

*Full Length Research Paper*

# River Usuma: A medium of assessing bioavailability of heavy metals in Abuja

Ugwu, A. I.<sup>1\*</sup>, Wakawa, R. J.<sup>2</sup>, Kana, M. Z.<sup>3</sup>, La'ah, E.<sup>1</sup> and Olotu, A.<sup>4</sup>

<sup>1</sup>Department of Physics, Federal Capital Territory (FCT) College of Education Zuba, Abuja, Nigeria.

<sup>2</sup>Department of Chemistry, Federal Capital Territory (FCT) College of Education Zuba, Abuja, Nigeria.

<sup>3</sup>Sheda Science and Technology Complex Abuja, Nigeria.

<sup>4</sup>Department of Integrated Science Federal Capital Territory College of Education Zuba Abuja, Nigeria.

Accepted 13 September, 2012

River Usuma was used as a substrate through which toxic elements and their sources were identified and measured due to anthropogenic activities in Federal Capital Territory (FCT), Abuja. It makes good public health sense, good economic and environmental sense to prevent water contamination at the source. Concentrations of heavy metals [Zinc (Zn), Manganese (Mn), Copper (Cu), Cadmium (Cd), Lead (Pb), Iron (Fe), and Chromium (Cr)] were measured in water and two fish species, catfish-*Synodontis membranaceus* and tilapia-*Oreochromis niloticus*, from River Usuma, FCT Abuja, Nigeria. As an attempt to understand metal bioavailability and assess the potential impact on aquatic biota, a study of seasonal variations of heavy metals fractionation in water column was achieved. In comparison to some organizations tolerable values, relatively high levels of total and dissolved Mn, Cu, Pb, and Fe were found in water samples. Availability of metals in water column established were in the rank: Cr < Fe < Pb < Zn < Cu < Mn. In addition, the potential toxicity of the metals was studied by evaluating correlations of the concentration of the metals in fish tissues and in water. High Cu and Fe levels were observed in liver tissue of both species, in agreement with higher total content of these metals in water. Correlations among metals' content in catfish's tissues and different fractions of metals in water were found.

**Key words:** Metal pollution, water, fish, speciation.

## INTRODUCTION

Anthropogenic activities have greatly taken their tolls on the natural environment. It is no longer a controversial issue; technology has brought negative impacts on the environment. Many human activities go on in many places around us without the knowledge of environmental pollution monitoring. In urban environment, it becomes difficult to identify and quantify sources of environmental pollution, especially in areas where many illegal human activities are going on. River Usuma stands out as a reliable option through which anthropogenic activities in a fast growing city such as Abuja can be identified and measured since it cuts across over three quarter of Abuja environment. Imperatively, studies (Yilmaz, 2005; Asuquo et al., 2004; Riba et al., 2003) have shown that heavy

metal burden in sediment, biota and water are important indicators of the pollution status of an aquatic environment. It becomes a guide on this study, therefore, that the extent to which Abuja environment is polluted in heavy metals' wish could be relatively estimated by determining the concentration levels of these metals in River Usuma.

It makes good public health sense, good economic and environmental sense to prevent water contamination at the source (USEPA, 2000). Thus, continuous monitoring is essential for detecting and assessing pollution level in Federal Capital Territory (FCT), and in this case, heavy metal pollution has been monitored. Therefore, this work will provide information on the concentrations and bioconcentration factors of some heavy metals in water and fish from the river and the result obtained would provide information on the level of some heavy metals in Abuja environment.

\*Corresponding author. E-mail: [aloyugwu@yahoo.com](mailto:aloyugwu@yahoo.com).

The aim of this study is to assess heavy metal bioavailability in Usuma River due to anthropogenic activities around FCT which collate in the River. This is pursued through the following objectives:

- 1) To determine the levels of total extractable heavy metals [Chromium (Cr), Cadmium (Cd), Copper (Cu), Iron (Fe), Manganese (Mn), Lead (Pb) and Zinc (Zn)] and study the fractionation of these metals in the water column because of their environmental implications.
- 2) To determine the levels of Cr, Cd, Cu, Fe, Mn, Pb, and Zn in some fish samples because of the health implications to human populations consuming fishes from the river.
- 3) To determine the levels of Cr, Cd, Cu, Fe, Mn, Pb, and Zn in some fish species and relate it to the concentration in water across the seasons.

It is hoped that the findings of the investigation will be useful in informing government policy on discharge wastes in the FCT, and people using the river will also understand the level of toxicity of the water they are using for domestic and other purposes. To the best of our knowledge, this is the first time chemical fractionation of heavy metals is performed on the river water.

## MATERIALS AND METHODS

### Sampling sites

The FCT falls within the Savannah zone vegetation of the West African sub-region. There are three seasons, including a warm, humid rainy season, from April to October, and a blistering dry season, when daytime temperatures can soar as high as 40°C (104°F). Between these seasons is a brief interlude of harmattan occasioned by the north-east trade wind, with characteristic dust haze, intensified coldness and dryness. The high altitudes and undulating terrain of the territory act as moderating influence on the weather of the territory. Rainfall in the FCT reflects the territory's location on the windward side of the Jos, Plateau and the zone of rising air masses. The annual total rainfall is in the range of 43.3 inches (1100 mm) to 63 inches (1600 mm). It is slightly west of the center of the country. Its area covers 7,315 km<sup>2</sup> (2,824 square miles) (Abuja, 2012). River Usuma with its source from Gurara River; enters through the northern part of FCT at Bwari and splits at Ushafa with one arm flowing eastwards towards Kpeyi and the other flowing westwards towards Paiko and its length stretches over 143 km across the breadth of FCT. The Usuma River drains the central part of Abuja in the north central zone of Nigeria flowing through towns, some of which with notable anthropogenic activities were designated as sampling points. The choice of River Usuma is hinged on its watershed that traverses more than three quarter of breadth of FCT and relatively to a large extent, the Savannah region which covers the north central zone of Nigeria.

Seven sampling sites were selected among the towns river Usuma traverses (Figure 1) and their locations are shown in Table 1. The first sampling site was located near Usuma River's mouth into FCT at Ushafa and a little distance after this point, the river splits towards east and west directions. The second was located at Kubwa; first town towards eastward flow of the river. In the descending order, three more sampling points were located, namely: Gwagwa, Gwagwalada and Paiko forming sampling sites

numbers: three, four and five, respectively. Two more sampling sites were located towards the eastward flow, namely Jabi and Kpeyi and they become sampling sites numbers six and seven, respectively.

