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SEASONAL VARIATIONS OF HEAVY METAL CONCENTRATIONS IN WATER AND FISH (*Malapterurus electricus*) FROM THE OBII STREAM, UFUMA, ANAMBRA STATE, NIGERIA

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Abstract
The seasonal variations of heavy metal concentrations in water and fish organs from the Obii stream, Ufuma in Orumba North, Anambra State, Nigeria, were determined. The heavy metals investigated were Cd, Pb, Ni, Cu, Zn and Fe and the fish organs used were kidney, muscle and liver. Samples were digested using standard methods and analyzed using Varian AA 240 Atomic Absorption Spectrophotometer (AAS). The mean concentrations and standard deviations of the heavy metals were determined using SPSS. Values obtained were compared with WHO and NESREA standards. Results obtained showed the water to be polluted with Pb, Ni and Cu in both seasons. The concentrations of heavy metals obtained in the fish organs indicated a certain degree of bioaccumulation. The order of bioaccumulation showed Cu>Pb>Zn>Ni>Cd>Fe in Kidney; Zn>Ni>Pb>Cd>Cu>Fe in muscle and Zn>Pb>Cd>Ni>Fe>Cu in liver. The heavy metals bio-accumulated in the fish organs in the order kidney>liver> muscle. The fish organs were polluted with Cd, Cu, and Zn. Based on the above findings, a close monitoring of metal pollution of, the Obii stream is strongly advocated, in view of possible health implications to consumers of the fish from the stream.

Introduction
In recent times, Nigerian water bodies have been subjected to degradation resulting from increase in industrialization, technological development, growing human population and oil exploration and exploitation. These factors pollute water and affect aquatic lives (Obasohan and Equavoen, 2008).

Concern over the ecological effects of the accumulation of heavy metal contaminants in the environment grows daily hence the need for its investigation. Slight changes in the concentration of these heavy metals in the water bodies above their acceptable levels whether due to natural or anthropogenic means, result in chronic stress conditions with the attendant negative effects on human health (Obasohan and Equavoen, 2008). Metals are ubiquitous in the environment as they are found in the aquatic, terrestrial and atmospheric compartments. Within each of these environments, they are present in association with water (freely dissolved metal or as organic and inorganic metal complexes), particles (sorbed, precipitated or incorporated) within a mineral phase, and air (Udombeh, 2015). Heavy metals have become the most important causes of pollution as they bio-accumulate in the tissue of crayfish and fish which are often at the top – of the aquatic food chain (Umar and Ebong, 2013). When compared with other forms of pollution, heavy metals are less visible but they have maximum effects due to their toxicity and ability to bio-accumulate in the aquatic organism (Edem *et al.,* 2008 and Ekpo *et al.,* 2013).

Heavy metal intake by fish in polluted environment depends on a variety of factors. These include exposure period, concentration of the element, pH, temperature and salinity of the aquatic environment. Jezierska and Witeska (2006) observed that the mechanism of accumulation and storage of heavy metals in aquatic animals are diverse, varying with chemical form of the metal, mode of uptake and animal species, exposure time, environmental conditions (pH, salinity, temperature, hardness) and intrinsic factors (fish ages, feeding habit). This study, therefore, investigates whether the trend of heavy metals concentration at Obii stream near a stone excavation site is sufficient enough to affect the environment as well as the health of the inhabitants of the area who use the stream for domestic purposes.

The study will show the effects of dry and rainy seasons on the heavy metal concentrations at the Obii stream. It will also give information on the extent of pollution of the stream, the order of bio-accumulation of the metals in the fish organs and in which fish organ the bio-accumulation is highest.

