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BIOACCUMULATION OF HEAVY METALS IN THE CATFISH *CHRYSICTHYS NIGRODIGITATUS* FROM TAYLOR CREEK, SOUTHERN NIGERIA

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ABSTRACT

The discharge of liquid effluents either untreated or with only primary treatment into Etelebou Creek, a tributary of Taylor Creek has led to the extensive contamination of Taylor Creek by heavy metals. The catfish species, *C. nigrodigitatus* and other environmental segments were collected from five sites along Taylor Creek, southern Nigeria, and some metals determined by flame atomic absorption spectrophotometry. The concentration levels of the metals in *C. nigrodigitatus* were higher than values reported in the literature for fresh fish and may lead to a higher risk and harmful effects. The bivariate regression models relating metals in *C. nigrodigitatus* and metals in the surface waters were significant ($R^2 \geq 0.7134$). The Log (bio-concentration factors or BCF) of Cr and Zn in *C. nigrodigitatus* were the highest, whereas Ni was the lowest. The ecological distribution of the log (BCF) values was, for all the heavy metals, moderately stable over the Creek. All log-transformed biomagnification factors (BMF) in the Creek were positive, which indicates that the metal concentration was higher in *C. nigrodigitatus* than in suspended particulate matter (SPM). The absolute log (BMF) values of heavy metals can therefore be ranked in order of decreasing magnitude: Fe (4.06) > Zn (2.87) > Mn (2.59) > Cr (1.95) > Pb (1.90) > Ni (1.82) > Cd (1.55). This sequence indicates that toxic metals such as Cd, Cr and Pb are undergoing significant bio-reduction from SPM to *C. nigrodigitatus.* The degree of correlation between the metals was different in *C. nigrodigitatus*, which suggests that the sources of the metals, polluting Taylor Creek were diverse.

KEYWORDS**:** Bioaccumulation; heavy metals; catfish; Taylor Creek; Southern Nigeria, suspended particulate matter.

INTRODUCTION

Catfishes (order Siluriformes) are a very diverse group of bony fishes. Despite their common name, not all catfish have prominent barbels; which define a fish as being in the order of the Siluriformes (Bruton, 1996). Catfishes are of considerable commercial importance; many of the larger species are fished for food. Most catfish are benthic in nature, meaning they normally associate with the bottom of the water column (i.e. the sediments). However, a variety of other lifestyles are also represented among the catfishes. A few species are pelagic in nature (Bruton, 1996).

The pollution of aquatic ecosystems by heavy metals is a significant problem (Rayms-Keller *et al.*, 1998), as heavy metals constitute some of the most hazardous substances that can bio-accumulate (Tarifeno-Silva *et al*., 1982). Metals that are deposited in the aquatic environment may accumulate in the food chain and cause ecological damage while also posing a risk to human health (Grimanis *et al*., 1978; Adams *et al*., 1992). Factors known to influence metal concentrations and accretion in catfishes include metal bioavailability, season of sampling, and hydrodynamics of the environment, size, sex, and changes in tissue composition and reproductive cycle (Risch, 1986). Seasonal variations have been related to a great extent to seasonal changes in flesh weight during the development of gonadic tissues (Risch, 1986).

Furthermore, the only perceptible activity in the area is oil industry activities. The Etelebou Flow Station, which is located on second order distributaries, discharges liquid effluents (either untreated or with only primary treatment) into Etelebou Creek, a tributary of Taylor Creek. Thus, Taylor Creek is a receptor of a highly polluted creek (Okafor and Opuene, 2007).

Taylor Creek has been the source for fish, prawns and molluscs to the residents living along the stem of the Creek. It is suspected that fishes from Taylor Creek, particularly at the convergence of Etelebou and Taylor Creeks will be highly contaminated with heavy metals, hence endangering the health of those who consume such fishes. To date, information regarding the accumulation of heavy metals in freshwater catfishes of Taylor Creek and its effects is very limited. However, the accumulation of heavy metals in fishes has been studied by different researchers (Nguyen *et al.*, 2005; Hung *et al*., 2001; Liu *et al.*, 2001; Agbozu *et al.*, 2007).

