2015 | Vol. 1 | Issue 1 | Pg. 1 - 8

Ewemen Journal of Analytical & Environmental Chemistry

Available online at http://ewemen.com/category/ejaec/

Full Length Research

HEAVY METALS LEVELS IN TILAPIA SAMPLES FROM NORTH CENTRAL NIGERIAN RIVERS

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Received 30 September, 2015
Revised on the 3 October, 2015
Accepted 6 October, 2015

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ABSTRACT

Heavy metal pollution in foods and the environment has remained a reoccurring decimal in sub-Saharan Africa and in Nigeria in particular. The determination of Cd, Cr, Mn, Ni, Pb contents in *Tilapia zilli* of the rivers of North-central Nigeria were made using Atomic Absorption spectrophotometric technique. Acid digestion consisting of 70% perchloric, concentrated nitric and concentrated sulphuric acid, in ration 1:5:1, was used to liberate the metals from the samples. The concentrations of the heavy metals (mg/kg) during the wet (rainy) season ranged from 0.0-25.4, 0.1-40.2, 1.4-435.1, 0.5-15.7, 0.4-25.4, for Cd, Cr, Mn, Ni and Pb, respectively, while in the dry season the concentrations ranged between 0.3-13.0, 0.8-31.2, 5.2-344.2, 0.6-25.1, 0.1-45.6, for Cd, Cr, Mn, Ni and Pb, respectively. The mean concentration of the heavy metals follow the pattern Mn>Cr>Pb>Ni>Cd during both seasons suggesting that once heavy metals are bio-accumulated they are either totally retained or lost through a very slow and gradual process. The results also show that the concentrations of Cd, Cr, Mn, Ni and Pb in the *T. zilli* samples were above the normal range in the WHO and FEPA guidelines and were therefore rendered the samples unfit for human consumption.

Key words: Aquatic organisms, heavy metals, bioaccumulation, river pollution, *T. zilli*.

INTRODUCTION

Heavy metals are reasonably dangerous to the aquatic environment. This can be due to their toxicity, wide sources, non-biodegradable properties, and accumulative tendencies (Mansouri *et al.,* 2012; Rezaee *et al.,* 2011; Salati and Moore, 2010). Usually, concentrations of heavy metals in aquatic ecosystems are monitored by measuring its concentration in water, sediments, and biota, which generally exist in lower levels in water and attain elevated concentration in sediments and biota (Ebrahimpour and Mushrifah, 2008).

Aquatic ecosystem is the ultimate sink of almost everything, heavy metals inclusive. Pollution of heavy metals in aquatic environment is a growing global problem and currently it has assumed an alarming proportion. There are numerous sources of heavy metals such as anthropogenic activities like mining of minerals, draining of sewage, dumping of hospital wastes and recreational activities. Conversely, metals also occur in small amounts naturally and can enter into aquatic system through leaching of rocks, airborne dust, forest fires and vegetation (Fernandez and Olalla, 2000). Heavy metals are continuously being deposited and incorporated in water, sediment and aquatic organisms as a result of their inability to be biodegraded (Linnik and Zubenko, 2000), thus causing heavy metal pollution in water bodies.

The indiscriminate disposal of industrial effluents and other wastes in river and lakes contribute greatly to the poor quality of river water (Chindah *et al.,* 2004; Emongore *et al*., 2005; Furtado *et al.*, 1998 and Ugochukwu, 2004). Among environmental pollutants, metals are of particular interest in view of their potential toxic effect and ability to bio-accumulate in aquatic ecosystems (Censi *et al*., 2006). Heavy metals including both essential and non-essential elements have a particular significance in ecotoxicology, as they are toxic to living organisms at certain levels (Storelli *et al*., 2005). Bioaccumulation and magnification is capable of leading to toxic level of these metals in fish even at minimal level of exposure. This work set out to investigate the concentration of heavy metals in *Tilapia zilli* in the rivers of North Central Nigeria with a view towards establishing their fitness for consumption and use of the river as safe sources of water for domestic use.