### Instrumentation

Metal determinations in the surface water and fish extracts were carried out by means of a computer controlled atomic absorption spectrometer (CCAAS 969) Solaar 32 AAA M series. Hollow cathode lamps having resonance lines at 213.9, 422.7, 285.2, 324.7, 309.3, 217.0, 248.3 and 357.9 nm were used as radiation sources for the determination of Zn, Mn, Mg, Cu, Cd, Pb, Fe and Cr, respectively. Acetylene and air flow rates were 2 and 1.0 L min<sup>-1</sup>, respectively, for all the elements. A centrifuge (Hettich Rotofix 32, Germany) for complete separation of the extracts from the residues, a Clifton shaker with end-over-end type, a Nel 900 pH-meter, and an electrical heater were used throughout all the experiments. Samples digestions were done by ultraviolet (UV) method.

### Sample collection and pre-treatment

#### Water collection and analysis

Surface water samples collection were carried out separately within the three seasons in a year. The water samples at each site were grabbed into 1 L high-density polyethylene bottles that were pre-washed with 10%, v/v HCl acid and also pre-rinsed with deionized water severally, to avoid any contamination from metal and non-metal ions. Prior to the sampling, the pre-washed bottles were stored in polyethylene bags until they were required. The pre-washed bottles were also rinsed thrice with water samples on the sites before the collection. At each of the seven sampling sites, surface water samples were collected in the pre-washed bottles and transported to the laboratory (Advanced Chemistry Laboratory, Sheda Science and Technology Complex Abuja-SHESTCO) in a cooler box. For total metal determination, 250 ml of samples from each sampling points were acidified with 2 mL<sup>-1</sup> HNO<sub>3</sub> of analytical grade, kept at temperature of -18°C until analysis. 0.2 ml of 65% HNO<sub>3</sub> and 0.125 ml of 70% HClO<sub>4</sub> (analytical grade) were added to 45 ml which were digested in a closed Teflon reactor for 8 hat 120°C, cooled and diluted up to 50 ml in a volumetric flask. The analysis was done using CCAAS 696.

The scheme of chemical fractionation of labile metals in water samples based on change of pH is shown in Figure 2. 250 ml of the water samples were acidified with 2 molL<sup>-1</sup> HNO<sub>3</sub> and kept at room temperature for 1 week and subsequently stored at -18°C until analysis was required. For inorganic labile fractionation, the metal fractionations were determined at this neutral pH which were denoted as C<sub>A</sub> and labeled F<sub>1</sub> (that is, F<sub>1</sub> = C<sub>A</sub>). For moderately inorganic labile metal fractionations, the neutral pH samples were conditioned to pH of 4.7 by adding 10 ml of 3 molL<sup>-1</sup> of acetate buffer and analyzed by CCAAS and the results labeled C<sub>C</sub>. The difference between C<sub>C</sub> and C<sub>A</sub> gives the values of moderately inorganic labile fractionations, F<sub>3</sub> (that is, F<sub>3</sub> = C<sub>C</sub> - C<sub>A</sub>). For organic labile fractionations, 15 ml of the neutral pH samples were treated with 50 µl of 30% H<sub>2</sub>O<sub>2</sub> and digested by UV for 2 h. The resulting values were labeled C<sub>B</sub>.

The labile organic fractionations F<sub>2</sub> were obtained by finding the difference between C<sub>A</sub> and C<sub>B</sub> (that is, F<sub>2</sub> = C<sub>B</sub> - C<sub>A</sub>). The moderately organic labile fractionations F<sub>4</sub> were determined by adding 50 µl of 30% of H<sub>2</sub>O<sub>2</sub> to the samples at pH 4.7 and digested for 1 h by UV. The analyzed values were denoted as C<sub>D</sub>. Then the moderately organic labile fractionations F<sub>4</sub> were calculated as follows: F<sub>4</sub> = (C<sub>D</sub> - C<sub>B</sub>) - (C<sub>D</sub> - C<sub>A</sub>).