The objectives of this study were to screen the catfish *C. nigrodigitatus* from Taylor Creek for heavy metal content/source, and verify its suitability as source of food and to determine the potential of using the catfish species as bio-indicator and bio-monitoring subject for heavy metal pollution in freshwater ecosystems.

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MATERIALS AND METHODS

Study area

The study area, comprising of five sampling sites, had earlier been described (Okafor and Opuene, 2006). The study area stretched from Agbia/Nedugo to Polaku along Taylor Creek (Fig. 1). The entire stretch from Agbia/Nedugo to Polaku is about 16km and lies between longitude 006°17' to 006°21' E and latitude 05°01' to 05°05' N respectively.

Sample collection

Sampling of surface waters were carried out monthly for the period January to December 2006 from the sampling sites. Surface water samples were collected with nitric acid pre-rinsed 1litre plastic containers. After collection, the samples were placed in cooler boxes with ice bags whilst being transported to the laboratory and kept at about 4°C before analysis.

Samples of the catfish *C. nigrodigitatus* were collected with pond nets and local fishing baskets each month from January to December 2006 from the sampling sites. All samples of *C. nigrodigitatus* were washed three times: in the freshwater, in distilled water and in freshwater again. The samples were then scrubbed in freshwater using a nylon brush, rinsed in distilled water and rinsed in freshwater again to remove epifauna.