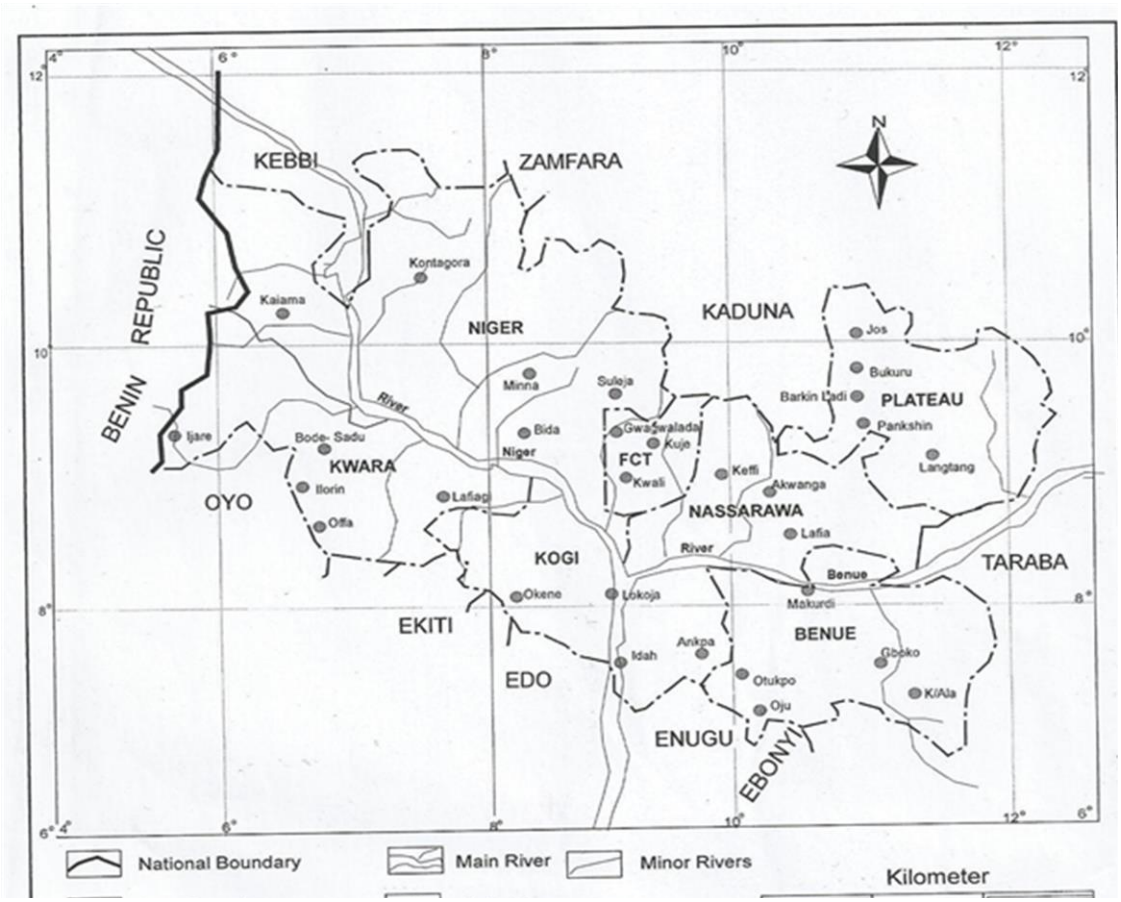

Figure 1: Map of North Central Nigeria Showing the Major and Minor Rivers.

MATERIALS AND METHODS

Materials

All reagents used were purchased from Kritz Scientific Enterprises, Makurdi, while reference standards were obtained from Sigma Aldrich. Reagents used were of analytical grade. The measurements were performed using the Perkin Elmer® Analyst 400 atomic absorption spectrophotometer at Central Science Laboratory Obafemi Awolowo University, Ife.

Methods

Sample Collection

Samples (fishes) were collected at the peak of both the dry (February-March) and wet season (August-September). The fish samples were collected using gill nets, baited hook and lines and traps. The fish samples were placed in plastic bags and stored in ice box and taken to the laboratory after cleaning with distilled water to remove any adhering dirt.