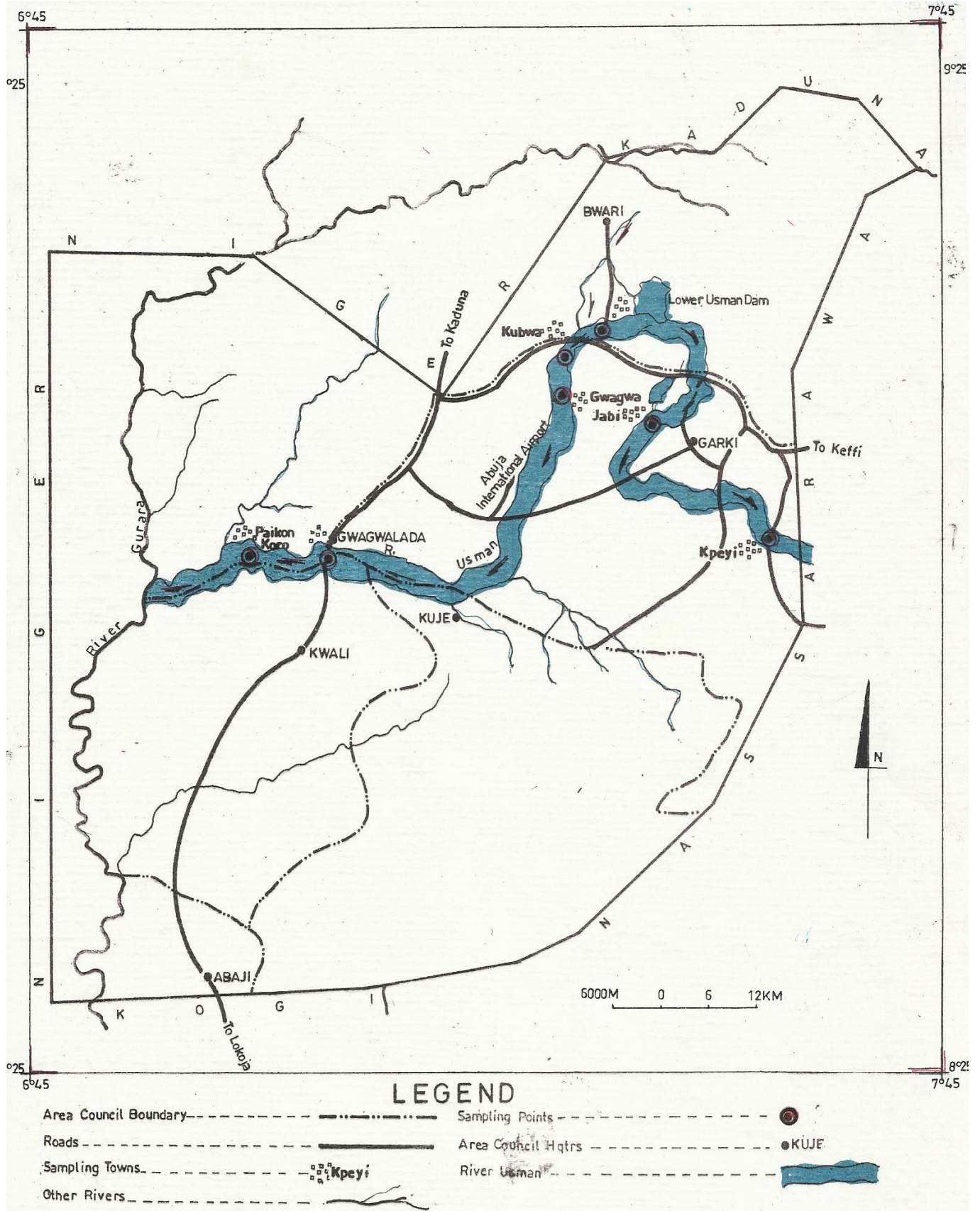
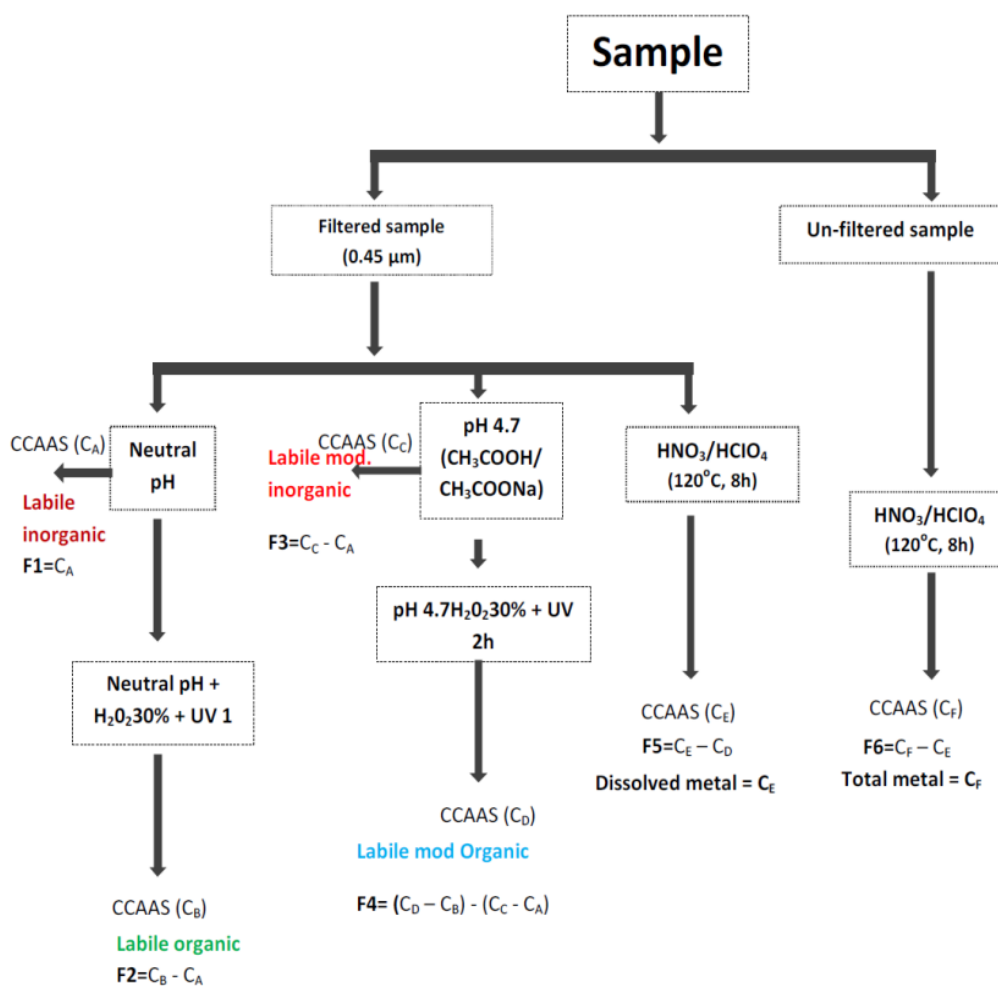


Figure 1. Area map of FCT, Abuja showing sampling towns locations. Source: Cartoprint Nigeria Ltd Kaduna, 2010.

**Table 1.** Names of the sampling locations and their coordinates.

Sampling sites no.	Name of sampling site	East latitude	North longitude	Elevation from sea level (m)
1	Ushafa	7° 24'	9° 11'	1500
2	Kubwa	7° 21'	9° 09'	1300
3	Gwagwa	7° 20'	9° 06'	1200
4	Gwagwalada	7° 06'	8° 56'	700
5	Paiko	7° 00'	8° 55'	500
6	Jabi	7° 26'	9° 02'	1400
7	Kpeyi	7° 34'	8° 57'	1300

**Figure 2.** Scheme of chemical fractionations of metal in water based on change of pH.

### Fish collection and analysis

The samples of matured *S. membranaceus* (catfish) and *O. niloticus* (tilapia) were collected at sampling sites and were transported in aerated tanks to the analysis laboratory (Advanced Chemistry Laboratory of Sheda Science and Technology Complex, Abuja). Catfish and tilapia are common table fishes within the study area (Owolabi, 2008). Fishes were dissected and tissue

sub-samples were taken out quickly from liver, gills and muscle and stored at -80°C. Samples were freeze-dried and digested by microwave heating. Gills and muscle samples (0.2 g) were digested with 7 ml of 65% HNO<sub>3</sub>, and liver samples (0.2 g) containing higher organic matter, were digested with 4 ml of 65% HNO<sub>3</sub> and 2 ml of 30% H<sub>2</sub>O<sub>2</sub>. The following microwave program was applied: 4 min for 200 W, 5 min for 400 W and as last step 10 min for 600 W. After microwave digestion, samples were diluted up to 25 ml with