Materials and Method

Study area

This study was conducted in an elongated area of the Obii stream, a tributary of Mamu River in Enugwu-Abo Ufuma, Anambra State, Nigeria (latitude 6d 3' 40N- 6d 7' 40N and longitude 7d 11'E- 7d 15'40E). The coordinates of the three sampling stations (1,2,3) are 6d 6'47.055N, 7d 13'37.077E, 6d 6'24.784N, 7d 13' 4.526E, and 6d 6' 3.54N, 7d 12' 34.716E. Enugwu-Abo Ufuma is known for its wet soil and large land mass for rice cultivation using both organic and inorganic fertilizer. The climate in the area is tropical with two major seasons; the wet (April – September) and dry (October – March) seasons. Rainfall is biomodal, peaking usually in June and again in August. The Obii stream has its source from rock and it combines with another stream from another rock located near the side of a stone excavation site. The land mass is mostly rocky. Domestic and agricultural activities such as fishing, bathing, washing are carried out in the stream. Runoffs from agricultural lands, flows into the stream at different points carrying both organic and inorganic matters. Land disturbing activities such as road construction and maintenance, timber harvesting, mining, and residential and commercial activities could also have contributed to the pollution of the stream.

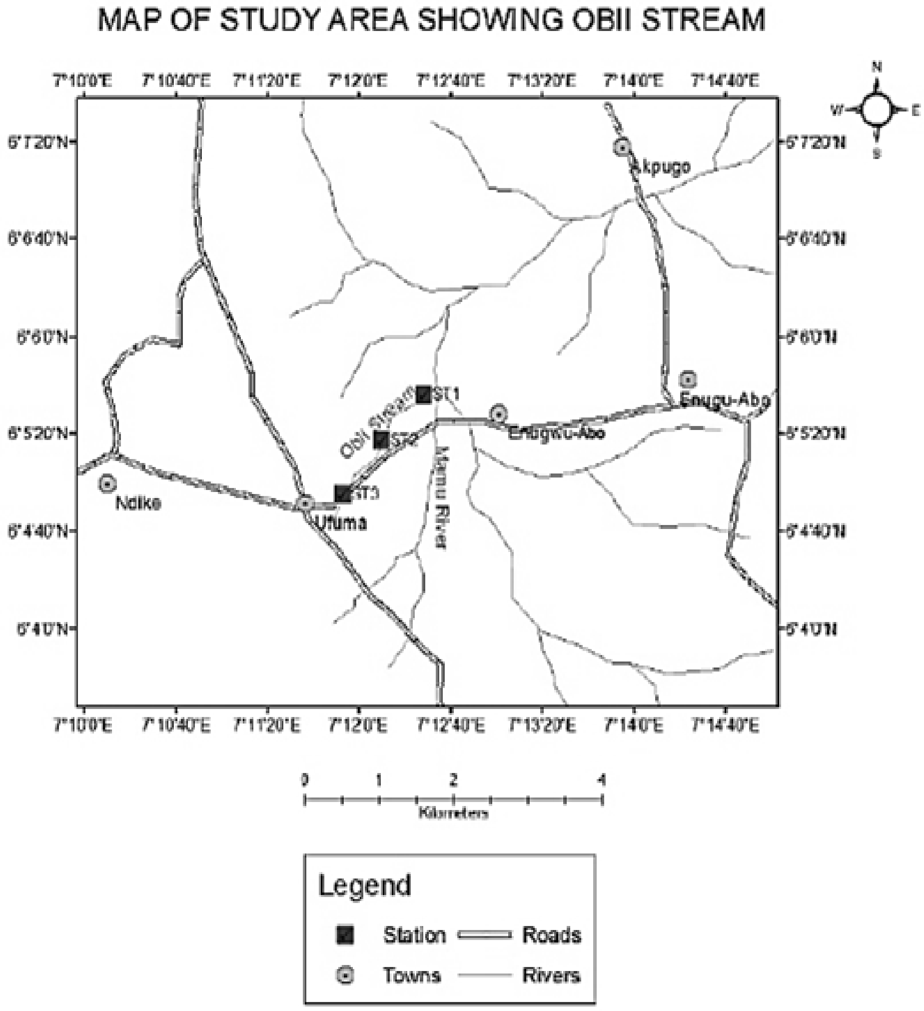


Fig 1: Map of the Obii stream showing the different sampling stations

Sample collection and treatment

Water sampling was carried out at stations 1, 2, and 3 representing downstream, midstream and upstream respectively for a period of six months. Water samples were collected randomly from six different points each at upstream, midstream and downstream using polythene bottles with caps. The bottles used for sample collections were washed with 5% nitric acid and rinsed with the water from the respective sampling sites before use. Water sampling using polythene bottles was carried out by dipping each mouth of the container against the flow direction to avoid trapping air bubbles in the bottle. The water samples were acidified immediately after collection by adding 5ml nitric acid (Analar grade) to minimize adsorption of heavy metals onto the walls of the bottles (APHA, 1989), to maintain the oxidation state of the elements present as well as to prevent microbial activities. Samples collected were properly labeled. Water sampling was done in the morning.

Fish sampling was done for six months. Two fish samples of the same kind (*Malapterurus electricus*) were caught with nylon nets of various mesh size, hooks and lines, local traps each month. They were identified by a Zoologist, Mr. Uyaeme Obinwa, a Senior Lecturer in the Department of Science Laboratory Technology, Federal Polytechnic, Oko. They were transported to the laboratory fresh and alive. The fish samples were cut using steel kitchen