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Bioaccumulation of chromium, copper, maganese, nickel and lead in a freshwater cichlid, *hemichromis fasciatus* from Ogba River in Benin City, Nigeria

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ABSTRACT: This study assessed and monitored the extent of Cr, Cu, Mn, Ni and Pb bioaccumulation by the freshwater fish (*Hemichromis fasciatus*) from Ogba River in Benin City, Nigeria between November, 2004 and October, 2005. The effects of Dry and Rainy seasons on the extent of bioaccumulation were specifically addressed. The results showed metals bioaccumulation levels differences (except Mn) at the sample stations, which were attributed to the influence of drainage effluents influx into the river. Seasonal levels of the metals were also different at the stations. Higher dry season levels were ascribed to higher water temperatures, while rainy season high levels, could result from pronounced leaching of metals. The finding that some metal accumulation levels exceeded WHO and PEPA recommended limits in food fish, indicated that the fish of Ogba River, might not be fit for human consumption. Consequently, close monitoring of metal pollution of Ogba River is strongly recommended.

Keywords: Bioaccumulation, Metals, Fish, River, Nigeria.

Introduction

The fact that aquatic organisms can accumulate pollutants such as metals and organic compounds from water is well documented (WHO 1985; USEPA, 1991; FEPA, 2003). Bioaccumulation measurements refer to studies or methods monitoring the uptake and retention of pollutants like metals or biocides by organisms such as fish (Roux, 1991; Nussey *et al*, 2000). The accumulation of metals in an organism's body can take place, if the rate of uptake by the organism exceeds the rate of elimination (Oronsaye, 1987; Oguzie, 2003).

Pollutants enter fish through a number of routes: via skin, gills, oral consumption of water, food and non-food particles. On absorption, pollutants are transported in the blood stream to either a storage point (i.e bone) or to the liver for transformation and/or storage (Nussey, *et al*, 2006). If transferred in the Liver, pollutants are either stored there or excreted in bile or passed back to the blood for possible excretion via gills or kidneys or stored in fat (Heath, 1991). These dynamic processes, which take place simultaneously within the body of the fish, eventually determine the concentrations of the pollutants in the fish. As fish constitute an important link in the food chain, its contamination by toxic metals causes a direct threat, not only to the entire aquatic environment, but also to humans that utilize it as food.

This study focuses on the extent of bioaccumulation of Chromium (Cr),

Copper (Cu), Manganese (Mn), Nickel (Ni), and Lead (Pb) by the freshwater Cichlid;

Hemichromis fasciatus from Ogba river, Benin City, Nigeria. The effects of seasons on the accumulation levels were also addressed. The choice of the fish is its ubiquitous nature, being found in every local

freshwater body or fishery. *H. fasciatus* is also of biological importance because it is a voracious carnivore and therefore an important link in the food chain in the freshwater ecosystem. It is a regular food item on the table of the local population that consumes it whole (dry or fresh).

Materials and Methods

Study Area.

The study area is a transect spanning a distance of 5.0 kilometers of the upper reaches of the river (Fig. 1). Within the area, the river drains and receives effluents from the Benin city drainage system, a Wood treatment factory and a Rubber processing factory as well as runoffs from the surrounding agricultural fields. The climate of the area is typically tropical with dry (November – March) and wet/Rainy (April – October) seasons. Rainfall is bimodal, peaking usually in July and again in September with a brief drop in August. Minimal rainfall is in January and February, followed by the onset of heavy rainfall in April. Annual temperature ranges between 22 to 32° C, while annual humidity is between 69 and 96%.

In the area, the secondary rain forest has been subjected to extensive land clearing and farming activities, including use of herbicides and pesticides. The marginal vegetation is composed by *Commelina, Ipomea, Emilia and Sonchifolia species*. The dominant macrophytes are *Nymphes, Azolla and Ceratophyllium species* (Kolade, 1998).

Field Sampling

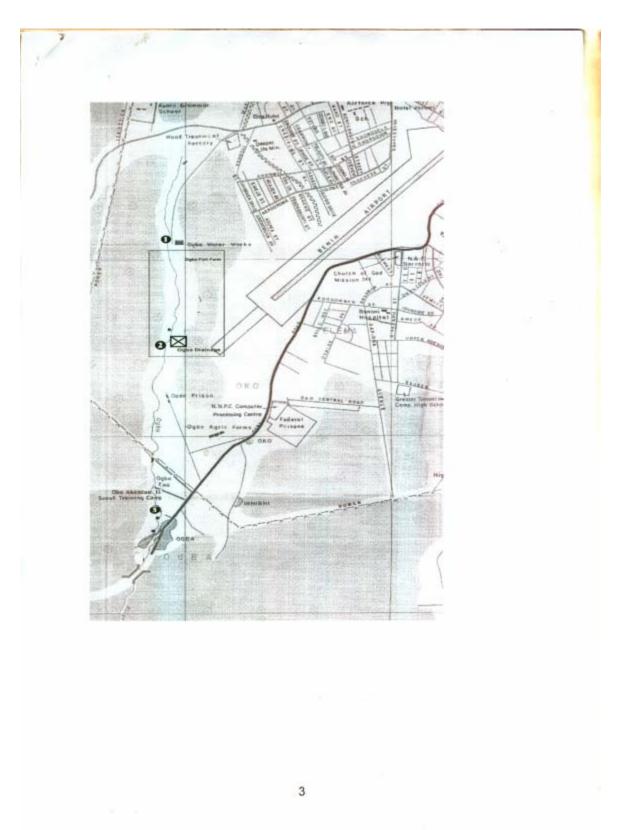
Three sample stations (1, 2 and 3) were established along the river for the purpose of the study (Fig.1). Station 1 (Control) was about 800m from the source of the river. The water of this point is relatively unpolluted. Station 2 was about 2.0km down stream, at the point where the drainage channel opened into the river, while Station 3 was another 2.0 km further downstream. Human activities such as, bathing, washing of clothes and sand excavation were more intensive at Stations 3.