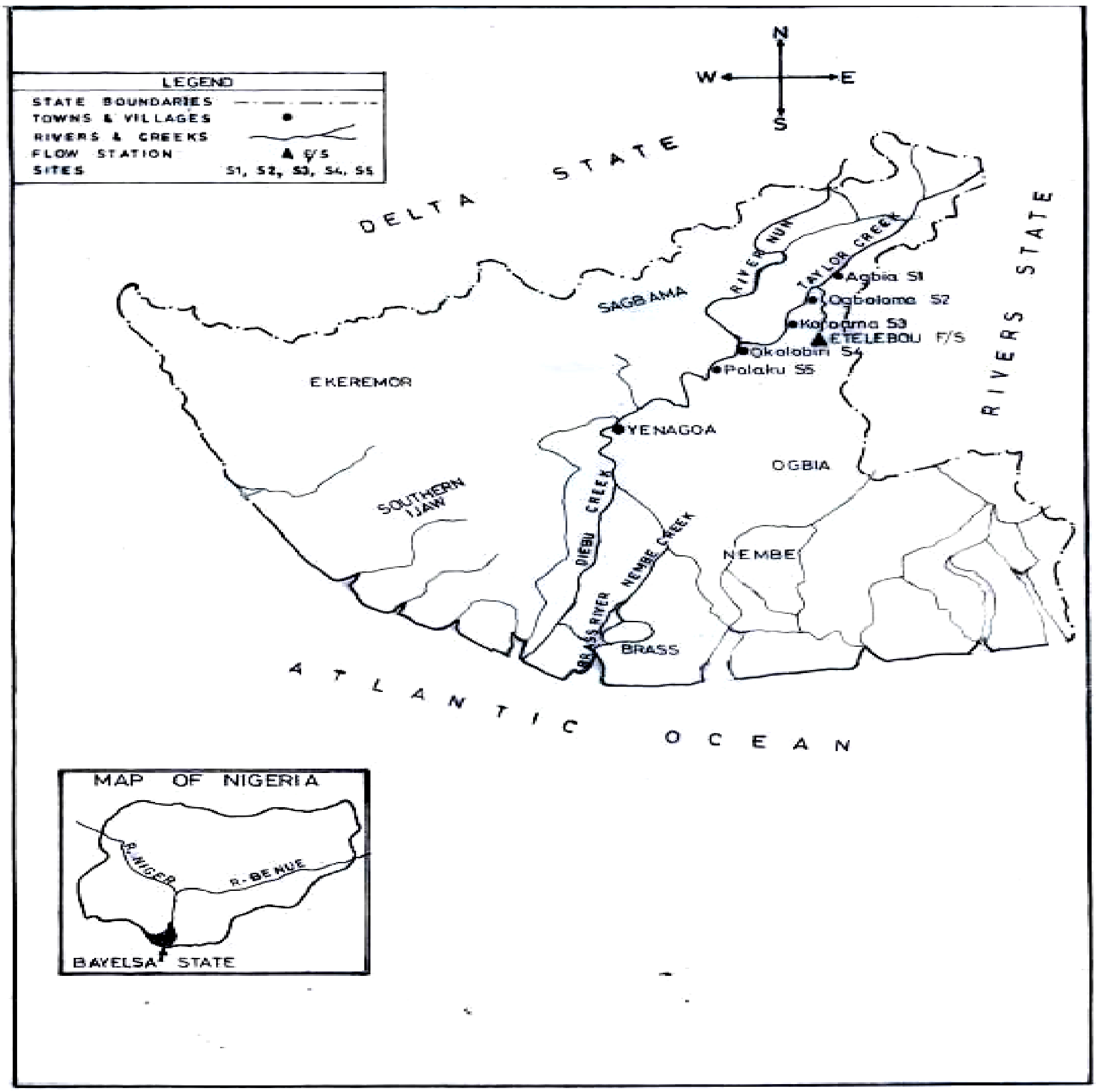

Fig. 1: Study Location and Sampling Site Map

Sample treatment and analysis

An aliquot of each water sample, after filtration with the 45 μm Whatman filter paper, was acidified and pre-concentrated. The non-filtered portions and residues were digested independently with a mixture of 10mL of conc. nitric acid and 2mL of conc. perchloric acid respectively.

The treatment of *C. nigrodigitatus* samples was based on established procedure (Okafor and Opuene, 2006). Before analysis, the catfishes were dehydrated to a constant weight using an oven at 65^{O}C for 20 hours and individual whole fish pulverized to a uniform particle size. Two grams (2g) of pulverized weight were weighed using a high precision micro-scale and put in a digestion flask and digested with a mixture of 10mL of conc. nitric acid and 2mL of conc. perchloric acid. The contents of the flask was, for each case, digested gently and slowly, by heating in a water bath until the contents got to near dryness. It was then set aside to cool. The digest was filtered into a 50mL volumetric flask, and made up to mark with distilled water.

Following acid digestion, all samples were analysed for 7 elements: Cd, Cr, Pb, Ni, Mn, Zn and Fe by flame atomic absorption spectrophotometry using Buck Scientific Model 200A Spectrophotometer, equipped with a high sensitivity nebulizer. Calibration of Buck Scientific Model 200A Spectrophotometer was performed before every run by successive dilution of a 100mgL^{-1} Multi-Element Instrument Calibration Standard solution (Fisher Scientific) that was in a range covering the concentration levels in the analysed samples. For each batch of elemental analysis, intra-run quality insurance standard (1mgL^{-1}, Multi-Element Standard Solution, Fisher Scientific) was checked for reading variation and precision of every 10 samples. Internal blanks were used to assess any background contamination originating from sample manipulation and preparation. Blanks were processed exactly as respective regular samples (Okafor and Opuene, 2006).

The accuracy of sample manipulation for the heavy metals was checked using samples of CASS-4 (seawater) and DOLT-3 (organism tissue) Matrix Certified Reference Materials with known concentration for certain metals and were found to be ≥89% for Cd, Fe, Pb, Ni, and Zn (Cantillo and Calder, 1990).

Statistical analysis

The relationship between inter-metal correlations in *C. nigrodigitatus* was tested using Pearson Product Moment Correlation Coefficient. Predictive regression models were developed for the indicator variables (catfishes) and the surface waters of the aquatic ecosystem for the heavy metals. All statistical analyses were done using Analysis Toolpak Software, with significance based on an α of 0.05 (Zar, 1996).