**Table 2.** Total metal concentrations and physiochemical parameters in water (Dry season; March, 2011).

Metal (mg/l) ± Rsd (%)	Sampling sites						
	1	2	3	4	5	6	7
	Ushafa	Kubwa	Gwagwa	Gwagwalada	Paiko	Jabi	Kpeyi
Zn ± Rsd	0.33 ± 0.40	0.44 ± 0.10	0.21 ± 0.90	0.55 ± 1.10	0.52 ± 0.30	0.33 ± 0.10	0.12 ± 0.10
Mn ± Rsd	0.31 ± 0.40	0.36 ± 0.40	0.26 ± 0.90	0.47 ± 0.70	0.39 ± 0.30	0.34 ± 0.90	0.24 ± 1.30
Mg ± Rsd	6.44 ± 0.40	8.25 ± 0.20	5.32 ± 1.90	7.39 ± 0.10	7.09 ± 0.30	7.13 ± 0.50	5.14 ± 1.10
Cu ± Rsd	0.51 ± 1.40	0.01 ± 1.20	0.35 ± 1.00	0.37 ± 1.70	0.32 ± 0.90	0.38 ± 1.30	0.33 ± 0.70
Cd ± Rsd	*BD	BD	BD	BD	BD	BD	BD
Pb ± Rsd	BD	0.07 ± 0.90	0.08 ± 0.10	0.05 ± 0.50	BD	BD	0.10 ± 1.10
Fe ± Rsd	0.50 ± 0.20	0.53 ± 0.80	0.31 ± 0.50	0.49 ± 0.50	0.54 ± 0.10	1.06 ± 1.90	0.26 ± 0.20
Cr ± Rsd	BD	0.29	BD	BD	0.54 ± 0.10	BD	0.18 ± 0.20
Na	1.15	1.60	1.05	2.10	1.20	2.71	1.55
K	0.80	0.45	0.35	1.00	1.40	2.45	0.62
pH	7.50	6.89	7.50	7.53	7.22	7.44	7.23
TDS (mg/L)	48.80	94.40	114.70	102.40	179.50	92.00	104.50
Cond µs	81.30	158.00	191.30	170.00	299.00	153.80	174.20
Alkalinity	2.19	1.56	2.46	2.72	2.10	1.84	3.16
%DO <sub>2</sub>	80	104	23	86	75	130	131
BOD	8.49	16.70	2.39	11.84	7.80	7.64	14.30
TSS (mg/L)	2.19	6.44	7.66	2.81	3.11	3.61	6.21
Turb	4.06	195.00	246.00	119.00	34.10	3.24	43.40
Sulphate (mg/L)	17.20	191.60	2012.00	1440.80	91.50	25.90	204.50
Phosphate (mg/L)	0.44	1.00	1.66	3.88	0.44	0.33	1.22
Nitrate (mg/L)	0.01	BD	0.07	BD	0.10	0.25	BD
Chloride (mg/L)	BD	BD	0.19	BD	BD	0.05	0.09

\*BD, Below detection limit.

deionized water. Metal concentrations of digested tissue samples were analyzed by CCAAS 969. Blanks were also performed and measured for all metals following the same procedure.

### Statistical analysis

Excel program tool was used for the analysis. Few heavy metals (Cd and Cr in all the seasons) had concentration below detection (BD) limits which were converted into a zero value for analysis purpose. The linear relationship between metals and physiochemical parameters was calculated using the correlation coefficient criterion. Pearson's correlation coefficient ( $r$ -square or  $r^2$ ) value closer to 1 indicates strong linear relationship between physiochemical parameters and other heavy metals. The correlation coefficient provides only information on strength of linear relationship, but does not state whether it is significant or merely occurred by chance.

## RESULTS AND DISCUSSION

### Metal concentrations in water

#### Total metal

The values of the physicochemical parameters and total

metal concentrations in water samples collected from Usuma River during three different seasons are shown in Tables 2, 3 and 4. The total metals recorded for the dry season from the seven sampling points ranged as follows: Zn: 0.12 to 0.55, Mn: 0.24 to 0.47, Cu: 0.01 to 0.51, Cd: BD limit, Pb: 0.05 to 0.10, Fe: 0.26 to 1.06 and Cr: 0.18 to 0.54 mg/L and ranked in the descending order: Pb < Mn < Cu < Cr < Zn < Fe. During the rainy season, the metal concentrations at the sampling sites ranged as follows: Zn: 0.11 to 0.56, Mn: 0.01 to 0.62, Cu: 0.29 to 0.58, Cd: BD, Pb: 0.08 to 0.30, Fe: 0.01 to 0.27 and Cr: 0.07 mg/L and ranked in the order: Cr < Fe < Pb < Zn < Cu < Mn. The harmattan (winter) values are: Zn: 0.24 to 1.10, Mn: 0.11 to 0.70, Cu: 0.01 to 0.48, Cd: BD, Pb: 0.01 to 0.16 and Fe: 0.23 to 0.87 mg/L and ranked in the order: Pb < Cr < Cu < Mn < Fe < Zn.

In order to assess the potential hazardous impacts, the heavy metal levels in water have been compared with quality guidelines for protection of aquatic life proposed by several organizations guidelines and imperative values of Nigerian standard for drinking water (Table 5). Metal concentrations studied were slightly above the limits provided by the several organization guidelines and Nigerian Industrial Standard.