Hemichromis fasciatus specimens were captured monthly at the sample stations during the study period (November, 2004 - October, 2005), using gill nets (50 - 120mm stretch mesh size), baited hooks and traps set overnight prior to collection. The fish were washed in flowing water to remove adhering dirt, transported in polythene bags to the laboratory and stored in deep freezer.

Laboratory Procedures

All previously frozen fish samples were allowed to thaw at room temperature $(27^{\circ}C)$ and then rinsed in distilled water. They were dried to constant weight at $105^{\circ}C$. The dried fish samples were then thoroughly ground to powder. One gram (1g) of each ground sample was put in a 250ml flash and 5ml of concentrated Nitric acid was added and allowed to stand for 2 hours to start the breakdown of fish protein. Then 1ml of 70% Perchloric acid was added, followed by the addition of 1ml of analar grade conc. Sulphuric acid (Sreedevi *et al*, 1992). The mixture was swirled gently and heated gently at low to medium heat on a hot plate at $100-105^{\circ}C$.

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Complete digestion was indicated by a milky coloured solution, after the disappearance of dense white chlorate fumes. The solution was allowed to cool and made up to 20ml by the addition of deionised water and aspirated into a Varian Atomic Absorption Spectrophotometer (Spectra AA-10) and the concentrations of Cr, Cu, Mn, Ni and Pb were determined. Bioaccumulation factors (Weiner and Giesy, 1979) between fish and water (BF) were calculated, using the mean metal concentrations in fish and the corresponding metal concentrations for water (Table 1) as previously reported (Obasohan *et al*, 2006).

Statistical Procedure

Tests of significance were carried out using the Analysis of Variance (ANOVA) of the Statistical Package for Social Sciences (SPSS) computer programme. Seasonal means were compared using the Duncan Multiple Range Test. The significance level throughout was P < 0.05.

Results

Bioaccumulation Levels of Metals

The concentrations of the respective metals in fish at the sample stations are presented in Table 2, while statistical comparisons of the annual mean values at the stations are in Table 3.

Cr was not detected (ND) in the months of November, January, March, April, July, August and October at Station 1. Where detected, the lowest value (0.01 mg/kg) was recorded in December and September at Station 1, while the highest value (1.16 mg/kg) was recorded in October at Station 2. Cr bio-concentration factors (BF) between fish and water based on annual values, ranged from 10 at Station 1 to 225 at Station 3 (Table 4). Annual mean levels of Cr at the stations were significantly different (P < 0.05).

Cu bioaccumulation levels ranged from a minimum of 1.93mg/kg in October at Station 1 to a maximum of 8.32mg/kg in August at Station 3. Annual mean levels of Cu were 3.82mg/kg (Station 1), 4.58 mg/kg (Station 2) and 6.28mg/kg (Station 3). The calculated bio-concentration factors (BF₁) in water were 111.71 (Station 2), 636.67 (Station 1) and 3140 (Station 3). Annual mean levels of Cu at the stations were statistically different (P< 0.05).

The highest Mn bioaccumulation value of 1.70mg/kg was recorded in August at Station 1, while the minimum value (0.49mg/kg) was recorded in June also at Station 1. Mn annual means were 0.88mg/kg (Station 1), 1.05mg/kg (Station 2) and 0.90mg/kg (Station 3). Bio-concentration factors of Mn at the stations were 880 (Station 1), 14 (Station 2) and 225 (Station 3). Statistical analysis showed that the annual mean values at the stations were not significantly different (P>0.05).

Nickel (Ni) accumulation levels were between a minimum of 0.01 mg/kg in September at Station 1 and a maximum of 0.99 mg/kg in February at Station 2. Annual mean levels were 0.06 mg/kg, 0.71 mg/kg and 0.15 mg/kg at Stations 1, 2 and 3 respectively. Ni calculated bio-concentration factors (BF) between fish and water ranged between 12.5 at Station 3 to 88.8 at Station 2 (Table 5) Annual mean levels of Ni at the stations were significantly different (P < 0.05).