Bio-accumulation factors

Relationships between the dissolved phase, particulate phase or suspended particulate matter (SPM) and catfish are discussed via the corresponding bio-concentration factor (BCF). Bio-magnification, the enrichment (positive value) or depletion (negative value) of the heavy metals at a higher trophic level versus food was also calculated. The BCF and BMF are metal- and organism-dependent (Okafor and Opuene, 2006). BCF represents the uptake of metals into an organism from the surrounding water alone. The accumulation process involves the biological sequestering of metals that enter the organism through respiration and epidermal (skin) contact with the metals. The sequestering results in the organism having a higher concentration of the metals than the concentration in the organism's surrounding environment (Okafor and Opuene, 2006). Furthermore, bio-magnification factor (BMF) refers to bioaccumulation of metals up the food chain by transfer of the metals in smaller organisms that are food for larger organisms in the chain. It generally refers to the sequence of processes that result in higher concentrations in organisms at higher trophic levels (Grimanis *et al*., 1978; Adams *et al.*, 1992). These processes result in an organism having higher concentrations of the metals than is present in the organism's food. BCF and BMF (Okafor and Opuene, 2006) were therefore calculated as follows:

$$BCF = \frac{[\text{Concentration of metal in } C.\ nigrodigitatus]\ (\mu g g^{-1})}{[\text{Concentration metal in dissolved phase}]\ (\mu g mL^{-1})}$$

$$BMF = \frac{[\text{Concentration of metal in } C.\ nigrodigitatus]\ (\mu g g^{-1})}{[\text{Concentration metal in SPM}]\ (\mu g g^{-1})}$$

Metal Pollution Index

To compare the total content of metals at the different sampling sites in *C. nigrodigitatus*, the Metal Pollution Index (MPI) was used. The MPI was obtained with the equation (AMA, 1992; Usero *et al.*, 1996):

$$MPI = (Cf_1 \times Cf_2 \ldots\ldots\ldots. Cf_K)^{1/n}$$

where,

Cf_1= concentration of metal 1 in *C. nigrodigitatus*

Cf_2 = concentration of metal 2 in *C. nigrodigitatus*

Cf_k = concentration of the kth metal in *C. nigrodigitatus*

n = number of selected metals studied

RESULTS AND DISCUSSION

Concentration levels of heavy metals in *C. nigrodigitatus*, the dissolved phase, SPM and surface waters are presented in Table 1 and Fig. 1 respectively. The metals, Fe and Zn were the most abundant in *C. nigrodigitatus*. The highest concentration of Zn in *C. nigrodigitatus* was found at site 3, which corresponds to one of the highest MPIs obtained in this study (Fig. 2). Besides, Zn was found to be higher than the concentration levels in fishes of the Rivers of South Carolina (Koli *et al*., 1978; Nwaedozie, 1998). While the highest Cd level was found at site 4, the highest Fe was at site 1, which may be attributed to the hydrodynamics of the environment. However, the lowest MPI was obtained for site 1. The maximum Mn concentration was found at site 5 that corresponds to the highest MPI (Fig. 2). Meanwhile, the highest concentration levels for the other metals for the sites were: Cr (site 4), Co (site 3), Pb (site3) and Ni (site 5), which are higher than mean metal concentrations in fishes of inland waters (Biney, 1991).