**Table 3.** Total metal concentrations and physiochemical parameters in water (Rainy season; July, 2011).

Metal (mg/L) ± Rsd (%)	Sampling sites						
	1	2	3	4	5	6	7
	Ushafa	Kubwa	Gwagwa	Gwagwalada	Paiko	Jabi	Kpeyi
Zn ± Rsd	0.39 ± 0.40	0.55 ± 0.10	0.11 ± 0.90	0.33 ± 1.10	0.26 ± 0.40	0.35 ± 0.10	0.12 ± 0.10
Mn ± Rsd	0.15 ± 0.40	0.24 ± 0.30	0.01 ± 0.90	0.62 ± 0.70	0.14 ± 0.30	0.16 ± 0.90	0.09 ± 0.60
Mg ± Rsd	8.71 ± 0.90	12.29 ± 0.40	15.09 ± 0.60	8.25 ± 0.10	9.12 ± 0.80	9.42 ± 0.30	9.13 ± 0.30
Cu ± Rsd	0.36 ± 1.40	0.47 ± 0.40	0.36 ± 1.00	0.58 ± 0.30	0.29 ± 0.90	0.58 ± 0.70	0.35 ± 0.70
Cd ± Rsd	BD	BD	BD	BD	BD	BD	BD
Pb ± Rsd	BD	0.16 ± 0.20	0.08 ± 0.60	0.09 ± 0.90	BD	0.30 ± 0.70	0.09 ± 0.80
Fe ± Rsd	0.19±0.20	0.22 ± 0.30	0.01 ± 0.10	0.20 ± 0.50	0.25 ± 0.10	0.27 ± 1.90	0.23 ± 0.10
Cr ± Rsd	BD	0.07 ± 0.80	BD	BD	BD	BD	BD
Na	2.29	2.46	1.50	2.56	2.79	3.12	1.55
K	1.24	1.26	0.82	1.29	2.13	3.15	0.62
pH	7.69	7.44	7.89	7.19	7.55	7.66	7.88
TDS (mg/L)	168.90	292.50	465.20	284.60	284.00	286.40	340.20
Cond µs	316.00	360.00	349.00	540.00	450.00	223.10	442.30
Alkalinity	3.49	2.91	2.15	5.44	3.89	2.46	3.55
%DO <sub>2</sub>	94.50	98.40	79.00	99.50	89.00	97.00	110.00
BOD	7.49	20.64	4.12	19.42	10.54	7.49	18.40
TSS (mg/L)	4.41	12.33	5.99	8.42	4.72	4.51	5.92
Turb	56.20	290.00	213.00	180.00	55.20	5.64	25.60
Sulphate(mg/L)	10.56	246.00	1920.00	920.00	105.00	23.40	150.4
Phosph(mg/L)	5.84	4.96	6.62	10.56	4.60	2.76	5.69
Nitrate (mg/L)	0.44	1.60	2.50	0.15	2.54	1.50	2.40
Chloride (mg/L)	0.14	0.56	1.80	1.75	2.19	0.15	1.80

\*BD, Below detection limit.

Conventionally, there is always significant difference between the seasonal variations of the dissolved metals having greater enrichment during the rainy seasons than the other seasons (Vincent-Martorell et al., 2009), which is not the case in many of the sampling points. Concentration values of Zn were lower than those proposed by Agency for Toxic Substances and Disease Registry (ATSDR) and Nigerian Industrial Standard; but above the criteria of maximum concentration (CMC) and criteria of continuous concentration (CCC), both established to prevent from acute and chronic toxicity to aquatic organisms, respectively. Pb and Cu exceeded all the referenced guidelines' limits.

Total Zn metal concentration lacks significant seasonality at the various sampling sites, except at sites 1 and 2 (Figure 3). Zn is an element commonly found in the earth's crust. It is released to the environment from both natural and anthropogenic sources; however, releases from anthropogenic sources are greater than those from natural sources. The primary anthropogenic sources of Zn in water environment are related to mining and metallurgic operations involving Zn and use of commercial products containing Zn (ATSDR, 2000).

The invariance in the seasonality of Zn concentration at

the different sampling points indicates low level of anthropogenic sources around the study environment. Also, environmental toxicity of Zn in water is dependent upon the concentration of other minerals and the pH of the solution, which affect the ligands that associate with Zn (Heijerick et al., 2002; Paquina et al., 2002). Pearson's product moment correlation coefficient (linear correlation coefficient),  $r^2$  between Zn and pH shows negative linear correlation (-0.62), indicating more of natural Zn occurrences at the sampling sites.

From Table 5, the results of present study when compared with the values from ATSDR and Environmental Protection Agency- National Oceanic and Atmospheric Administration (EPA-NOAA) show that Zn concentration within the study environment is much below the critical values. There is no defined significant seasonal variation in Mn at the sampling points. The present study recorded values that are below the critical values posted by ATSDR, but well above the values given by EPA-NOAA.

Cu and its compounds are naturally present in the earth's crust. Much of the Cu that enter environmental waters are associated to particulate matter. Cu is a natural constituent of soil and will be transported into

**Table 4.** Total metal concentrations and physiochemical parameters in water (Harmattan; February, 2012).

Metal (mg/L) ± Rsd (%)	Sampling sites						
	1	2	3	4	5	6	7
	Ushafa	Kubwa	Gwagwa	G/Lada	Paiko	Jabi	Kpeyi
Zn ± Rsd	0.35 ± 0.40	0.62 ± 0.10	0.34 ± 0.90	0.42 ± 1.10	0.37 ± 0.30	0.32 ± 0.10	0.24 ± 0.10
Mn ± Rsd	0.14 ± 0.40	0.62 ± 0.40	0.11 ± 0.90	0.70 ± 0.70	0.41 ± 0.30	0.20 ± 0.90	0.39 ± 1.30
Mg ± Rsd	6.44 ± 0.40	7.78 ± 0.20	5.18 ± 1.90	6.57 ± 0.10	6.67 ± 0.30	6.87 ± 0.50	4.85 ± 1.10
Cu ± Rsd	0.27 ± 1.40	0.48 ± 1.20	0.11 ± 1.00	0.18 ± 1.70	0.02 ± 0.90	0.23 ± 1.30	0.01 ± 0.70
Cd ± Rsd	BD	BD	BD	BD	BD	BD	BD
Pb ± Rsd	BD	0.16 ± 0.90	BD	0.01 ± 0.50	BD	BD	BD
Fe ± Rsd	0.25 ± 0.20	0.24 ± 0.80	0.30 ± 0.50	0.40 ± 0.50	0.42 ± 0.10	0.87 ± 1.90	0.23 ± 0.20
Cr ± Rsd	BD	0.18	BD	BD	BD	BD	BD
Na	1.92	1.78	1.84	1.88	1.99	2.15	1.61
K	0.89	0.89	0.88	0.94	0.95	0.97	0.91
pH	7.73	7.12	7.46	7.23	7.49	7.55	7.14
TDS (mg/L)	133.20	256.3	284.00	274.30	243.10	208.40	320.10
Cond µs	284.00	18	223.10	497.00	340.00	227.60	356.10
Alkalinity	1.77	1.28	0.57	4.38	2.10	0.56	1.89
%DO <sub>2</sub>	95.00	96.20	88.00	95.00	93.00	92.00	91.00
BOD	8.49	22.56	7.19	19.23	15.46	9.46	15.80
TSS (mg/L)	5.11	8.94	5.77	7.62	5.88	5.62	4.62
Turb	2.89	18.90	246.00	76.30	4.62	1.56	3.45
Sulphate (mg/L)	8.14	222.00	680.00	182.00	88.90	9.46	144.00
Phosphate (mg/L)	4.55	3.62	8.22	4.41	3.66	0.88	2.80
Nitrate (mg/L)	BD	BD	BD	0.09	0.12	BD	0.15
Chloride (mg/L)	BD	BD	0.24	BD	0.11	0.10	0.08

\*BD, Below detection limit.