Table 1: Sample codes and Sample Locations

Sampled States	Sample Locations	Sample Codes (Wet Season)	Sample Codes (Dry Season)	Intra State State Sample Distance (km)
Benue	Wadata	A	M	7
	Wurukum	B	N	
Kogi	Ganaja	C	O	10
	Lokoja Town	D	P	
Kwara	Jebba	E	Q	15
	Jebba Bridge	F	R	
Nassarawa	Yelwa	G	S	45
	Gudi	H	T	
Niger	Shiroro	I	U	120
	Kainji	J	V	
Plateau	Kalong	K	W	20
	Shendam Town	L	X	

Sample Treatment

The fish samples after defrosting were dissected to get the gills, liver and muscle, using stainless steel dissection instruments. After dissection, all tissue samples were separately oven-dried at 105 ^{o}C to constant weight and were each ground to powder. 1 gram of each powdered sample was digested using a mixture of 1.5.1, 70% perchloric, concentrated nitric and concentrated sulphuric acid at 80 ± 5 ^{o}C in a fume chamber, until a colourless liquid was obtained, which was used for the analyses.

Stock Solutions

Cadmium: 1.0 g of cadmium metal was dissolved in 20 mL of 1M HCl and then diluted to 1000 mL to make 1000 mgL^{-1} Cd stock solution. An intermediate stock solution of 100 mgL^{-1} Cd was made from the stock solution, and a series of working standards of 0.0, 0.5, 1.0, 2.0, 3.0, 5.0 mgL^{-1} Cd concentrations were prepared. The absorbance was taken on AAS at a wavelength of 228.9 nm.

Chromium: 2.828 g of anhydrous potassium dichromate ($K_2Cr_2O_7$) was dissolved in 200 mL distilled water and 1.5 mL concentrated HNO_3 was added, and then diluted to 1000 mL with distilled water to make 1000 mgL^{-1} Cr. An intermediate stock solution of 100 mgL^{-1} Cr was made from the stock solution and a series of working standards of 0.0, 0.5, 1.0, 2.0, 3.0, 5.0 mg L^{-1} Cr concentrations were prepared. The absorbance was taken on AAS at a wavelength of 357.9 nm.

Manganese: 1.0 g of manganese metal was dissolved in 50 mL of conc. HCl. The solution was then made up to 1L in a volumetric flask with distilled deionized water.
Nickel: 1.0 g of nickel was dissolved in 20 mL of conc. HNO_3. The solution was diluted to 1L in a volumetric flask with distilled deionized water.

Lead: 1.598 g of lead nitrate $Pb(NO_3)_2$ was dissolved in 200 mL distilled water and 1.5 mL concentrated HNO_3 was added and then diluted to 1000 mL to make 1 000 mgL-1 Pb. An intermediate stock solution of 100 mgL^{-1} Pb was made from the stock solution and a series of working standards of the following concentrations were prepared: 0.0, 0.5, 1.0, 2.0, 3.0, 5.0, mgL-1 Pb. The absorbance was determined on AAS and wavelength set at 283.7 nm (APHA, 1990).

Instrumentation

The measurements were performed in a Perkin Elmer® Analyst 400 atomic absorption spectrophotometer (PerkinElmer, Inc. Shelton, CT, USA) equipped with WinLab32™ for AA version software. The AAS was equipped with Perkin Elmer high efficiency double beam optical system and solid–

state deuterium background correction to eliminate most interference, and Perkin Elmer corrosion – resistant nebulizer, which can be used for solutions containing HF. A single slot air-acetylene 10 cm burner head was used for all air-acetylene experiments.

RESULTS AND DISCUSSION

The concentrations of the heavy metals in the different organs of Tilapia during the wet season and dry season are as presented in Table 1 and 2 respectively, and figures 2 to7.