knife. The decapitated fish parts (liver, kidney and muscle), for each of the fishes were homogeneously mixed and placed in a porcelain crucible and then dried in an oven. The dried muscle, kidney and liver parts were homogenized using mortar and pestle. The finely homogenized fish samples were stored in a well-labeled plastic bag before digestion. During digestion, each of the finely homogenized fish samples (2.0g) was put in a crucible and burned in a furnace until it turned to ash. The ash was leached with $5cm^3$ of 6M HCl in a volumetric flask and made up to $50cm^3$ using distilled water. The digested samples were stored in plastic containers with plastic covers and labeled appropriately. They were later used for the determination of the concentrations of the heavy metals. Determination of the elements in all samples (water and fish parts) was done using Varian 240 Atomic Absorption Spectrophotometer.

Statistical Analysis

Analysis of variance (ANOVA) was used to evaluate the difference between the stations. **A hypothesis test was stated to ascertain the significant difference in the observed value compared with WHO and NESREA standards. Differences were considered significant at $P < 0.05$ and insignificant at $P > 0.05$**. The mean concentrations between groups were compared using Post hoc test (LSD). T –test was used to compare each parameter with standards (WHO and NESREA) using Microsoft Office Excel 2007.

Results and Discussions

Table 1: Cadmium concentrations in water and fish for both seasons

Samples	Seasons	Stations	Mean Conc.	WHO	P-value	NESREA	P-value
Water (mg/L)	Dry	1	0.187±0.225				
		2	0.046±0.069				
		3	0.184±0.166				
		Mean	**0.139±0.080**	0.003	0.09	0.003	0.09
	Rainy	1	0.213±0.294				
		2	0.087±0.075				
		3	0.106±0.145				
		Mean	**0.135±0.067**	0.003	0.07	0.003	0.07
Fish parts (mg/kg)	Dry	Kidney	0.103±0.084				
		Muscle	0.081±0.086				
		liver	0.131±0.184				
		Mean	**0.105±0.025**	0.50	0.00	-	-
	Rainy	Kidney	0.114±0.114				
		Muscle	0.057±0.018				
		Liver	0.159±0.158				
		Mean	**0.109±0.051**	0.50	0.00		

From Table 1, the mean cadmium level in the water samples from the three stations varied from 0.046 mg/L at midstream (station 2) to 0.187 mg/L at downstream (station 1) during the dry season and from 0.087 mg/L at midstream to 0.213 mg/L at downstream during the rainy season. In the fish samples, the mean cadmium concentration was found to be the same in the order: Liver>kidney>muscle for both seasons. Cd levels for both seasons were not significantly different (P>0.05) at the stations. These implied that the Obii stream was not contaminated with cadmium. The mean cadmium levels in the different fish parts for both seasons were all significantly different from the WHO limit of 0.50 mg/kg. Hence it may be inferred that the fish samples from the stream were polluted by cadmium.

