

## SPATIAL DISTRIBUTION OF HEAVY METALS IN RIVER USUMA SEDIMENTS AND STUDY OF FACTORS IMPACTING THE CONCENTRATION

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### ABSTRACT

Concentrations of heavy metals (Zn, Mn, Cu, Cd, Pb, Fe, and Cr) were measured in sediment and two fish species, catfish-*synodontis membranaceus* and tilapia-*oreochromis niloticus*, from River Usuma, Federal Capital Territory (FCT) Abuja Nigeria based on its economic standing. As an attempt to understand metal bioavailability and assess the potential impact on aquatic biota, a study of seasonal variations of heavy metal speciation of sediments was achieved. In comparison to some organizations tolerable values; most of the determined metals in the sediments, except Fe; were below guideline values. Availability of metals established were in the ranking: Cr < Fe < Pb < Zn < Cu < Mn. The potential hazardous impact of the determined metals and their validity were studied by evaluating correlations of metal levels in fish tissues and metal levels in fractions of sediment. High Cu and Fe levels were observed in liver tissue of both species, in agreement with higher total content of these metals in the sediment. Correlations among metals' concentration levels in fishes' tissues and sediments' fractions were found.

**Keywords:** *Metal pollution, Sediment, Fish, Metal Speciation*

### 1. INTRODUCTION

Water bodies receive metals from natural and anthropogenic sources. Naturally, the concentration of metals in sediments depends on types of soils or rocks present along the watershed. From anthropogenic activities, since after the Industrial Revolution, point sources from mining, municipal waste, industries and non-point sources from both agriculture and urban stormwater runoff have accumulated in water resources, settling to the bottom areas of waterbodies. Contaminated sediments pose a risk to the environment in two basic mechanisms: (1) ecological risk to aquatic and piscivorous animals and (2) toxic risks on terrestrial habitat when contaminated area is dredged and placed on land (Khan et al., 2000).

The analysis of bottom sediments has been used to determine the extent and source of heavy metal contamination in aquatic environment. Sediment have the capacity for accumulating heavy metals and other contaminants over time and serve to integrated assessment of contamination that has occurred in water body (Mark et al, 1982; Youssel et al., 1994) indicated that the transport of metals through sediments is a very slow process since the sediments possess high metal retaining capacity. Quantification of total metal concentration, alone however is not an enough evidence of potential toxic effect as the relationship between metal concentration and their bioavailability are not clearly established (Burton et al, 1994).

River Usuma's watershed traverses more than three quarter of breadth of Federal Capital Territory (FCT) and relatively to an extent, some part of Savannah region which covers the north central zone of Nigeria. River Usuma supplies fishes which are being sold to public for human consumption and its bank is being used for dry season farming. Data on Usuma river water quality and the health status are scare, it becomes necessary to carry out a detailed water quality assessment of the river and investigate the potential risk of water column contamination from river sediments for the municipal water works that relies on good quality source of water. It makes good public health sense, good economic and environmental sense to prevent water contamination at the source (USEPA, 2000).

The work studies the distribution of heavy metals' speciation from the sediments of River Usuma and their potential impact on aquatic biota. For this purpose, concentrations of heavy metals (Zn, Mn, Cu, Cd, Pb, Fe, Cr) were measured in tissues (gill, liver and muscle) of two fishes' species (catfish-*synodontis membranaceus* and tilapia-*oreochromis niloticus*) with pelagic and benthic behaviours, respectively (Owolabi, 2008; Peña-Mendoza et al, 2005). The sampling points were designated in some towns through which River Usuma traverses. Analyses of metal concentrations in samples were performed by computer controlled Atomic Absorption Spectrometer (AAS 969). Metals' speciations in sediment were achieved by the method of sequential extraction of the Standards, Measurements and Testing programme of the European Union (SM & T—formerly BCR).

2. MATERIALS AND METHODS

2.1 Sampling sites

The Federal Capital Territory falls within the Savannah Zone vegetation of the West African sub-region. It is slightly west of the center of the country. Its area covers 7,315 square km (Abuja, 2012). River Usuma with its source from Gurara River; enters through the northern part of Federal Capital Territory (FCT) at Bwari and splits at Ushafa with one arm flowing eastward towards Kpeyi and the other flowing westward towards Paiko and its length stretches over 143km 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.