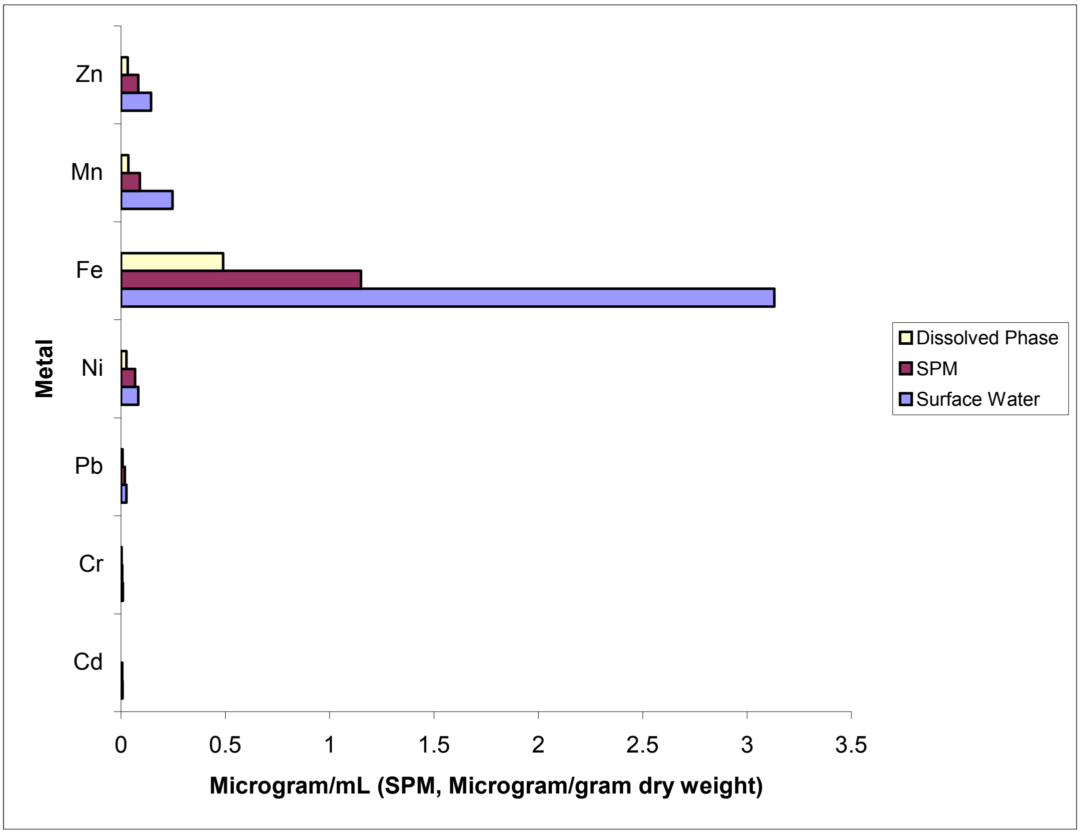

Fig. 1: Mean levels of heavy metals in SPM, dissolved phase and the Surface Waters

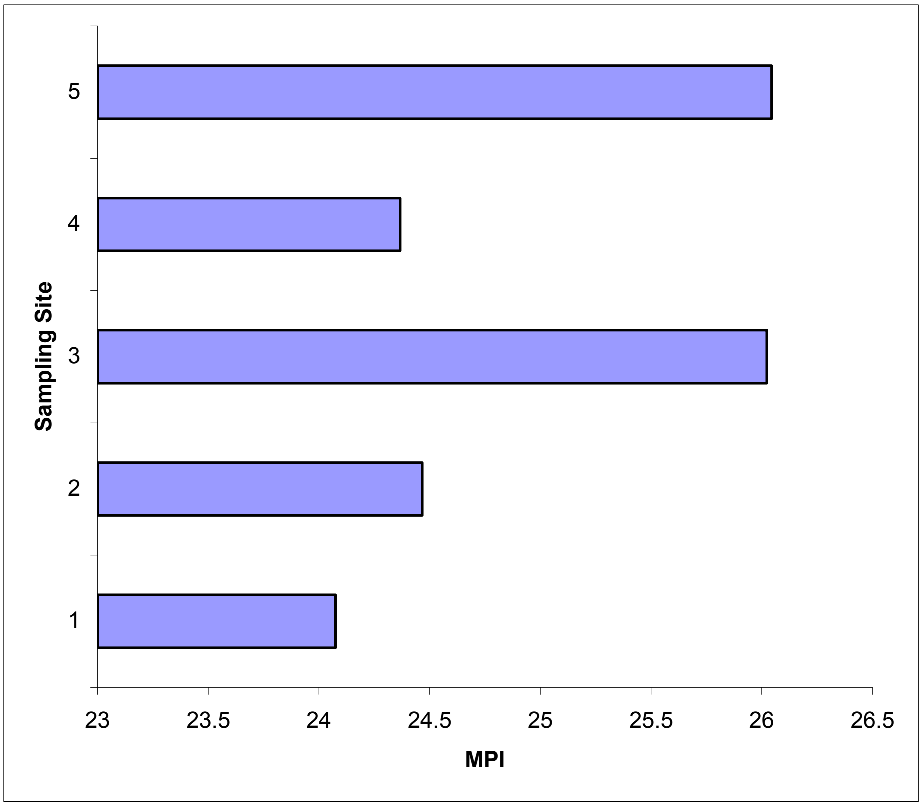

Fig. 2: Metal Pollution Index for the Sampling Sites

Table 1: Ranges and Mean of Heavy Metals in *C. nigrodigitatus* from Taylor Creek