Table 2: Elemental concentrations (mg/kg) in organs of *Tilapia zilli* during the wet season

Sample code	Gill					Liver					Muscle				
	Cd	Cr	Mn	Ni	Pb	Cd	Cr	Mn	Ni	Pb	Cd	Cr	Mn	Ni	Pb
A	3.1	0.9	1.4	3.0	12.0	0.8	5.4	13.3	2.9	11.1	0.3	7.0	23.6	5.0	13.2
B	0.3	8.7	79.5	9.4	7.0	5.8	22.3	31.1	2.8	13.4	0.1	4.5	22.3	0.9	12.6
C	0.7	13.1	17.6	1.3	0.7	2.8	25.5	26.3	11.6	1.2	3.8	18.3	5.3	3.6	4.4
D	0.0	31.8	94.4	6.6	4.1	15.1	9.3	11.9	2.2	14.2	8.7	4.9	27.7	0.5	0.4
E	10.8	40.2	70.4	12.6	0.7	18.2	4.6	31.4	1.7	13.2	1.6	4.8	3.0	12.2	4.2
F	13.0	20.2	8.2	2.1	12.1	1.6	26.7	27.6	14.0	6.9	11.6	2.4	30.8	0.9	4.4
G	2.6	9.7	171.5	10.6	14.4	0.2	7.8	435.1	4.5	12.0	0.5	5.2	40.3	10.8	1.1
H	2.1	7.7	165.3	1.6	6.4	0.7	16.6	220.4	0.8	3.4	0.8	26.4	12.8	0.9	12.6
I	1.5	17.1	12.8	1.3	15.2	0.5	6.9	24.6	0.7	25.4	0.6	6.9	28.4	1.2	7.8
J	1.4	12.5	23.6	6.5	2.1	1.6	15.2	14.4	0.7	0.9	7.8	4.2	38.2	3.7	0.5
K	4.7	21.6	80.0	5.7	9.8	3.4	24.0	35.6	15.7	11.2	0.9	16.0	9.2	0.8	0.9
L	0.6	24.8	40.0	8.4	13.1	2.5	16.9	40.4	9.7	2.7	0.3	6.0	36.0	1.5	0.5

Table 3: Elemental concentrations (mg/kg) in organs of *Tilapia zilli* during the dry season

Sample code	Gill					Liver					Muscle				
	Cd	Cr	Mn	Ni	Pb	Cd	Cr	Mn	Ni	Pb	Cd	Cr	Mn	Ni	Pb
M	2.5	10.5	112.1	7.3	0.1	13.0	26.6	142.4	16.7	15.1	2.0	1.2	11.0	1.2	16.8
N	5.3	27.9	178.1	1.1	13.4	2.2	0.9	66.8	17.4	13.5	1.4	22.1	11.0	1.4	7.0
O	2.8	28.4	5.2	1.8	1.0	3.8	23.0	68.2	21.4	7.0	1.4	11.9	16.2	1.2	14.2
P	1.5	20.5	6.4	12.3	4.5	0.8	25.1	18.4	7.8	41.4	6.0	17.3	12.0	3.7	6.7
Q	4.0	19.5	21.2	7.6	5.3	1.6	19.3	18.4	1.3	10.4	1.5	5.0	8.0	12.2	1.1
R	6.7	8.1	13.7	1.0	14.2	2.2	1.0	21.5	1.22	23.0	3.1	31.2	394.7	8.5	8.2
S	10.6	1.2	179.6	1.6	1.0	10.6	0.0	77.9	1.7	14.5	1.2	17.4	16.3	15.5	1.7
T	2.7	29.0	105.1	6.6	7.2	2.7	17.8	38.3	6.9	3.4	1.2	9.4	33.2	2.8	0.3
U	2.1	23.0	105.1	0.6	8.2	11.0	19.7	344.2	4.1	11.4	2.0	23.0	15.9	1.0	12.6
V	0.5	15.1	37.8	6.6	0.7	1.5	19.5	152.5	1.1	14.2	0.3	21.2	94.1	1.2	9.6
W	11.0	7.3	104.9	1.9	10.6	2.4	15.8	39.2	7.2	3.9	2.3	8.9	10.0	0.8	7.4
X	0.6	26.0	134.0	1.5	7.0	1.6	29.1	33.6	12.0	1.0	2.6	20.8	59.7	25.1	45.6