Lead (Pb) was not detected in fish in the months of November, March, April, July and August at station 1, but where detected, the values ranged from 0.01mg/kg in January, May, June and September at Station 1 to 1.10mg/kg in December at Station 2. Pb annual mean values were 0.09, 0.75 and 0.64mg/kg at Stations 1, 2 and 3 respectively, while the calculated bio-concentration factors (BF) between fish and water were 90 (Station 1), 14.12 (Station 2) and 213.33 (Station 3). Statistically, annual Pb values were significantly different (P<0.05) between the stations.

Seasonal Variations of Bioaccumulation

Seasonal bioaccumulation levels of the metals in fish were also determined during the investigation (Table 3). The seasonal mean values of Cr ranged from 0.02 mg/kg in the dry and rainy seasons at Station 1 to 0.84 mg/kg in the dry season at Station 2. Seasonal mean levels of Cr on fish at the stations were statistically different (P<0.05). The differences were caused by the high concentrations of Cr in the fish at Station 2.

TABLE 1:MONTHLY AND SEASONAL VARIATIONS OF HEAVY METALS IN WATER OF OGBA RIVER, OBTAINED AT THE SAMPLESTATIONS DURING THE PERIOD NOVEMBER 2004 TO OCTOBER, 2005

Season	Month of	STATION 1				STATION 2				STATION 3						
	Survey	Cr	Mn	Cu	Ni	Pb	Cr	Mn	Cu	Ni	Pb	Cr	Mn	Cu	Ni	Pb
	Nov. 2005	0.001	0.001	0.004	0.001	0.001	0.009	0.010	0.049	0.010	0.009	0.001	0.006	0.003	0.010	0.003
	Dec. 2005	0.007	0.001	0.006	0.002	0.001	0.006	0.010	0.063	0.009	0.031	0.003	0.006	0.003	0.009	0.002
DRY	Jan. 2005	0.001	0.002	0.007	0.001	0.002	0.006	0.09	0.041	0.008	0.029	0.003	0.007	0.002	0.012	0.005
	Feb. 2005	0.001	N. D.	0.006	0.002	0.001	0.007	0.09	0.046	0.011	0.030	0.001	0.004	0.001	0.013	0.004
	Mar. 2004	N. D.	N. D.	0.004	0.001	0.001	0.009	0.07	0.039	0.010	0.026	0.003	0.003	0.002	0.009	0.002
DRY Season Me	an	0.001	0.001	0.006	0.001	0.001	0.007	0.09	0.048	0.010	0.025	0.002	0.005	0.002	0.011	0.003
	April 2005	N. D.	N. D.	0.001	0.001	N. D.	0.008	0.05	0.031	0.009	0.029	0.002	0.003	0.001	0.012	0.003
	May 2005	0.001	0.001	0.001	0.004	N. D.	0.009	0.06	0.036	0.007	0.001	0.002	0.004	0.002	0.013	0.004
	June 2005	0.001	0.001	0.006	0.002	N. D.	0.010	0.06	0.026	0.006	0.009	0.001	0.002	0.002	0.014	0.002
	July 2005	0.002	0.002	0.009	0.002	0.001	0.009	0.05	0.020	0.006	0.008	0.002	0.003	0.001	0.009	0.004
RAINY	Aug. 2005	N. D.	0.002	0.007	N. D.	N. D.	0.008	0.07	0.041	0.009	0.009	0.002	0.004	0.001	0.009	0.003
(WET)	Sept. 2005	0.001	0.001	0.009	0.001	0.001	0.008	0.07	0.044	0.006	0.010	0.002	0.005	0.002	0.014	0.004
	Oct. 2005	0.001	0.001	0.009	0.001	0.002	0.006	0.009	0.051	0.009	0.009	0.002	0.005	0.003	0.014	0.005
RAINY Season N	Aean	0.002	0.001	0.006	0.002	0.002	0.008	0.053	0.036	0.007	0.011	0.002	0.004	0.002	0.012	0.004
Annual Mean		0.001	0.001	0.006	0.002	0.001	0.008	0.075	0.041	0.008	0.017	0.002	0.004	0.002	0.012	0.003

Source: Obasohan et al, 2006.