Table 1. Names of the sampling locations and their coordinates

Sampling no.	sites	Name of sampling site	East latitude	North longitude	Elevation (m)
1		Ushafa	7° 24'	9° 11'	1500
2		Kubwa	7° 21'	9° 09'	1300
3		Gwagwa	7° 20'	9° 06'	1200
4		G/lada	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

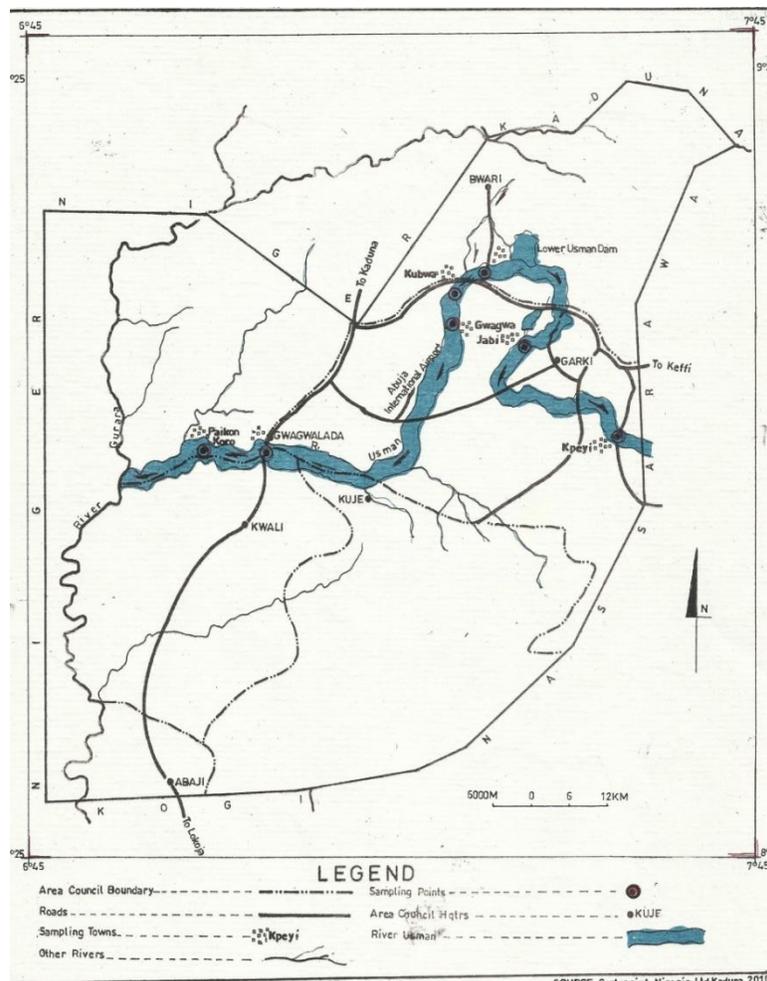


Figure 1. Area map of Federal Capital Territory Abuja showing sampling towns locations

Seven sampling sites were selected among the towns river Usuma traverses (Figure 1). The first one 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 one 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.

Metal determinations in sediments and fish extracts were carried out by means of a computer controlled Atomic Absorption Spectrometer (AAS 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, Cr respectively. 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 the experiments. Samples digestions were done by UV method.

### 3. SAMPLE COLLECTION AND PRE-TREATMENT

#### 3.1 Sediments collection and analysis

Sediment samples were collected from the surface sediment (2–20 cm) using grab method, and immediately placed into 1 litre high-density polyethylene (HDPE) bottles that were pre-washed with 10%, v/v HCl acid and also pre-rinsed with deionised water and transported to the laboratory where they were stored at  $-4^{\circ}\text{C}$  until analysis. Samples were air dried, grinded using an agate mortar, sieved through a stainless steel mesh in order to obtain fine particle-size fractions and stored in polyethylene bottles until sequential extraction analysis. The sequential extraction procedure was performed according to the procedure recommended by the Standards, Measurements and Testing programme of the European Union (SM & T—formerly BCR), for the determination of 8 heavy metals (Zn, Mn, Mg, Cu, Cd, Pb, Fe, Cr) in sediments collected from different sampling sites (Tokalio-Glu et al., 2003). The BCR (Community Bureau of Reference) sequential extraction procedure is summarized in Table 2.