Table 2: Lead concentrations in water and fish for both seasons

Samples	Seasons	Stations	Mean Conc.	WHO	P-value	NESREA	P-value
Water (mg/L)	Dry	1	0.197±0.196				
		2	0.045±0.031				
		3	0.329±0.233				
		Mean	**0.190±0.014**	0.01	0.00	0.01	0.00
	Rainy	1	0.093±0.104				
		2	0.038±0.062				
		3	0.004±0.007				
		Mean	**0.041±0.044**	0.01	0.34	0.01	0.34
Fish parts (mg/kg)	Dry	Kidney	1.380±1.627				
		Muscle	0.141±0.160				
		liver	0.263±0.430				
		Mean	**0.594±0.682**	2.00	0.07	0.02	0.28
	Rainy	Kidney	0.071±0.036				
		Muscle	0.115±0.092				
		Liver	0.304±0.400				
		Mean	**0.163±0.123**	2.00	0.00	0.02	0.18

From Table 2, lead level in water samples was found to be highest during the dry season and ranged from 0.045 mg/L at midstream to 0.329 mg/L at upstream (station 3). These concentrations in water samples were found to decrease during the rainy season and ranged from 0.004 mg/L at upstream to 0.093 mg/L at downstream. In the fish samples, lead concentrations were in the order: kidney>liver>muscles during the dry season but as rainy season set in, they showed a different trend: liver >muscle> kidney. Pb levels in water samples for dry season showed a significant difference from the standard. This implied the stream was polluted with Pb

Table 3: Nickel concentrations in water and fish for both seasons

Samples	Seasons	Stations	Mean Conc.	WHO	P-value	NESREA	P-value
Water (mg/L)	Dry	1	0.320±0.398				
		2	0.210±0.124				
		3	0.151±0.062				
		Mean	**0.227±0.086**	0.02	0.05	0.02	0.05
	Rainy	1	0.110±0.090				
		2	0.124±0.143				
		3	0.085±0.112				
		Mean	**0.106±0.020**	0.02	0.01	0.02	0.01
Fish parts (mg/kg)	Dry	Kidney	0.199±0.250				
		Muscle	0.047±0.081				
		liver	0.099±0.172				
		Mean	**0.115±0.077**	0.60	0.00	0.50	0.01
	Rainy	Kidney	0.600±0.715				
		Muscle	0.626±0.824				
		Liver	0.249±0.241				
		Mean	**0.492±0.211**	0.60	0.46	0.50	0.95

From Table 3, the nickel levels in the water samples ranged from 0.151 mg/L at upstream to 0.320 mg/L at downstream during the dry season and from 0.085 mg/L at upstream to 0.124 mg/L at midstream during the rainy season.

In the fish samples, nickel concentrations were found to be highest in kidney during dry season and least in the muscle. However, as rainy season set in, muscle showed the highest concentrations. The order for nickel in the fish parts during the dry and rainy seasons was kidney>liver>muscle and muscle>kidney>liver. Ni seasonal levels were significantly different from the control in water samples during the rainy season. The fish parts also showed a nickel level significantly different from WHO and NESREA during the dry season. Hence, water and fish from this stream were polluted with Ni.

From Table 4, the mean copper concentrations for the water samples ranged from 0.104 mg/L at midstream to 0.159 mg/L at downstream during the dry season and from 0.034 mg/L at upstream to 0.250 mg/L at midstream during the rainy season. Copper concentrations were only detected in the kidney (2.653 mg/kg). No copper was detected in the muscle and the liver parts of the fish sample during the dry season. However, during the rainy season, copper concentration was found to be in the order: liver>muscle>kidney. Cu seasonal levels for both water and fish samples showed a significant difference from the control in dry and rainy seasons. This implied that the water and fish samples were polluted with this heavy metal.