Season	Month of	STATION 1					STATION 2				STATION 3					
	Survey	Cr	Mn	Cu	Ni	Pb	Cr	Mn	Cu	Ni	Pb	Cr	Mn	Cu	Ni	Pb
	Nov. 2004	N.D.	0.78	2.64	0.08	N. D.	1.00	1.00	4.11	1.00	0.92	0.33	0.72	6.04	0.09	0.94
	Dec. 2004	0.01	0.76	3.00	0.09	0.49	1.10	1.44	3.20	1.10	0.33	0.92	0.67	5.85	0.09	0.93
DRY	Jan. 2005	N.D.	0.93	4.22	0.04	0.01	0.62	1.12	5.21	0.62	0.73	0.61	1.10	4.74	0.19	0.92
	Feb. 2005	0.02	1.00	6.44	0.04	0.07	0.87	1.10	4.14	0.87	0.99	0.68	1.00	7.11	0.58	1.02
	Mar. 2005	N.D.	0.79	6.02	0.02	N. D.	0.61	0.89	4.72	0.61	0.79	0.49	0.93	6.57	0.19	0.52
Dry Sease	on Mean	0.02	0.85	4.46	0.05	0.19	0.84	1.11	4.28	0.75	0.83	0.61	0.88	6.06	0.23	0.87
	April 2005	N.D.	0.62	2.03	0.03	N. D.	0.56	1.02	3.39	0.41	0.51	0.01	0.71	6.69	0.08	0.17
	May 2005	0.03	0.61	4.11	0.09	0.01	0.53	0.10	3.91	0.93	0.43	0.07	0.99	7.28	0.09	0.20
	June 2005	0.02	0.49	4.46	0.06	0.01	0.61	1.02	4.59	0.51	0.61	0.10	1.00	4.92	0.02	0.27
RAINY	July 2005	N.D.	1.10	3.90	0.07	N. D.	N.D.	0.97	5.04	0.63	0.34	0.48	0.96	7.91	0.09	0.80
	Aug. 2005	N.D.	1.70	3.50	0.10	N. D.	0.54	1.00	5.83	0.71	0.99	0.70	0.87	8.32	0.05	0.01
(WET)	Sept. 2005	0.01	0.99	3.61	0.01	0.01	0.61	1.11	6.12	0.94	1.00	0.37	0.92	4.77	0.11	0.86
	Oct. 2005	N.D.	0.81	1.93	0.11	0.02	1.16	0.88	4.68	0.60	1.01	0.66	0.89	5.18	0.17	0.09
Rainy Sea	ason Mean	0.02	0.76	3.36	0.07	0.13	0.57	1.01	4.79	0.68	0.70	0.34	0.91	6.44	0.09	0.49
Annual N	Iean	0.02	0.88	3.82	0.06	0.09	0.75	1.05	4.58	0.71	0.75	0.45	0.90	6.28	0.15	0.64

TABLE 2:MONTHLY AND SEASONAL VARIATIONS OF HEAVY METALS IN FISH (Hemichromis fasciatus)FROM OGBA RIVER, OBTAINEDAT THE SAMPLE STATIONS, DURING THE PERIOD NOVEMBER, 2004 TO OCTOBER, 2005

Cu seasonal mean levels were between a minimum of 3.36 mg/kg (Dry season) at Station 1 and a maximum of 6.44 mg/kg (Rainy season) at Station 3. Cu seasonal means were not significantly different (P>0.05) at the stations.

The seasonal bioaccumulation levels of Mn were a minimum of 0.76mg/kg (Rainy season) at Station 1 and a maximum of 1.11mg/kg (Dry season) at Station 2. The differences in Mn levels at the stations were not significant (P>0.05).

Ni seasonal mean levels ranged from 0.05mg/kg (Dry season) at Station 1 to 0.75mg/kg at Station 2. Statistically, seasonal levels of Ni at the stations were not significantly different (P>0.05).

The seasonal levels of Pb ranged between a minimum of 0.13 mg/kg (Rainy season) at Station 1 and a maximum of 0.87 mg/kg (Dry season) at Station 3. Seasonal means at the stations were statistically different (P<0.05).

Seasonal bio-concentration factors (BF) of the various metals were also calculated between seasonal concentrations in fish and water and the values are as presented in Table 4.

Cr bio-concentration factors ranged between a minimum of 20 at both seasons at Stations 1 to a maximum of 305 in the dry season at Station 3. For Cu, the values were between 89.17 in the dry season at Station 1 to 3220 in the rainy season at Station 3. The BF values for Mn were a minimum of 12.33 in the season at Station 2 and a maximum of 850 in the dry season at Station 1. For Ni, the BF seasonal values ranged from 7.5 in the rainy season at Station 3 to 97.14 in the rainy season at Station 2, while for Pb, the BF seasonal values were a minimum of 33.2 in the dry season at Station 2 and a maximum of 290 in the dry season at Station 3.

Table 3: Statistical comparison of annual mean metal levels in fish at the sample station.

METALS		PROBABILITY						
-		STATIONS						
	1	2	3					
Cr	0.02	0.75	0.45	P < 0.05				
Cu	3.82	4.58	6.28	P < 0.05				
Mn	0.88	1.05	0.90	P > 0.05				
Ni	0.06	0.71	0.15	P < 0.05				
Pb	0.09	0.75	0.64	P < 0.05				

Conc. in mg/kg

Discussion

Metals Bioaccumulation in fish

Fish, on exposure to high levels of metals in an aquatic environment, absorb the bio-available metals either through gills and skin or through ingestion of contaminated water or food. Metals in fish are regulated (uptake and loss system) in the fish body to a certain level beyond which bioaccumulation of the metals takes place (CIFA, 1991; Heath, 1991).

The concentration of heavy metals in fish is related to several factors such as the food habits and foraging behaviors of the organism (Obasohan and Oronsaye, 2004); tropic status, source of a particular metal, distance of the organism from the contamination source and presence of other ions in the milieu (Giesy and Wiener, 1977); bio-magnification and/or bio-diminishing of a particular metal (Barlas, 1999); food availability, metallothioneins and other metal detoxifying proteins in the body of the animal (Deb and Fukushima, 1999); temperature, transport of metal across the membrane and the metabolic rate of the animal (Oronsaye, 1989); physical and chemical properties of the water and the seasonal changes in the

taxonomic composition of the different trophic levels affecting the concentration and accumulation of heavy metals in the body of the fish (Chen and Folt, 2000) and the adaptation capacity of the fish to heavy metal load (Shah and Altindag, 2005).