**Exchangeable metals:** 40 mL of  $0.11 \text{ mol L}^{-1}$  acetic acid was added to 1.00 g of dry soil sample in a 50-mL polypropylene tube. The mixture was shaken for 16 hours at  $22\pm 3^{\circ}\text{C}$  (overnight) at 400 rpm. The extract was separated from the solid phase by centrifugation at 3800 rpm for 20 min. The supernatant liquid was decanted into a 100-mL beaker and then covered with a watch-glass. The residue was washed by adding 20 mL of double-distilled water, shaking for 15 min, and then centrifuging. The second supernatant liquid was discarded without any loss of residue.

**Metals bound to iron and manganese oxides (Reducible).** Metals bound to iron and manganese oxides were extracted by adding 40 mL of  $0.1 \text{ mol L}^{-1}$  hydroxylammonium chloride (adjusted to pH 2 with  $2 \text{ mol L}^{-1}$  nitric acid) onto the residue from the first step.

**Table 2.** The BCR (Community Bureau of Reference) three-stage sequential extraction scheme

Extraction Steps	Reactive / concentration / pH	Solid Phase
1	Acetic acid: $\text{CH}_3\text{COOH}$ ( $0.11 \text{ mol/l}$ ), pH 2.85	Exchangeable, water and acid soluble (e.g., carbonates)
2	Hydroxylammonium chloride: $\text{NH}_2\text{OH}\cdot\text{HCl}$ ( $0.1 \text{ mol/l}-1$ ) at pH 2	Reducible (e.g., iron/manganese oxides)
3	Hydrogen peroxide: $\text{H}_2\text{O}_2$ ( $8.8 \text{ mol/L}$ ), followed by ammonium acetate: $\text{CH}_3\text{COONH}_4$ ( $1.0 \text{ mol/L}$ ) at pH 2	Oxidisable (e.g., organic substance and sulphides)
(Residual) <sup>a</sup>	Aqua regia: $3\text{HCl} + \text{HNO}_3$	Remaining, non-silicate bound metals

<sup>a</sup>Digestion of the residual material is not a speciation of the BCR protocol.

After shaking the mixture for 16 hours at  $22\pm 3^{\circ}\text{C}$ , it was centrifuged for 15 min, and then decanted into a beaker. Using 20 mL of distilled water, the residue was washed, centrifuged, and the supernatant discarded.

**Metals bound to organic matter and sulphides (Oxidisable).** 10 mL of  $8.8 \text{ mol L}^{-1}$  hydrogen peroxide was carefully added in small aliquots to the residue in the centrifuge tube. The tube ingredients were digested at room temperature for 1 hour with occasional manual shaking. The procedure was continued for 1 hour at  $85^{\circ}\text{C}$  and the

volume reduced to a few millilitres by further heating in a water bath. A second aliquot of 10 mL of hydrogen peroxide was added to the residue and the digestion procedure was repeated. The solution was heated to near dryness, and 50 mL of 1.0 mol L<sup>-1</sup> ammonium acetate solution (adjusted to pH 2 with nitric acid) was added to the moist residue. The sample solution was shaken and centrifuged, and the extract was separated as described above.

**Residual.** The analysis of the residue was performed using aqua regia for metals insoluble in the previous steps. For this purpose, first 6 mL of double-distilled water and then aqua regia solution in a sequence of 15 and 10 mL were added to the remaining residue. After adding each aqua regia solution, the residue was evaporated to near dryness on a water bath. The extract was filtered through filter paper by adding 1 mol L<sup>-1</sup> HNO<sub>3</sub> solution in small amounts on the last residue in the centrifuge tube. The tube walls were carefully washed with the same acid solution and then the dregs were collected in a beaker. The extracts acquired after each extraction stage applied, sequentially were evaporated to near dryness. Each extract was completed to 5 mL with 1 molL<sup>-1</sup> HNO<sub>3</sub>; the extract of ammonium acetate was made up to 6 mL. The determinations of Zn, Mn, Mg, Cu, Cd, Pb, Fe, and Cr in the extracts were performed by AAS.