The maximum concentration of cadmium during the wet and dry season were detected in the liver as 18.2 and 13.0 mg/kg, corresponding to sample E (Jebba area of Kwara state) and sample M (Wadata area of Benue state), respectively. Samples C, D, F and J had significant high amount of cadmium (>1 mg/kg) in the wet season, while only sample V (0.3 mg/kg) had less than 1 mg/kg in the dry season. It was however not clear if a particular organ accumulate the metal more. According to European Food Safety Authority (EFSA) regulation EC No. 1881/2006 and No 629/2008, the maximum limit of Cd in muscles of meat of fish is 0.05 mg/kg of wet weight (FSAI, 2009; AFFI, 2015). Thus the fishes from the various rivers could be potential sources of cadmium poisoning. Cadmium is a highly toxic non–essential heavy metal and it plays no role in biological process in living organisms. The FSAI (2009) reported that the principal toxic effect of cadmium is its toxicity to the kidney, and has been associated with lung damage through lung tumor, and skeletal changes in occupationally exposed populations. Though cadmium is poorly absorbed into the body, it is slowly excreted like other metals once absorbed, and accumulates in the kidney causing renal impairment. As a result, even in low concentration, cadmium could be harmful to living organisms (Tsui

and Wang, 2004). The levels of Cd present in the selected organs of *T. zilli* may be due to agricultural activities in the investigated area (Ambedkar and Muniyan, 2011).