Table 4: Copper concentrations at different stations in water and fish for both seasons

Samples	Seasons	Stations	Mean Conc.	WHO	P-value	NESREA	P-value
Water (mg/L)	Dry	1	0.159±0.233				
		2	0.104±0.093				
		3	0.151±0.088				
		Mean	**0.138±0.030**	2.00	0.00	1.00	0.00
	Rainy	1	0.049±0.048				
		2	0.250±0.366				
		3	0.034±0.044				
		Mean	**0.111±0.121**	2.00	0.00	1.00	0.00
Fish parts (mg/kg)	Dry	Kidney	2.653±4.595				
		Muscle	BDL				
		liver	BDL				
		Mean	**-**	3.00	-	0.50	-
	Rainy	Kidney	0.060±0.054				
		Muscle	0.113±0.096				
		Liver	0.117±0.052				
		Mean	**0.097±0.032**	3.00	0.00	0.30	0.00

BDL = below detection limit

Table 5: Zinc concentrations in water and fish for both seasons

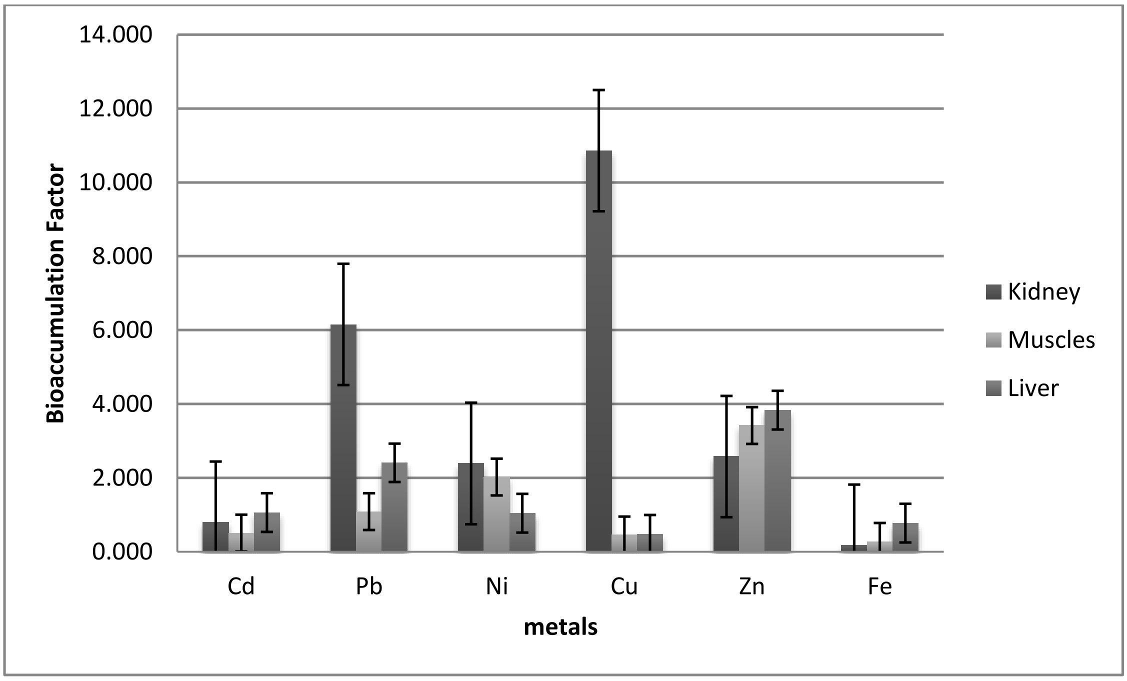
Samples	Seasons	Stations	Mean Conc.	WHO	P-value	NESREA	P-value
Water (mg/L)	Dry	1	1.641±2.061				
		2	0.647±0.639				
		3	0.211±0.261				
		Mean	**0.833±0.733**	3.00	0.03	0.02	0.19
	Rainy	1	0.837±1.304				
		2	0.387±0.519				
		3	0.100±0.107				
		Mean	**0.441±0.371**	3.00	0.00	0.02	0.18
Fish parts (mg/kg)	Dry	Kidney	1.783±1.016				
		Muscle	1.451±0.530				
		liver	1.610±0.459				
		Mean	**1.615±2.559**	10.00	0.03	75.00	0.00
	Rainy	Kidney	1.500±1.294				
		Muscle	2.904±2.000				
		Liver	3.272±4.088				
		Mean	**2.559±0.935**	10.00	0.03	75.00	0.00