### 3.2 Fish collection and analysis

The samples of matured *synodontis membranaceus* (catfish) and *oreochromis niloticus* (tilapia) were collected at sampling sites and were transported in aerated tanks to the analysis laboratory. Catfish and tilapia are commonly 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 7mL of 65% HNO<sub>3</sub>, and liver samples (0.2 g), containing higher organic matter, were digested with 4mL of 65% HNO<sub>3</sub> and 2mL of 30% H<sub>2</sub>O<sub>2</sub>. The following microwave program was applied: 4min for 200W, 5min for 400W and as last step 10min for 600W. After microwave digestion, samples were diluted up to 25mL with deionised water. Metal concentrations of digested

**Table 3.** Total metal concentrations and physiochemical parameters in sediment dry season, March 2011

Metal/mg/l ±Rsd(%)	Sampling Sites						
	1 Ushafa	2 Kubwa	3 Gwagwa	4 G/Lada	5 Paiko	6 Jabi	7 Kpeyi
Zn ±Rsd	0.92±0.40	1.26±0.10	1.01±0.90	0.91±1.10	1.52±0.40	1.33±0.10	1.46±0.10
Mn ±Rsd	1.82±0.40	0.64±0.30	1.86±0.90	1.21±0.70	1.32±0.30	0.93±0.90	1.40±0.60
Mg ±Rsd	25.67±0.90	12.28±0.40	33.19±0.60	14.42±0.10	31.22±0.80	11.28±0.30	11.52±0.30
Cu ±Rsd	1.02±1.40	0.64±0.40	1.74±1.00	0.96±0.30	1.09±0.90	1.13±0.70	0.80±0.70
Cd ±Rsd	*BD	BD	BD	BD	BD	BD	BD
Pb ±Rsd	0.52±0.80	0.52±0.20	0.24±0.60	0.51±0.90	0.10±0.60	0.34±0.70	0.42±0.80
Fe ±Rsd	0.93±0.20	2.55±0.30	1.03±0.10	1.11±0.50	1.24±0.10	0.96±1.90	1.33±0.10
Cr ±Rsd	0.70±0.20	0.45±0.80	0.48±0.50	0.79±0.20	0.86±0.60	0.80±0.50	0.23±0.70
Na	4.84	6.10	5.10	5.75	2.79	6.00	4.40
K	3.70	2.90	1.62	2.05	2.90	1.60	2.80
pH	9.55	8.14	8.49	9.14	9.13	9.14	8.89
TDS(mg/l)	633	564	849	655	884	558	497
Cond µs	492	479	795	792	794	499	521
Alkalinity	4.44	2.88	3.58	5.14	3.18	3.89	5.81
%DO <sub>2</sub>	91	92	88	46	45	69	92
BOD	11.25	22.30	16.10	36.00	42.40	56.10	36.50
TSS(mg/l)	51	124	11.46	98	6.55	56	88
Turb	110	204	253	246	152	162	192
Sulph/mg/l	17.2	191.6	2012.0	1440.80	91.5	25.90	204.50
Phos/mg/l	0.44	1.00	3.88	1.66	0.44	0.33	1.22
Nitrat/mg/l	0.01	BD	0.07	BD	0.10	0.25	BD
Chlor/mg/l	BD	BD	0.19	BD	BD	0.05	0.09

BD: Below detection limit

**Table 4.** Total metal concentrations and physiochemical parameters in sediment; rainy Season, July 2011

Metal(mg/l) ±Rsd(%)	Sampling Sites						
	1 Ushafa	2 Kubwa	3 Gwagwa	4 G/Lada	5 Paiko	6 Jabi	7 Kpeyi
Zn ±Rsd	1.12±0.40	0.75±0.10	1.25±0.90	0.76±1.10	1.09±0.30	1.21±0.10	0.79±0.10
Mn ±Rsd	2.09±0.40	0.55±0.40	1.81±0.90	1.34±0.70	1.72±0.30	1.73±0.90	1.92±1.30
Mg ±Rsd	29.14±0.40	16.72±0.20	31.18±1.90	15.49±0.10	33.29±0.30	12.06±0.50	17.01±1.10
Cu ±Rsd	1.33±1.40	0.94±1.20	1.83±1.00	1.09±1.70	1.55±0.90	1.33±1.30	0.94±0.70
Cd ±Rsd	0.08±1.20	0.09±0.80	*BD	0.08±1.00	BD	0.12±0.30	BD
Pb ±Rsd	0.62±0.80	0.52±0.90	0.53±0.10	0.26±0.50	BD	0.48±0.70	0.53±1.10
Fe ±Rsd	0.95±0.20	1.27±0.80	1.28±0.50	0.46±0.50	1.60±0.10	0.91±1.90	0.93±0.20
Cr ±Rsd	1.16	1.21	1.28±0.70	1.63±0.80	0.78±0.10	0.95±	0.79±0.20
Na	4.97	4.16	5.40	5.59	4.36	3.49	4.51
K	3.27	2.91	2.18	2.46	2.51	1.58	2.49
pH	9.68	7.89	8.89	9.81	9.45	9.24	9.12
TDS(mg/l)	659.00	482.00	649.00	642.00	778.00	496.00	556.00
Conductivity µs	428.00	567.00	668.00	819.00	810.00	348.00	467.00
Alkalinity	5.99	5.61	5.71	9.42	4.52	5.12	7.49
%DO <sub>2</sub>	92	99	89	99	97	96	97
BOD	13.00	45.80	14.50	21.00	44.30	29.40	33.00
TSS(mg/l)	19.00	20.00	17.40	56.00	7.89	39.00	48.00
Turbidity	76.00	256.00	83.00	140.00	94.00	124.00	49.00
Sulphate(mg/l)	55.10	230.00	2516.00	1567.00	152.00	1256.00	305.00
Phosphate(mg/l)	5.44	3.79	6.23	9.46	4.15	3.54	4.13
Nitrate (mg/l)	2.64	3.14	3.41	2.89	2.96	4.15	0.94
Chloride (mg/l)	0.56	0.84	3.54	1.96	1.20	2.46	1.89