METAL	PERIOD	STATION 1	STATION 2	STATION 3
	Annual	$\frac{3.82}{0.006} = 636.67$	$\frac{4.58}{0.041} = 111.71$	$\frac{6.28}{0.002} = 3140$
Cu	Dry Season	$\frac{4.46}{0.006}$ = 743.33	$\frac{4.28}{0.048}$ = 89.17	$\frac{6.06}{0.002} = 3030$
	Rainy Season	$\frac{3.36}{0.006} = 560$	$\frac{4.79}{0.036} = 133.06$	$\frac{6.44}{0.002} = 3220$
Cr	Annual	$\frac{0.02}{0.002} = 10$	$\frac{0.75}{0.008} = 93.75$	$\frac{0.45}{0.002} = 225$
	Dry Season	$\frac{0.02}{0.001} = 20$	$\frac{0.84}{0.007} = 120$	$\frac{0.61}{0.002} = 305$
	Rainy Season	$\frac{0.02}{0.001} = 20$	$\frac{0.57}{0.008} = 71.25$	$\frac{0.34}{0.002} = 170$
	Annual	$\frac{0.88}{0.001} = 880$	$\frac{1.05}{0.075} = 14$	$\frac{0.90}{0.004} = 225$
Mn	Dry Season	$\frac{4.46}{0.006} = 850$	$\frac{1.11}{0.09}$ = 12.23	$\frac{0.88}{0.005} = 176$
	Rainy Season	$\frac{0.76}{0.001} = 760$	$\frac{1.01}{0.053}$ = 19.05	$\frac{0.91}{0.004} = 227.5$
	Annual	$\frac{0.06}{0.002} = 30$	$\frac{0.71}{0.008} = 88.8$	$\frac{0.15}{0.012} = 12.5$
Ni	Dry Season	$\frac{0.05}{0.001} = 50$	$\frac{0.75}{0.010} = 75$	$\frac{0.23}{0.011} = 20.91$
	Rainy	$\frac{0.07}{0.002} = 35$	$\frac{0.68}{0.007} = 97.14$	$\frac{0.09}{0.012} = 7.5$
	Annual	$\frac{0.09}{0.001} = 90$	$\frac{0.75}{0.017}$ = 14.12	$\frac{0.64}{0.003} = 213.33$
Pb	Dry Season	$\frac{0.19}{0.001} = 190$	$\frac{0.83}{0.025} = 33.2$	$\frac{0.87}{0.003} = 290$
	Rainy Season	$\frac{0.13}{0.002} = 65$	$\frac{0.70}{0.011}$ = 63.64	$\frac{0.49}{0.004} = 122.5$

Table 4: Metal bioconcentration factors in water at the sample stations.

The bioaccumulation levels of Cr in fish from the three stations were different (Table 3). Fish from Station 2 recorded significantly higher Cr than those from Stations 1 and 3. This is as expected as Station 2

is a point source of pollution and the fish at the station were probably exposed to higher concentration of Cr. Obasohan *et al* (2006) also reported significantly different Cr levels in water in the study stretch of Ogba River. The calculated Cr bio-concentration factor (BF) between fish and water at the respective stations, which is an indication of bioavailability of the metal, however did not correlate, as the BF was higher at Station 3. This could be attributed to various physicochemical properties of the water. Similar results have been reported for the Witbank Dam in South Africa (Nussey *et al*, 2000).

Cr bioaccumulation in fish has been reported to cause impaired respiratory and osmoregulatory functions through structural damage to gill epithelium (Heath, 1991). The values of Cr (0.02 - 0.75 mg/kg) recorded in fish in this study were above WHO and FEPA limiting standards of 0.15 mg/kg for food fish. Based on the above finding, the consumption of fish from Ogba River could presumably lead to Cr induced health hazards.

Cu accumulation levels were significantly higher (P<0.05) in fish from Stations 3 in comparison to those from Stations 1 and 2. This correlated with the calculated BF, which was highest at the station (Table 4). The higher concentration in fish at Station 3 could result from local sources. The station is subjected to more human activities such as bathing, washing of clothes, which could affect the pH of the water due to high basic chemicals in soap used while washing.

The concentrations of Cu recorded in fish in this study, ranged from 3.82 to 6.28mg/kg. These levels exceeded WHO and FEPA recommended limit (3.0mg/kg) in inland freshwater fish. The implication is that the fish from Ogba River, based on the recorded Cu concentrations, may not be suitable for consumption

Copper (Cu) is an essential element that serves as a cofactor in a number of enzyme systems for most living organisms. Cu bioaccumulation has been reported to be related to copper toxicity and the pH of water is a determinant factor in the process (Carvalho *et al*, 2004). Fresh water fish are killed by less than 1ppm copper (Simpkins and Williams, 1989). Fish gill is the primary target organ for the toxic action of copper. Impairment of the respiratory and the ion regulatory functions may occur due to structural changes and an increased ion permeability of the gill epithelia (Oronsaye and Obano, 2000) and inhibition of the Na⁺/K⁺ ATPase activity (Oronsaye, 1989). These effects result in biochemical and physiological changes in fish blood and can be an indicator of the physiological state of fish (Heath, 1991).