Metal	Sampling Sites				
	1	2	3	4	5
Cd	12.200 -1.100 (3.840±2.540)	11.750-2.100 (3.890 ± 2.350)	11.350-2.000 (4.010 ± 2.410)	11.750-1.800 (3.980 ± 2.450)	11.700-1.600 (4.052 ± 2.62)
Cr	38.40-0.500 (9.620 ±12.68)	38.80-0.500 (10.720 ± 13.68)	40.00-0.500 (10.150 ±14.24)	40.40-0.500 (10.040 ± 14.46)	39.20-0.500 (9.990 ± 13.98)
Pb	32.50-3.100 (8.670± 7.09)	27.00-1.470 (8.650 ± 5.64)	27.00-3.100 (10.460 ± 5.88)	21.50-1.000 (8.860 ± 4.53)	21.50-1.000 (7.990 ± 4.83)
Ni	25.00-2.100 (7.320± 6.40)	25.00-2.100 (7.340 ± 6.34)	26.50-2.100 (7.470 ± 7.32)	26.50-1.700 (7.620 ± 6.92)	27.50-2.100 (7.610 ± 7.59)
Fe	1900.50-183.2 (1289.8±700.2)	1906.50-188.4 (1287.6 ± 700.1)	1881.50-192.0 (1295.1 ± 701.7)	1910.50-188.0 (1295.0 ± 702.6)	1880.50-201.6 (1280.6 ± 705.2)
Mn	142.50-17.00 (37.16± 28.59)	291.30-17.00 (45.230 ± 62.78)	76.80-17.00 (42.410 ± 28.33)	248.20-17.200 (59.680 ± 64.34)	150.10-22.400 (39.940 ± 31.39)
Zn	293.60-24.26 (81.150±104.7)	304.00-24.70 (79.870 ± 107.6)	310.00-24.55 (86.230 ± 107.8)	304.00-23.67 (83.560 ± 104.9)	305.00-23.08 (84.800 ± 109.5)

Furthermore, the surface waters, dissolved phase, and SPM that were also screened for similar metals had elevated values (FEPA, 1991). Whereas, it is apparent that the concentration levels of the metals in the surface waters may be due to catchments in-washings (Ibok *et al.*, 1989), and oil industry activities (Nwadinigwe and Nwaorgu, 1999), the results of the bivariate regression statistics show that the metals in *C. nigrodigitatus* and metals in the surface waters are significantly correlated ($R^2 \geq 0.7134$), which indicates that the metals are bio-accumulated from the dissolved phase and SPM respectively (Table 2).

Table 2: Predictive model summary of criterion and predictor variable

Linear Regression Model	R^2
Cd in *C. nigrodigitatus* = .0027Cd in Surface Water + 3.8163	.9656
Cr in *C. nigrodigitatus* = .01184 Cr in Surface Water + 9.5102	.8852
Pb in *C. nigrodigitatus* = .000257 Pb in Surface Water + 7.2574	.7844
Ni in *C. nigrodigitatus* = .00043 Ni in Surface Water + 7.2574	.9236
Mn in *C. nigrodigitatus* = .2517 Mn in Surface Water + 32.299	.8133
Fe in *C. nigrodigitatus* = .2834 Fe in Surface Water + 688.24	.7134
Zn in *C. nigrodigitatus* = .0819Zn in Surface Water + 79.03	.9879

The absolute value of R^2 at § =0.05 indicates the correlation between the observed and predicted values of the dependent variable, with larger absolute values indicating stronger relationship.

The availability of metals in the dissolved phase and SPM provides an opportunity for *C. nigrodigitatus* to biomagnify/remobilize them through the food chain, which is considered to be one of the principal risks to fish consumers. As a result, the efficiency of bioaccumulation was studied by assessing Bio-concentration Factor (BCF) and Bio-magnification Factor (BMF) (Nguyen *et al.*, 2005).