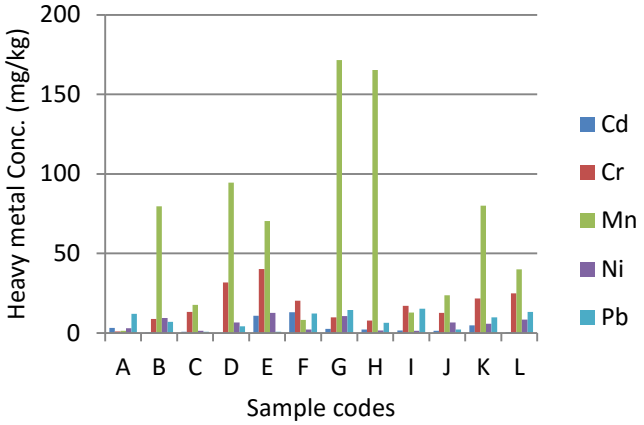

Figure 2: Level of heavy metals in *T. zilli* gills during the wet season

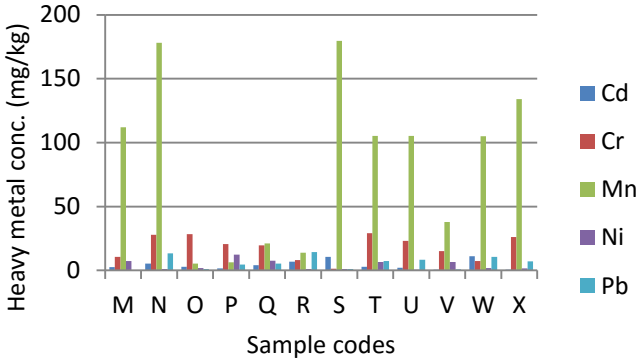

Figure 3: Levels of heavy metals in *T. zilli* gills during the wet season

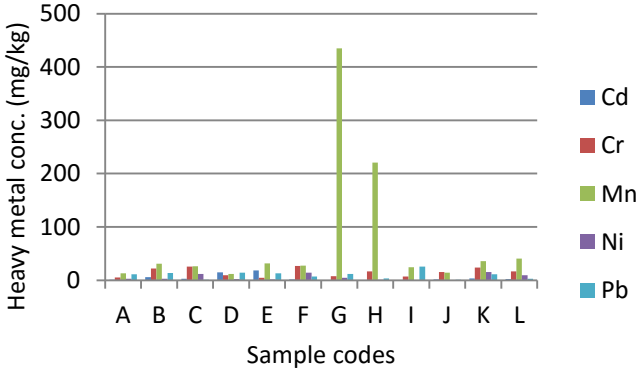

Figure 4: Levels of heavy metals in *T. zilli* livers during the wet season

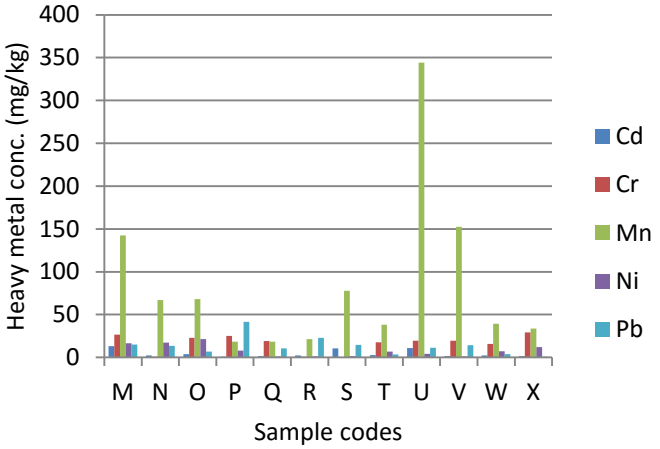

Figure 5: Levels of heavy metals in *T. zilli* liver during the dry season

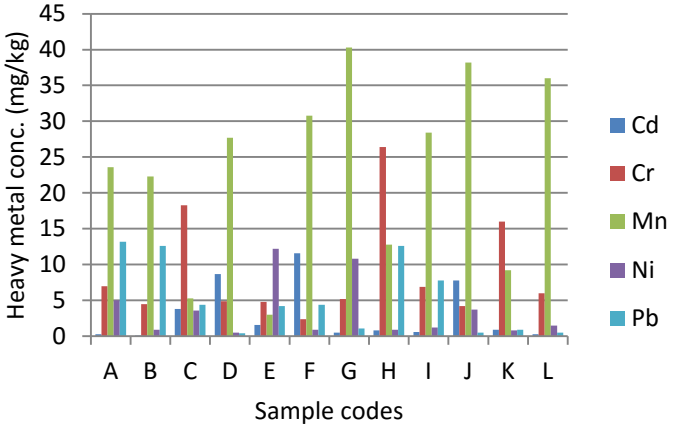

Figure 6: Levels of heavy metals in *T. zilli* muscles during the wet season

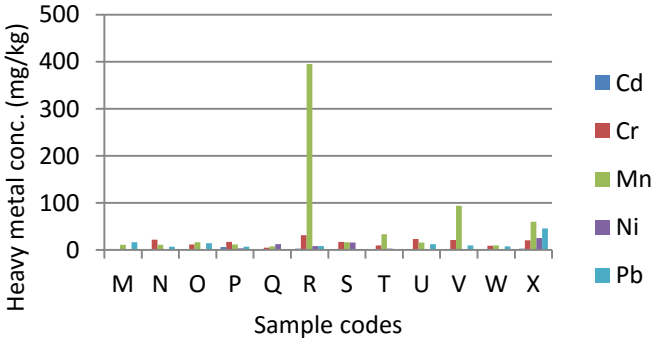

Figure 7: Concentration of heavy metals in *T. zilli* muscles during the dry season

Chromium concentration during the wet season in the gills was 40.2 mg/kg from sample E (Jebba area of Kwara state), in the liver was 26.7 mg/kg (sample H from Gudi in Nasarawa) and in the muscles was 26.4 mg/kg (sample F from Jebba Bridge). For the dry season, the concentration of chromium was highest in the muscles at 31.2 mg/kg from sample R (Jebba bridge), followed by liver at 29.1 mg/kg in sample X (Shendam Town), and gills at 29.0 mg/kg in sample T (Gudi). Chromium levels in the samples were generally above the WHO and FEPA standards limits of 0.15mg/kg for fish food (FEPA, 1991; WHO 1989). Chromium plays an important role in glucose metabolism. Chromium bioaccumulation in fish had been implicated in impaired respiratory and osmoregulatory functions through structural damage to gill epithelium (Heath, 1991). The concentration of chromium levels in the different organs of the freshwater fish may be linked to waste water discharge from the agricultural related activities that are prevalent in the investigated areas.