**Table 5.** Guideline levels of metals in water described in the literature.

Parameter	Zn (mg/L)	Mn (mg/L)	Cu (mg/L)	Cd (mg/L)	Pb (mg/L)	Fe (mg/L)	Cr (mg/L)
<b>ATSDR</b>							
GMMC (water)	2.00	1.00	0.40	0.04	0.10		0.80
<b>NOAA-EPA</b>							
CMC (pH:7.50)	1.20	0.23	0.13	0.02	0.065		0.57
CCC (pH: 8.7)	1.20	0.08	0.09	0.0025	0.0025	0.10	0.074
Nigeria standard for water	3.00	0.20	1.00	0.003	0.01	0.30	0.05
<b>Present study</b>							
Dry season	0.11 - 0.56	0.24 - 0.47	0.01 - 0.51	BD	0.05 - 0.10	0.26 - 1.06	0.18 - 0.54
Rainy season	0.11 - 0.55	0.01 - 0.62	0.29 - 0.58	BD	0.08 - 0.30	0.01 - 0.26	0.07
Harmattan	0.24 - 0.62	0.11 - 0.70	0.00 - 0.48	BD	0.01 - 0.16	0.23 - 0.87	0.18

GMMC, Geometric mean maximum concentration; CMC, Criteria of maximum concentration; CCC, criteria of continuous concentration.

streams and waterways in runoff either due to natural weathering or anthropogenic soil disturbances. 68% of releases of Cu to water are estimated to derive from these processes (ATSDR, 2000). Seasonality was fairly observed in five out of the seven sampling points for Cu concentration distribution within the study area (Figure 3).

For Cu, there is very week negative linear correlation in its seasonal variation ( $r^2 = -0.10$ ). The physiochemical parameters do not suggest that the study area is polluted by Cu metal since there is no correlation between them. The concentrations of Cu metal exceeded the values posted by the two organizations (Table 5).

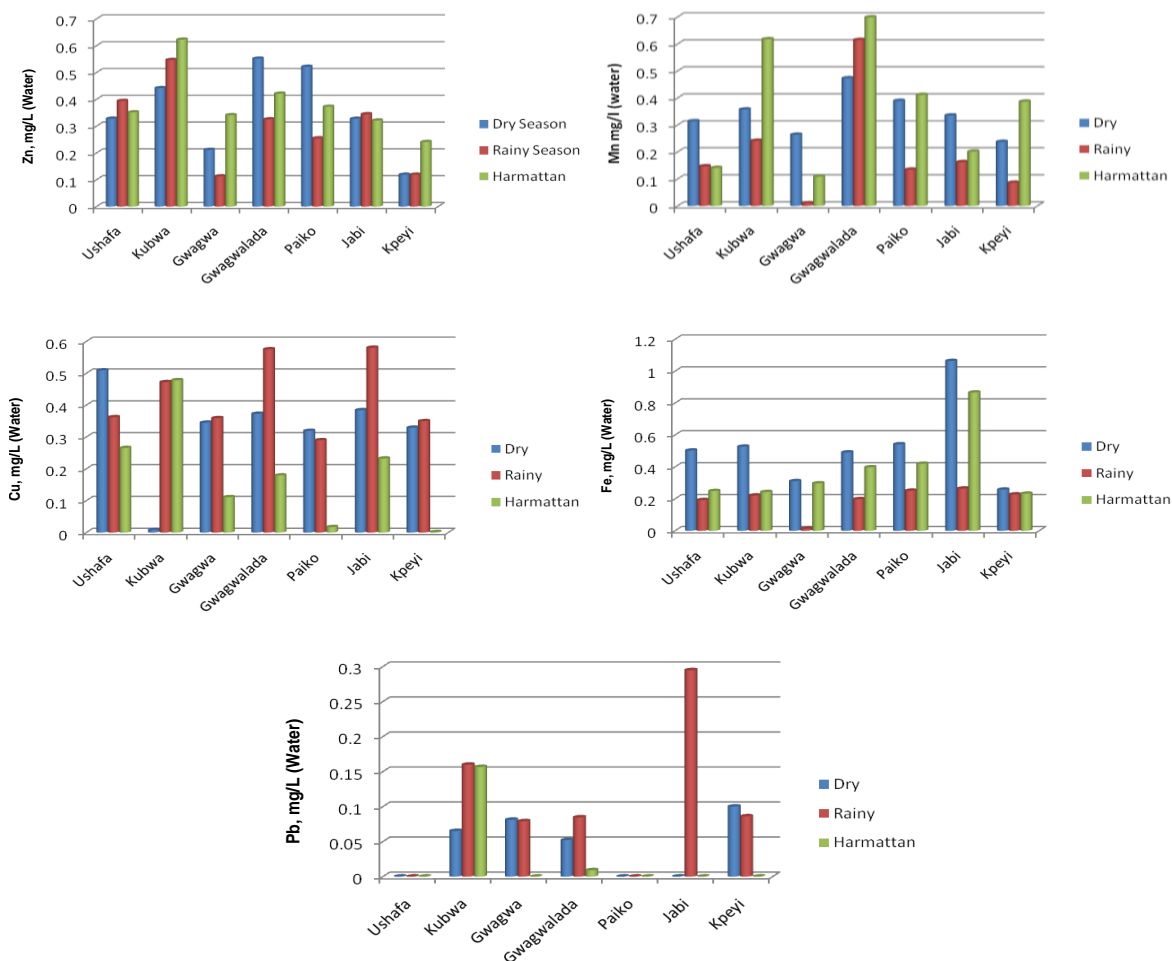


Figure 3. Seasonal variation for total metal concentration in water at the sampling sites.