From Table 5, the mean zinc values for the water samples ranged from 0.211mg/L at upstream to 1.641mg/L at downstream during the dry season and from 0.100 mg/L at upstream to 0.837 mg/L at downstream during the rainy season. It was found to be highest at downstream (1.641mg/L) during the dry season. However, in the fish samples, the zinc concentrations were found to be highest in the liver during the rainy season and lowest in the muscle during the dry season. Zn levels in fish parts for both seasons showed a significant difference since $P < 0.05$. Hence, fish from this stream was contaminated with Zn.

Table 6: Iron concentrations in water and fish for both seasons

Samples	Seasons	Stations	Mean Conc.	WHO	P-value	NESREA	P-value
Water (mg/L)	Dry	1	18.867±17.396				
		2	21.423±20.467				
		3	16.828±17.352				
		Mean	**19.039±2.302**	0.30	0.00	0.30	0.00
	Rainy	1	0.538±0.533				
		2	0.509±0.668				
		3	0.497±0.672				
		Mean	**0.515±0.021**	0.30	0.00	0.30	0.00
Fish parts (mg/kg)	Dry	Kidney	2.216±1.886				
		Muscle	1.753±0.885				
		liver	11.268±11.423				
		Mean	**5.079±5.365**	0.50	0.27	-	-
	Rainy	Kidney	1.227±1.214				
		Muscle	3.654±3.934				
		Liver	3.803±3.470				
		Mean	**2.895±1.446**	0.50	0.10	-	-

From Table 6, the concentrations of iron in the water samples for dry season ranged from 16.828 mg/L at upstream to 21.423 mg/L at midstream. It decreased and ranged from 0.497 mg/L at upstream to 0.538 mg/L at downstream during the rainy season. Its levels in the fish parts were in the order liver>muscle>kidney during the rainy season and liver>kidney>muscle during the dry season. Water sample from the stream was polluted with Iron since $P < 0.05$ for both seasons. However, in the fish parts, Fe levels were not significantly different. This implied that the fish sample may not be polluted with Fe.



The kidneys of the analyzed fish had the highest concentration of all the metals; while the muscles had the least values. This implied that muscle was the least preferred site for bioaccumulation. The low concentration of metals in muscles could be because of its low metabolic activity. The order of bioaccumulation of the heavy metals in the various fish parts showed Cu>Pb>Zn>Ni>Cd>Fe in kidney; Zn>Ni>Pb>Cd>Cu>Fe in muscle and Zn>Pb>Cd>Ni>Fe>Cu in liver. The heavy metals were found to bio-accumulate in the fish organs in the order: Kidney>Liver>muscle.

Conclusion

This work showed that heavy metal concentrations in water and fish *(M.electricus*) of the Obii stream were affected by seasons. The dry season concentrations were found to be higher than the rainy season concentrations. Cd levels in water sample showed no significant difference since $P > 0.05$. The null hypothesis was rejected for Cu and Fe levels in water sample for both seasons. The fish sample was not polluted with Fe and Pb since $P > 0.05$. The results of this finding, therefore, present a valuable baseline data on the heavy metals in the water and fish from the Obii stream, Enugwu Abo, Ufuma, Anambra state. Also metal concentrations in fish showed that considerable amounts of different metals might be deposited in fish tissues without causing mortality and that most of the accumulated heavy metals are found in kidney and liver more than in muscle. Based on the above findings, a close monitoring of metal pollution of the Obii stream is strongly advocated, in view of possible health implication to consumers of the fishes of the stream.

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