BD: Below Detection limit

tissue samples were analysed by computer controlled Atomic Absorption Spectrometer (AAS 969). Blanks were also performed and measured for all metals following the same procedure.

## 4. RESULTS AND DISCUSSIONS

### 4.1 Metal concentrations in sediment

Non-anthropogenic factors taken into consideration in this study which are likely to impact metal concentration in sediments are: pH, texture of sediment, and organic matter content. Usually, a pH level above six tends to show more metals adsorbed into sediment than a lower pH. Fine-grained clay particles with more surface area contained more metals than coarse grained sand (Horowitz et al., 1987). Sediments containing high levels of organic matter are likely to contain higher concentration of heavy metals as compared to sediments lacking organic matter.

Rivers are zones of complex interaction due to urban storm water runoff that trap heavy metals bonded in the fine-grained sediments into rivers. Depositional acceleration of clay mineral due to salinity change, favouring the entrapment and accumulation of metal adsorbed on clay particles can occur at the riverbed (Martorell et al, 2008). Due to this process of co-precipitation that happen when metal rich storm water runoff mix with river water and undergo a notable increase of pH, the content of metal in sediment of riverbed are higher than the content in the rivers as many author has described (Galan et al, 2003; Morillo et al, 2002).

### 4.2 Total metal concentration in sediments

The total metal concentrations and average values for each sampling sites found in sediment of River Usuma in this study are shown in Tables 3, 4 and 5; for dry, rainy and harmattan seasons respectively. Also, their seasonal variations are shown in figure 2. Metal concentrations ranged as followings: (for the dry season values) Zn: 0.91–1.52mgkg<sup>-1</sup>; Mn: 0.64–1.86mgkg<sup>-1</sup>; Cu: 0.64–1.74mgkg<sup>-1</sup>; Pb: 0.10–0.52mgkg<sup>-1</sup>; Fe: 0.96–1.32mg kg<sup>-1</sup>; Cr: 0.23–0.86mgkg<sup>-1</sup>, and the mean concentration in decreasing order is: Pb < Cr < Fe < Zn < Cu < Mn. The rainy season values range as: Zn: 0.76 – 1.25mgkg<sup>-1</sup>; Mn: 0.55 – 2.09mgkg<sup>-1</sup>; Cu: 0.94 – 1.55mgkg<sup>-1</sup>; Cd: 0.08 – 0.12mgkg<sup>-1</sup>; Pb: 0.26 – 0.62mgkg<sup>-1</sup>; Fe: 0.46 – 1.60mgkg<sup>-1</sup>; Cr: 0.78 – 1.63mgkg<sup>-1</sup> and ranked in increasing order as: Cd < Pb < Zn < Cu < Fe < Cr. The harmattan values are: Zn: 0.99 – 1.66, Mn: 0.76 – 1.90, Cu: 0.77 – 1.98, Pb: 0.16 – 0.65, Fe: 0.89

– 2.76 and Cr: 0.06 – 0.91mg/kh. Their order of ranking is: Pb < Cr < Zn < Mn < Cu < Fe. It is worthy to note that higher mean values were found in the last sampling sites (5 & 7) near the mouth of the Usuma, according to process of metal deposition. Only Cd has higher mean values in Ushafa site.