Log (BCF) values of Fe and Zn in *C. nigrodigitatus* were the highest, whereas the lowest was Cd (Table 3). The ecological distribution of the log (BCF) values was, for all trace metals, moderately stable over the creek. Furthermore, Table 3 illustrates the absolute values of log (BCF) and log (BMF) of *C. nigrodigitatus* in the creek. All log-transformed BMF values in the creek are positive, which indicates that the metal concentration was larger in *C. nigrodigitatus* than in SPM. Conversely, Nguyen *et al.* (2005) reported that all log-transformed BMF values in Lake Balaton are negative, which means that the metal concentration was larger in suspended matter than in the organism studied. For Ni, positive but low values (log (BMF)=1.68) reveal the degree of bio-magnification of this metal across the Creek.

Table 3: Absolute values of log (BCF) and log (BMF)

Trace metal	log (BCF)	log (BMF)
Cd	1.40	1.55
Cr	1.81	1.95
Fe	3.92	4.06
Pb	1.75	1.90
Mn	2.45	2.59
Zn	2.73	2.87
Ni	1.68	1.82

The absolute log (BMF) values of heavy metals in Taylor Creek can therefore be ranked in order of decreasing magnitude: Fe (4.06) > Zn (2.87) > Mn (2.59) > Cr (1.95) > Pb (1.90) > Ni (1.82) > Cd (1.55). This sequence indicates that toxic metals such as Cd, Cr and Zn are undergoing significant bio-reduction from the SPM to *C. nigrodigitatus* (Nguyen *et al.*, 2005).

For the levels of Cd, Cr, Co, Fe, Pb, Ni, Mn and Zn, inter-metal correlations appear to be different in *C. nigrodigitatus* (Table 4). Significant inter-metal relationship exists between Cd-Zn (r=0.86), Cd-Ni (r=0.86), Co-Fe(r=0.78), Co-Mn (r=0.83), Pb-Fe (r=0.77) and considerable correlations between Ni-Zn (r=0.69), Ni-Mn (r=0.53), and Fe-Mn (r=0.51) for *C. nigrodigitatus*, which are comparable to correlation coefficients reported elsewhere (Hung *et al.*, 2001; Liu *et al.*, 2001). This, thus, implies that the sources of the metals, polluting Taylor Creek, were not from the same source.

Table 4: Pearson product moment correlation coefficients between metal levels in *C. nigrodigitatus*

	Cd	Cr	Pb	Co	Ni	Fe	Mn	Zn
Cd	1							
Cr	0.04	1						
Pb	0.122	0.0926	1					
Ni	0.863	-0.145	-0.127	0.058	1			
Fe	-0.156	-0.041	0.7701	0.776	-0.06	1		
Mn	0.202	0.2469	0.0538	0.827	0.53	0.514	1	
Zn	0.86	-0.272	0.4776	-0.226	0.69	0.167	0.05	1

The levels of the heavy metals found in *C. nigrodigitatus* were also compared to the monthly fish consumption limits for carcinogenic/non-carcinogenic health end-points of US EPA (2000), as there appeared to be no sources within the Nigerian context for heavy metal guidelines in fish. The US EPA (2000) monthly fish consumption limits for carcinogenic/non-carcinogenic health end-points lists, by chemical contaminant, the maximum number of fishmeals per unit time (monthly) that may be safely consumed. Therefore, the concentration levels of heavy metals in *C. nigrodigitatus* from the aquatic environment had shown that the Risk Based Consumption Limits, based on an adult body weight of 70kg and 16 Fish Meals/Month were exceeded. Although fish species chronically exposed to polluted environments may acquire compensatory adaptive mechanisms (Bruton, 1996), the catfish *C. nigrodigitatus* from Taylor Creek is not suitable for human consumption.

CONCLUSION

The concentration levels of heavy metals in the catfish *C. nigrodigitatus* from Taylor Creek indicates that the catfish is a good bio-accumulator of heavy metals and would not be suitable for human consumption. In addition, *C. nigrodigitatus* may well serve as an excellent bio-monitoring subject for heavy metal pollution in freshwater ecosystems.

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