Manganese concentration was virtually higher than all other metals in all the organs investigated during the wet season and in the gills and liver during the dry season. The maximum concentration of Mn during the wet season was detected in sample G from Yelwa in Nasarawa State. The concentration in the liver was 435.1 mg/kg, followed by gills (171.5 mg/kg) and then Muscles (40.3 mg/kg). However, during the dry season the concentration was highest in the muscles of sample R from Jebba Bridge (394.7 mg/kg), followed by livers of sample U (344.2 mg/kg). The highest concentration in the gills was in sample M from Wadata in Benue State (178.1 mg/kg) (Fig. 4&5). The health effects of manganese exposure in humans are not well understood. Although dietary manganese is an essential nutrient, high intake of manganese have been shown to be toxic (Institute of Medicine Food and Nutrition Board, 2002). Manganese is best characterized as neurotoxin, occupational exposures are associated with characteristic syndrome called manganism which involves both psychiatric symptoms and Parkinsonism features (Dobson, *et al.,* 2004).

The highest reported concentration of nickel during the wet season was 15.7 mg/kg in the liver sample from K. The highest concentration in the gills was 12.6 mg/kg in samples from E, and in the muscle it was 12.2 mg/kg from E. During the dry season, the highest Ni concentration was in the muscles of sample X (25.2 mg/kg). The highest levels in the gills and liver were in samples P (12.3 mg/kg) and O (21.4 mg/kg) respectively. None of the organs had less than 0.6 mg/kg during both seasons. Nickel concentrations in foodstuffs usually range from about <0.1 mg/kg to 0.5 mg/kg (Cempel and Nikel, 2006). According to the US FDA (1993), the estimated maximum limit for nickel in foods is 70-80 mg/kg. The concentrations of Ni in all the samples were far below the stipulated limit. The major source of Ni for humans is food and uptake from other sources, as well as food processing. Increased incidence of cancer of the lung and nasal cavity caused by high intake of Ni had been reported in workers in Ni smelters.

The maximum concentration of Pb during the wet season (25.4 mg/kg) was detected in the liver from sample I (Shiroro) while it was highest (45.6 mg/kg) in the muscle of sample X (Shendam Town) during the dry season. No sample had <0.1 mg/kg in both seasons. Lead is a well-known toxicant that has several deleterious effects even at very low concentrations (Eneji*et al*., 2011). The maximum tolerable limit (MTL) of Pb in fish meat is 0.3 mg/kg, whereas in the European Union it is 0.2 mg/kg (European Commission, 2000). It is highly toxic to aquatic organisms, especially fish. The biological effects of sub-lethal concentrations of lead include delayed embryonic development, suppressed reproduction, and growth inhibition, elevated mucous formation, neurological problems, and kidney dysfunction (Rompala, *et al.,* 1984; Leland and Kuwabara, 1985).

The pattern of metal concentration in *Tilapia zilli* appeared to be Mn>Cr >Pb> Ni > Cd during both the wet and dry seasons. On the other hand, the concentration of heavy metals in the organs appeared to be Cd: liver>gills>muscle, Cr: gills>liver>muscle, Mn: liver>gills>muscle, Ni: gills>liver>muscle, Pb: liver>gills>muscle, during the wet season. The accumulation pattern for Cd, Cr and Mn seemed to be liver>gills>muscle but was liver>muscle>gills for Ni and Pb. A comparison of the concentration of heavy metals in the various organs at $p<0.05$ reveals there was no significant difference in concentrations of the heavy metals in the organs of fishes as well as between the two seasons.

CONCLUSION

Based on the results obtained from this study it could be seen that the fishes in these Rivers have been severely affected by heavy metals, especially Cd, Mn and Pb, and pose serious health implications for human consumption. The study also reveals that the heavy metals concentrations in the fish species were not sensitive to the seasonal changes as heavy metals are lost slowly or not at all once bioaccumulated. The level of heavy metals found in the rivers were above normal level recommended by WHO and FEPA and therefore the fishes (*T. zilli*) in these rivers were found not to be suitable for human consumption. It is recommended that more studies should be conducted to determine the culpable sources of these metals pollution so as to address the environmental challenge.

ACKNOWLEDGMENT

The authors wish to acknowledge the Staff of Central Science Laboratory for their inputs during the elemental analysis.

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Article's Citation:

Ogah E, Abiaziem CV, Malu SP, Ushie OA, Longbap BD (2015). Heavy metals levels in Tilapia samples from North Central Nigerian rivers. *Ew J Anal & Environ* 1(1): 1-8.