Mn accumulation levels in fish at the three stations were not significantly different (P>0.05). This correlated with Mn levels in water, which were also not statistically different among the stations. The implication is that Mn distribution in water at the stations is uniform and *H. fasciatus*, being a pelagic species were probably exposed to even Mn bioavailability.

Mn levels (0.88-1.05mg/kg) detected in this study were higher than the 0.19-0.44mg/kg reported in fish of River Niger (Okoronkwo, 1992) and the 0.02-0.04mg/kg reported in fish of Ikpoba River (Oguzie, 2003). The levels were, however, comparable with the 1.07mg/kg and 0.21-1.21mg/kg recorded in fish of Ikpoba River reservoir in Benin City (Fufeyin, 1998) and Warri River (Ezemonye, 1992) respectively. The bioaccumulation levels of Mn detected in fish in this study exceeded the WHO and FEPA recommended standards (0.5mg/kg) in food fish. The implication of this finding is that consumption of the fish could lead to Mn induced health hazards.

Manganese (Mn) is an essential micronutrient and does not occur naturally as a metal in aquatic ecosystems (<1.0mg/I⁻¹), but is found in various minerals and salts for example Rhodocrosite (MnCaCo3), Pyrolusite (MnO₂) and Rhodonite (MnSiO₃), with oxides being the only important Mn containing minerals mined (Garvin, 1996). Mn demonstrates some significance as a pollutant and is one of the first metals to show elevated concentrations in acidified waters (Bendell-Young and Harvey, 1986). Mn is of moderate toxicity to aquatic organisms (Nussey *et al*, 2000). Its uptake in fish has been reported to be mainly through gills and to a lesser degree through gut via food (Katz *et al*, 1972). The toxicity of Mn to fish is reported to be associated with the physicochemical form of the free divalent manganous ions (Andrew *et al*, 1976).

Fish are known to accumulate Ni in different tissues when exposed to elevated levels in their environment (Nussey *et al*, 2000; Obasohan and Oronsaye, 2004). Ni is also extensively bio-accumulated from intake of contaminated food (Singh and Ferns, 1978). In this study, Ni accumulation levels in *H. fasciatus* were found to be different (P<0.05) at the sample stations, due to the high levels in fish at Station 2. This station receives large influx of municipal wastes from Benin City through a major drainage channel. Municipal wastes from the City have been reported to contain high levels of Nickel (Oguzie, 2003; Ezemonye and Kadiri; 1998). The high levels of Ni at Station 2 coincided with the high BF value calculated for the metal at the station. This implied that the fish at Station 2 were exposed to higher bioavailability of Ni and consequently bio-accumulated higher levels of Ni at the station.

The high level of Ni (0.71mg/kg) recorded in fish (*H. fasciatus*) in this study is high, when compared to the 0.28mg/kg recorded for the same fish species in Ikpoba River in the same locality (Fufeyin, 1998). The levels are also higher than WHO and FEPA recommended limits (0.5-0.6mg/kg) in food fish, indicating that the fish of Ogba River is contaminated with nickel.

Nickel (Ni) is a natural ubiquitous element of the earth and in water. In aquatic ecosystems, Ni toxicity has been shown to very significantly with organism species, pH and water hardness (Birge and Black, 1980). Ni toxicity is generally low, but elevated levels have been reported to cause sub-lethal effects (Nussey *et al*, 2000).

Pb accumulation levels in fish recorded in this study also varied significantly among the stations. The maximum levels of Pb recorded in fish from Station 2 coincided with the maximum levels of most of the other metals except Cu, which maximum values were in fish from Station 3. The higher levels of Pb in the fish at Station 2 did not correlate with the calculated BF between fish and water, which was highest at Station 3 (Table 4). Other factors such as the physicochemical properties of the water could affect the bioavailability of the metal at the stations.

Pb levels (0.0-0.75mg/kg) recorded in this study were high when compared to the 0.13mg/kg reported for *H. fasciatus* from Warri River by Ezemonye, 1992. Oguzie (2003) also reported lower levels (0.007-0.022mg/kg) for fishes of Ikpoba River in the same locality. Pb levels recorded in this study, were, however, lower than WHO and FEPA standard limit of 2.0mg/kg for food fish. This implies that the consumption of Ogba River fish as far as Pb contamination is concerned is safe for now.

Pb exists in various oxidation states (O, I, II and IV), which are of environmental importance. The divalent from Pb (II) is reported to be the form in which most Pb is bio-accumulated by aquatic organisms (Dwarf, 1996). Pb is known to accumulate in fish tissues (bone, gills, liver, kidneys, scales), while gaseous exchange across the gills to the blood stream is reported to be the major uptake mechanism (Oguzie, 2003). Pb toxicity is dependent on life stage of fish, pH, hardness of water and presence of other organic materials (Merkini and Pozzi, 1977). In man, Pb toxicity is known to cause musculo-skeletal, renal, ocular, neurological immunological, reproductive and developmental effects (Todd *et al*, 1996; ATSAR, 1999).

