Table 4: Mean Heavy metals concentrations in *Mormyrus macrophthalmus* based on Location

Concentration (mg/kg) Month				
Heavy Metals	**Sampling locations**	**Oct**	**Nov**	**Dec**
Pb	Upstream	0.369^{b}±0.522	0.025^{c}±0.030	0.005^{h}±0.001
	Downstream	0.031^{e}±0.030	0.019^{e}±0.022	0.028^{e}±0.018
Cd	Upstream	0.007^{g}±0.008	0.020^{d}±0.018	0.016^{d}±0.000
	Downstream	0.485^{b}±0.438	0.008^{f}±0.001	0.006^{f}±0.007
Cr	Upstream	0.014^{f}±0.004	0.020^{d}±0.018	0.023^{e}±0.001
	Downstream	0.012^{e}±0.012	0.022^{e}±0.004	0.018^{d}±0.018
Cu	Upstream	0.050^{d}±0.071	0.000^{e}±0.000	0.000^{g}±0.000
	Downstream	0.050^{d}±0.071	0.000^{e}±0.000	0.000^{g}±0.000
Zn	Upstream	0.500^{a}±0.000	0.450^{a}±0.071	0.550^{a}±0.071
	Downstream	0.450^{a}±0.071	0.450^{a}±0.071	0.500^{a}±0.000
Mn	Upstream	0.155^{c}±0.021	0.170^{b}±0.042	0.175^{b}±0.021
	Downstream	0.090^{c}±0.113	0.200^{b}±0.099	0.250^{b}±0.849

Results are presented as Mean ± Standard deviation (SD). Means having the similar alphabets in a row are not significantly different ($p > 0.05$).

The results of concentrations between locations presented in Table 4 above between location, some metal, such as Zn, Mn, Cu, did not show variation but Cr, Cd and Pb values showed variations. Also Heavy metals concentration showed variation with time. The highest Zn values (0.500 mg.kg) and (0.450mg/kg) gotten in the two location was for October, lower (0.000mg/kg) was reported for Cu in November and December during the study period. Lead (Pb) values (0.005mg/kg - 0.369mg/kg) were generally observed to be low in the muscle of *M. macrophthalmus* throughout the study period. The Pb values were within the 2.0mg/kg recommended by WHO/FAO (2004) [19] and FEPA (2003) [14] for fish and fish products. However Mn, Cr, and Cd showed significance difference ($p<0.05$) with time compare to other metals. The variation of the above metals may not be unconnected with their high solubility and mobility as reported by Mustapha (2003) [22].

Conclusion

This study reported on some importance water quality parameters (temperature, pH, D.O., Electrical conductivity (EC) and TDS,) which were found to be within acceptable levels which will enhance fish growth in the wild, also occurrence of heavy metals (Pb, Cr, Cu, Mn, Cd, Zn) for muscles in two commercially important species *Synodontis courteti* and *Mormyrus macrophthalmus* of lower River Benue at Ibi, in Taraba. Values Pb, Cd, Cr, Cu, Mn, Zn reported for the fish species were lower compared to the safe limits for fish and its products. Lead (Pb) values were generally low during the study period for both species except in the month of October which was higher. Though Pb, Cd and Cr Values were within the safe limits recommended for fish and fisheries products. However, lead (Pb) value were observed to be higher for October indicating the need for monthly or routine evaluation of load for fish from lower River Benue. Also the need for continuous monitoring which will enable the conservation of the fish and fisheries resources of lower river Benue waters.

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