Due to its high abundance within the earth's crust, Fe is ubiquitous in all freshwater environments and often reaches significantly higher concentrations in water and sediments than other trace metals (Kari-Matti, 1995). Fe concentration and speciation in water depends on redox and light condition, pH, and amount and type of dissolved organic matter. The oxidation of Fe(II) is accelerated by trace metals, phosphate, fluoride and particles. Large fluctuations in the fluxes and concentrations of Fe in river water occur particularly during storms and rapid floods (Vincent-Martorell et al., 2009). Fe showed seasonality and significant reduction in values during the rainy season (Figure 3, and Tables 2, 3, 4 and 5). The linear correlation coefficient,  $r^2$  of Fe between the seasons shows a positive value (0.52) in conformity with literature. The observed values were above the values posted by ATSDR and NOAA, but below the value suggested by Nigerian Industrial Standard for water.

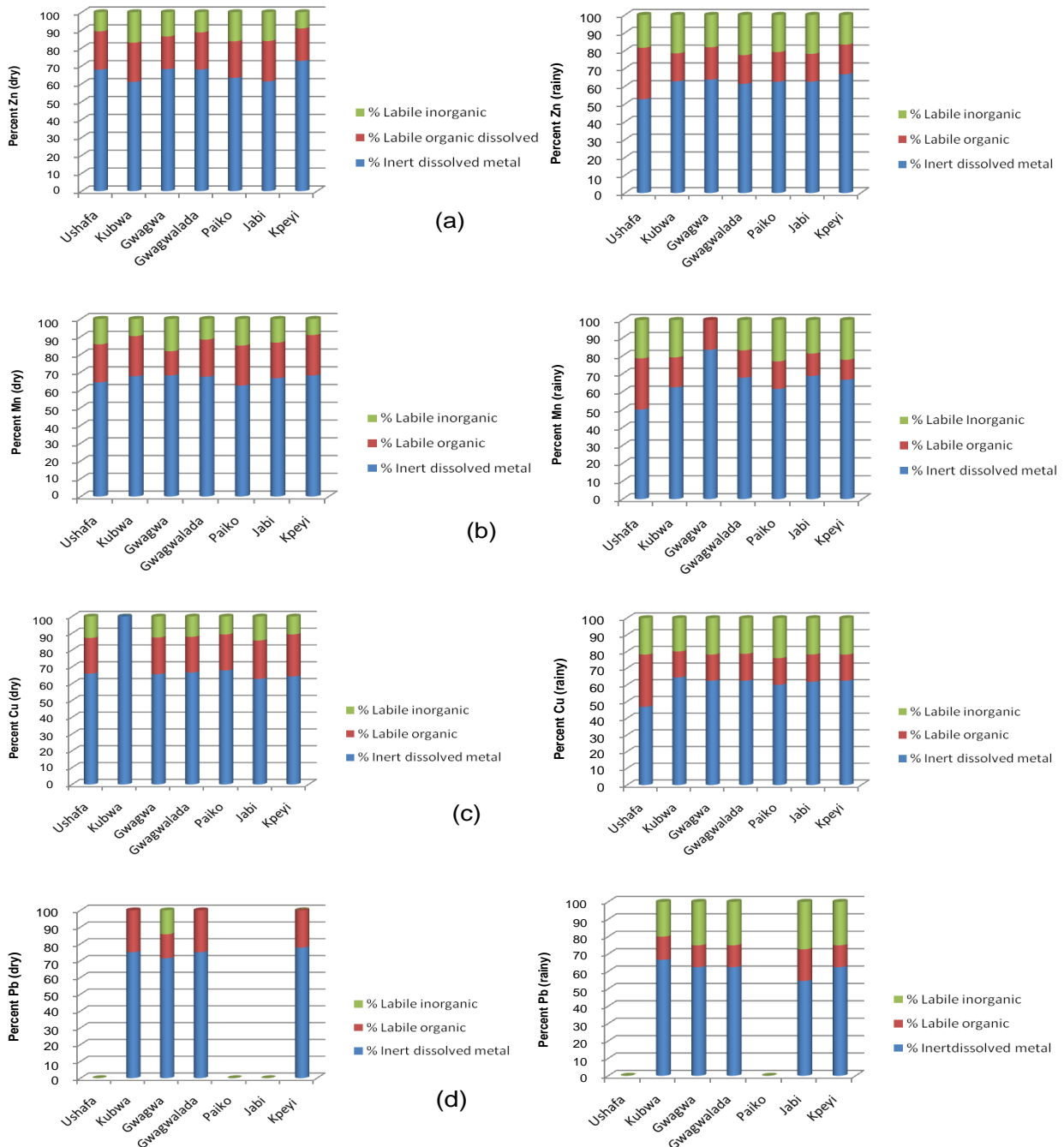
Cd is BD limit, throughout the seasons in surface water samples (Tables 2, 3 and 4). Pb has some level of significance, especially during the rainy season period

and its observed values just exceeded the values posted by EPA-NOAA (Tables 2, 3, 4 and 5, and Figure 3), but well below the ones posted by ATSDR. Cr has insignificant concentration values in the surface water at the sampling points, indicating non-occurrence of anthropogenic sources related to these metals (Tables 2, 3 and 4).

### Speciation of dissolved Zn, Mn, Cu, Cd, Pb, Fe, and Cr

Metal toxicity is not related to the total but rather to the free or labile metal ion concentration. Pollution of surface waters has led to strict regulations on maximum metal concentrations allowed in natural waters. However, it is often found that the uptake of heavy metals by organisms does not depend only on the total metal concentrations in solution. Instead, better correlations have been found between metal uptake and free metal ion concentrations (Slaveykova and Wilkinson, 2002) or labile metal





**Figure 4.** (a), Speciation of dissolved Zn in water from sampling sites (dry/rainy season); (b), speciation of dissolved Mn in water from sampling sites (dry/rainy season); (c), speciation of dissolved Cu in water from sampling sites (dry/rainy season); (d), speciation of dissolved Pb in water from sampling sites (dry/rainy season).

concentrations (Mylon et al., 2003). Free metal ion concentration is, in most cases, the key factor in predicting bioavailability.

Metal fractionation associated to dissolved metal (Zn, Mn, Cu, Cd, Pb, Fe, and Cr) were obtained following the scheme of speciation based on different pH sequential dilution (Figure 2). They were labile inorganic metal ( $F_1$ ), labile organic metal ( $F_2$ ), moderately labile inorganic

metal ( $F_3$ ), moderately labile organic metal ( $F_4$ ) and inert fraction metal ( $F_5$ ). It is important to emphasize that inert fractions are the most available. The results obtained from metal speciation (Figure 4a to d) suggested the following behaviours of metal in the studied area:

i) Zn concentrations at various sampling sites have between 58 to 70% inert dissolved fractions of the metal.