Seasonal Variations

The levels of Cu, Mn and Pb (Station 1); Cr, Mn, Ni and Pb (Station 2) and Cr, Ni and Pb (Station 3) were higher in the dry season, while those of Ni (Station 1), Cu (Station 2) and Cu and Mn (Station 3) were higher in the rainy season. The higher dry season concentrations in fish could be attributed to the generally higher water temperatures associated with the dry season in the area. Higher temperatures can result in higher activity and ventilation rates in fish. High temperatures tend to lower oxygen affinity of the blood and thus increase the rate of pollutant accumulation (Grobler, 1988). A higher temperature could also lead to higher metabolic rates, which could induce more feeding and in turn result in increased metal concentration, if the metals are taken up via food chain (Nussey *et al*, 2000).

Higher metal concentrations in the rainy season as recorded in the cases of Ni (Station 1), Cu (Station 2) and Cu and Mn (Station 3) could result from pronounced leaching of metals into the river. Obasohan and Oronsaye (2004) reported increased influx of municipal effluents into the river in the rainy season, while Oguzie, 2003 reported higher metal concentrations in the municipal wastes in the Benin City locality. The increased volume of metals-laden municipal wastes entering the river in the rainy season could have increased metal bioavailability in water, which could in turn lead to increased bioaccumulation in fish. Similar reports have been reported for freshwater bodies in Burkina-faso (Etienne *et al*, 1997), Witbank Dam, South Africa (Nussey *et al*, 2000) and Olomoro water bodies, Nigeria (Idodo-Umeh, 2002).

Conclusion

The levels of the heavy metals (except Mn) in the fish of Ogba River were different at the sample stations. Station 2 which is a point source of drainage effluents in the river recorded higher metal pollutant levels and implicated municipal effluents influx at the station. The higher metal concentrations during this study did not always correlate with the higher metal concentrations in the water and can probably be attributed to various physicochemical properties of the water. Significantly higher dry season levels in comparison to the rainy season levels were ascribed to probable higher metal bioaccumulation due to increased metabolic rates in fish induced by higher water temperatures associated with the dry season.

The finding in the study that the bioaccumulation levels of some of the metals, exceeded WHO and FEPA recommended limits in food fish is worrisome and indicated that the fish of Ogba River might not be suitable for human consumption. Close monitoring of metal contamination levels involving bio-monitoring of field data and controlled experimental exposure conditions is therefore strongly recommended

References

- Andrew R.W. *et al* (1976): Toxicity to Biota of metal forms in natural waters. Inter. Joint Commission, Great Lakes Research, Windsor, Ontario. 187 193.
- ATSDR (Toxicological Profile for Lead) (1999): US Department of Health and Human Services, Public Health Service 205-93-0606.
- Barlas, N (1999): A pilot study of heavy metal concentration in various environments and fishes in the upper Sakaryia River basin, Turkey. *Environ. Toxicol.* 14:367-373.
- Bendell-Young, L.I. and Harvey, H.H. (1986): Uptake and tissue distribution of manganese in the white sucker (*Catostomus commersoni*) under conditions of low pH. *Hydrobiol.* **113**. 117-125.
- Birge, W.S and Black, J.A (1980): Aquatic toxicology of nickel. In J.O. Nriagu (ed) Nickel in Environment. John Wiley and Sons Inc. USA 349-266
- Carvalho, C.S. *et al* (2004): Hepatic metallothionein in a teleost (*Prochilodus scrofa*) exposed to copper at pH 4.5 and 8.0. *Comp. Biochem. Physiol.* **137** (*B*): 225-234.
- Chen, C. Y; Folt, C.L. (2000): Bioaccumulation and diminution of arsenic and lead in a freshwater good web. *Environ. Sci. Technol.* **34**: 3878-3884.
- CIFA (Committee for Inland Fisheries of Africa) (1991): Working Party on Pollution and Fisheries, Accra, Ghana, 25-29 Nov. 1991. FAO Fisheries Report **471**: 7-25
- Deb, S.C.; and Fukushima, T. (1999): Metals in aquatic ecosystems: Mechanism of uptake, accumulation and release. *Int. J. Environ. Stud.* 56. 385-492.
- DWAF (Department of Water Affairs and Forestry) (1996): South African Water Quality Guidelines (2nd Ed.) Vol. 7: *Aquatic Ecosystems*. 159pp.
- Etienne, B. *et al* (1997): Physical chemical and biological characteristics of reservoirs in Burkina Faso. Tech. Centre for Agric. and Rural Co-operation, ACP-EU. 28-42.
- Ezemonye, L.I. and Kadiri, M.O (1998): Find Report of Studies on Ikpoba and Ogba Rivers in Benin City, University of Benin, Benin City, Nigeria. 120pp.
- Ezemonye, L.I. (1992): Heavy metals concentrations in Water, Sediment and elected fish fauna in Warri River and its tributaries.
- Ph.D. Thesis, University of Benin, Benin City. 199pp.
- F.E.P.A.(Federal Environmental Protection Agency). (2003); Guidelines and Standards for Environmental Pollution Control in Nigeria. 238pp.
- Fufeyin,T.P. (1998): Heavy metal levels in some dominant fish of Ikpoba Reservoir in Benin City, Nigeria. *Environmental Review* **2**:61-69.
- Garvin, R.M. (1998): Occurrence of metals in water. An overview: Water SA 22(1). 7-18
- Giesy, J.P and Weiner, J.G. (1977): Frequency distribution of trace metals concentrations in five freshwater fishes. *Trans. Am. Fish. Soc.* **106**. 393-403.
- Grobler, E (19988). Die Effek van Atrasien, Sink en Yster op die Hematogie en Suurstofverbruik van *Tilapia sparmanii* (Cichlidae) M.Sc. Thesis, Rand Afr. University, South Africa.
- Heath, A.G. (1991): Water Pollution and Fish Physiology. Lewis Publishers. Boca Raton, Florida, USA 359pp.
- Idodo-Umeh, G. (2002): Polution assessments of Olomoro water bodies using physical, chemical and biological indices. Ph.D. Thesis, University of Benin, Benin City, Nigeria 485pp.
- Katz, M. et al (1972): Effects on freshwater fish. J. W. P.CO.F. 44 (6): 1226-1250.
- Kolade, R. O. (1998): Bioaccumulation of heavy metals by shrimps (*Macrobracium vollenhovenii*) in a transect of Ogba River in Benin City. M.Sc. Thesis, University of Benin, Benin City, Nigeria. 79pp.
- Merlini, M. and Pozzi, G. (1977): Lead and freshwater fishes. Part 2 iconic lead accumulation. *Environ Pollut*. **13**:119-126.
- Nussey, G. et al (2000): Bioaccumulation of Chromium, Manganese, Nickel and Lead in the Tissues of the moggel, Labeo umbratus (Cyprinidae), from Witbank Dam, Mpumalanga.S Africa. Water SA. Vol. 26 (2): 269-284.
- Obasohan, E.E. and Oronsaye, J.A.O. (2004): Bioaccumulation of heavy metals by some cichlids from Ogba River, Benin City, Nigeria. Nigerian Annals of Natural Sciences Vol. 5 (2) 11 – 27.
- Obasahan, E. E. et al (2006): Heavy metals concentrations in Malapterurus electricus and Chrysichthys nigrodigitatus from Ogba River in Benin City, Nigeria. African Journal of Biotechnology, Vol. 5 (10). 974-962.
- Oguzie, F.A (2003): Heavy metals in fish, water and effluents of lower, Ikpoba River in Benin City, Nigeria. *Pakistan Journal of Science and Industrial Research*, Vol. **46** (3) 156 160

- Oronsaye, J.A.O. (2000): The uptake and loss of dissolved copper by *Clarias angullaris* fingerling. *Pakistan Journal of Science and Industrial Research, Vol.* **43** (6) 359 362.
- Oronsaye, J.A.O. (1989): Historical changes in the kidneys and the gills of stickleback (*Gesterosteus aculeatus*) exposed to cadmium. *Ecotoxicol and Environ. Safety* **17**:279-290
- Oronsaye, J.A.O. (1987): Uptake and loss of absorbed cadmium by the stickleback *Gasterosteus aculeatus* (L) *Ecotoxicol and Environ. Safety* **14**. 88-96.
- Roux, D (1994): Role of Biological monitoring in water quality assessment and a case study on the Crocodile River Eastern Transvaal. M.Sc. Thesis Rand Afr. University, South Africa.
- Shah, S.L. and Attinag, A. (2005). Effects of heavy metals accumulation on the 96-h Lc50 values in Tench (*Tinca tinca L.*) 1758. *Turk. J. Vet. Anim. Sci.* 29: 139-144.
- Simpkins, J. and Willaims, J. I. (1989): Advanced Biology (3rd Edition). English Language Book Society / Unwin Hyman. 760pp.
- Sreedevi, P. et al (1992): Bioaccumulation of nickel in the organs of the freshwater fish Cyrino carpio and the freshwater mussel Lamelliolens marginalis, under lethal and sublethal nickel stress. Chemisphere. 24 (1): 29-36.
- Singh, S.M. and Ferns, P. (1978): Accumulation fo heavy metals in Rainbow trout Salmo gairdneri maintained on a Chet containing activated sewage sludge. J.fish. Biol. 13. 2277-2286.
- Todd, A.C. et al (1996): Long-term effects of Biosolids Applications on Heavy metals Bioavailability in Agricultural Soils. J. Environmental Quality 26:966-974.
- USEPA (United States Environmental Protection Agency (1991): Assessment and Control of Bioconcentratable contaminants in surface waters. Office of Health and Environmental Assessment, USEPA. Cincinnati, Ohio.
- Weiner, J.G and Gresy J.G (1979): Concentrates of Cd, Cu, Mn, Pb and Zn in fishes in a highly organic soft water pond J. fish. Res. Bd. Can. 36:270-279.
- WHO (World Health Organization) (1985): Guidelines for drinking water quality.Vol. 1. Recommendations, W.H.O. Geneva. 130pp.