**Table 6.** Average metal concentrations in tissue of *O. niloticus* (tilapia) and *S. membranaceus* (catfish) in River Usuma.

Fish	Tissue	Zn (mg/kg)	Mn (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Fe (mg/kg)	Cr (mg/kg)
Tilapia	Gill	0.04	BD	0.16	BD	BD	0.11	BD
	Liver	0.07	0.38	0.26	BD	BD	1.40	BD
	Muscles	0.52	0.05	0.26	BD	BD	0.17	0.56
	Total	0.63	0.43	0.68	BD	BD	1.68	0.56
Catfish	Gill	0.02	0.05	0.12	BD	BD	0.59	BD
	Liver	0.05	0.33	0.23	BD	BD	1.23	BD
	Muscles	0.13	0.03	0.15	BD	BD	0.24	BD
	Total	0.20	0.41	0.50	BD	BD	2.06	BD

The maximum value was observed at sampling site 7-Kpeyi, close to the eastern exit of Usuma River from FCT. The minimum value was observed at site 2-Kubwa, which is close to source of Usuma river into FCT. The percentages of inorganic and organic labile fractions indicate levels below the values given by ATSDR and EPA-NOAA.

ii) The speciation of the metals is a linear function of the total metal concentrations in solutions. The total metals at the sites observed in this study are below the tolerable values given in the literature. Thus, the percentages of labile metals were inductively, below the tolerable values and they are shown in Figure 4a to d.

### Metal concentrations in fish tissues

The metal concentrations in muscle, gill and liver of *S. membranaceus* (catfish) and *O. niloticus* (tilapia) are shown in Table 6. McGeer et al. (2003) observed that the level of metal concentrations found in tissues of fishes is directly related to the exposure concentrations in water.

In studying the bioavailability of heavy metal in Usuma River, the values of metals' concentration in the fish tissues, were compared with some tolerable values posted by some organizations (Table 5). Various tissues of fish measured in the two species have no significant values when compared to tolerable values posted in Table 5. It is remarkable to note that metals' concentration in tissues of catfish is significantly lower than those in tilapia as observed by Owolabi (2008). This observation confirms the benthic nature of tilapia and equally correlates with higher consideration of metals associated with sediments. Concentration of metals in catfish tissues also shows relationship between pelagic fish and water column (Vicente-Martorell et al., 2009).

Correlations with labile forms, that is, labile and moderately labile inorganic; labile and moderately labile organic with the total metal correlations determine the relative bioavailability of these metals in these phases. This statement could not hold in this study because of non-correlation between these phases and the total metal

concentrations in water. The departure from the literature could be low level concentrations and non-seasonality observed through the study.

### Conclusions

The metallic contamination of River Usuma water column and biota were investigated in this study. Zn, Mn, and Fe showed the highest concentrations among the metals investigated, but below the tolerable values posted in the literature. The heavy metal concentrations were compared with quality guidelines values and non-significant toxicity was observed. Also, none of the metals showed significant availability in River Usuma. The effect of this pollution was studied by evaluation of metal accumulations in two species of fish (*O. niloticus*; tilapia and *S. membranaceus*; catfish). For that, analysis of metal concentrations in gill, liver and muscle were accomplished. High concentration of Fe was found in the two species. In addition, no correlation among metal content in tissues and different fractions of metal in water speciation studies were found.

### ACKNOWLEDGEMENTS

The present study was supported by Tertiary Education Trust Fund (TET Fund) and Advanced Chemistry Laboratory of Sheda Science and Technology Complex (SHESTCO) Abuja, Nigeria.

### REFERENCES

- Abuja (2012). New World Encyclopedia. <http://www.newworldencyclopedia.org/entry/Abuja>.
- Asuquo FE, Ewa-Oboho I, Udoh PJ (2004). Fish Species Used as Biomarker for Heavy Metals and Hydrocarbon Contaminations for the Cross River, Nigeria. *Environmentalist* 24:29-37.
- ATSDR (2000). Toxicological Profile for Manganese. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, GA.
- Heijerick DG, Karel AC, De S, Janssen RC (2002). Predicting acute zinc toxicity for *Daphnia magna* as a function of key water chemistry

- characteristics: Development and validation of a biotic ligand model. *Environ. Toxicol. Chem.* pp. 139-151.
- Kari-Matti V (1995). Direct and indirect effects of iron on river ecosystems. *Ann. Zool. Fennici.* 32:317-329.
- McGeer JC, Brix KV, Skeaff JM, DeForest DK, Brigham SI, Adams WJ, Green A (2003). Inverse relationship between bioconcentration factor and exposure concentration for metals: Implications for hazard assessment of metals in the aquatic environment. *Environ. Toxicol. Chem.* 22:1017-1037.
- Mylon SE, Twining BS, Fisher NS, Benoit G (2003). Relating the speciation of Cd, Cu, and Pb in two Connecticut rivers with their uptake in algae. *Environ. Sci. Technol.* 37:1261-1267.
- Owolabi OD (2008). The dietary habits of the upside-down catfish, *Synodontis membranaceus* (Osteichthyes: Mochokidae) in Jebba lake, Nigeria. *Int. J. Trop. Biol.* 56(2):931-936.
- Paquina PR, Gorsuchb JW, Aptec S (2002). The biotic ligand model: a historical overview. *Comp. Biochem. Physiol. Part C* 133:3-35.
- Riba I, Gracia- Lague E, Blasco J, Del Vallsi TA (2003). Bioavailability of Heavy Metals Bound to Estuarine Sediments as Function of pH and Salinity Values. *Chem. Speciation Bioavailab.* 15:101-114.
- Slaveykova VI, Wilkinson KJ (2002). Physicochemical aspects of lead bioaccumulation by *Chlorella vulgaris*. *Environ. Sci. Technol.* 36:969-975.
- United State Environmental Protection Agency (USEPA) (2000). 2000 National Water Quality Inventory. <http://www.Epa.gov305b2000report> retrieved August 6, 2003.
- Vicente-Martorell JJ, Galindo-Riaño MD, García-Vargas M, Granado-Castro MD (2009). Bioavailability of heavy metals monitoring water, sediments and fish species from a polluted estuary. *J. Hazard. Mater.* 162:823-836.
- Yilmaz AB (2005). Comparism of Heavy Metals of Grey Mullet (*M. cephalus* L.) and Sea Bream (*S. aurata* L.) Caught in Iskenderun Bay (Turkey). *Turk. J. Vet. Anim. Sci.* 29:257-262.