**Table 5.** Total metal concentrations and physiochemical parameters in sediment Harmattan season, Feb. 2012

Metal(mg/l ±Rsd(%))	Sampling Sites						
	1 Ushafa	2 Kubwa	3 Gwagwa	4 G/Lada	5 Paiko	6 Jabi	7 Kpeyi
<b>Zn ±Rsd</b>	1.01±0.40	1.36±0.10	1.31±0.90	0.99±1.10	1.63±0.40	1.13±0.10	1.66±0.10
<b>Mn ±Rsd</b>	1.90±0.40	0.76±0.30	1.84±0.90	1.31±0.70	1.42±0.30	0.83±0.90	1.53±0.60
<b>Mg ±Rsd</b>	28.67±0.90	12.48±0.40	36.10±0.60	16.02±0.10	33.12±0.80	12.48±0.30	13.72±0.30
<b>Cu ±Rsd</b>	1.66±1.40	0.77±0.40	1.98±1.00	1.00±0.30	1.11±0.90	1.03±0.70	0.79±0.70
<b>Cd ±Rsd</b>	*BD	BD	BD	BD	BD	BD	BD
<b>Pb ±Rsd</b>	0.65±0.75	0.58±0.20	0.54±0.60	0.63±0.90	0.16±0.86	0.35±0.70	0.52±0.80
<b>Fe ±Rsd</b>	0.89±0.20	2.76±0.30	1.23±0.10	1.57±0.50	1.48±0.10	0.98±1.90	1.24±0.10
<b>Cr ±Rsd</b>	0.06±0.84	0.47±0.80	0.47±0.87	0.72±0.30	0.91±0.70	0.78±0.58	0.29±0.66
<b>Na</b>	4.89	6.33	5.25	5.71	2.69	5.79	4.00
<b>K</b>	3.70	2.70	1.82	2.08	2.87	1.65	2.65
<b>pH</b>	9.21	8.11	8.24	9.11	9.25	9.02	5.74
<b>TDS(mg/l)</b>	623	439	633	622	746	481	504
<b>Cond µs</b>	399	507	628	722	782	302	444
<b>Alkalinity</b>	4.15	2.11	4.01	5.88	4.01	3.99	5.16
<b>%DO<sub>2</sub></b>	94	95	92	96	89	91	98
<b>BOD</b>	15.00	23.00	12.40	19.00	24.70	24.20	28.00
<b>TSS(mg/l)</b>	14	14	16.40	44	8.01	33	41
<b>Turb</b>	66	251	77	130	88	102	55
<b>Sulph/mg/l</b>	44.20	221	2213	1440.80	152	110.10	311
<b>Phospmg/l</b>	3.12	2.19	5.61	4.09	1.88	1.89	1.85
<b>Nitrat/mg/l</b>	0.19	2.15	0.89	1.55	1.46	1.24	0.16
<b>Chlor/mg/l</b>	0.12	0.12	0.21	1.61	0.55	1.08	0.19

BD: Below detection limit

Table 6 shows the results of the present study compared with guideline levels given by ATSDR, EPA and US National Oceanic and Atmospheric Administration (NOAA). Concentrations of all metals studied in sediments were lower than guidelines values recommended by the three organizations, except the Fe value that is little above the guideline levels.

#### 4.3 Sequential extraction of metal

The seasonal distribution of metals in sediment following BCR procedure is shown in Figure 3. Cr was the most mobile metal mainly bound to weak acid and carbonates (80% and 75% in dry and rainy season respectively). Pb has similar values of about 80% mobile metal especially in few sampling sites during the rainy season.

Other elements have their residual components dominating the fractionation in the water sediment samples. In the same way, Zn showed a high mobility appearing mainly bound to most labile fractions (exchangeable fraction ranging over 10–25%), probably due to the incorporation into these phase of Zn that precipitates as coating onto amorphous or poorly crystallized components of the sediments. Cu showed the highest percentage of reducible fraction (ranging from 5% to 60% in the dry season), probably due to Cu forms easily complexes with organic matter associated to reducible fraction. The organic fraction released in the reducible step is not considered very available because it is thought to be associated with stable high-molecular weight humic substances that release small amounts of metal slowly (Morillo et al, 2003).

Fe has little but insignificant mobility, as it was associated to reducible, oxidisable and residual fractions. From the results, the availability patterns of metals were similar in water and sediment samples.

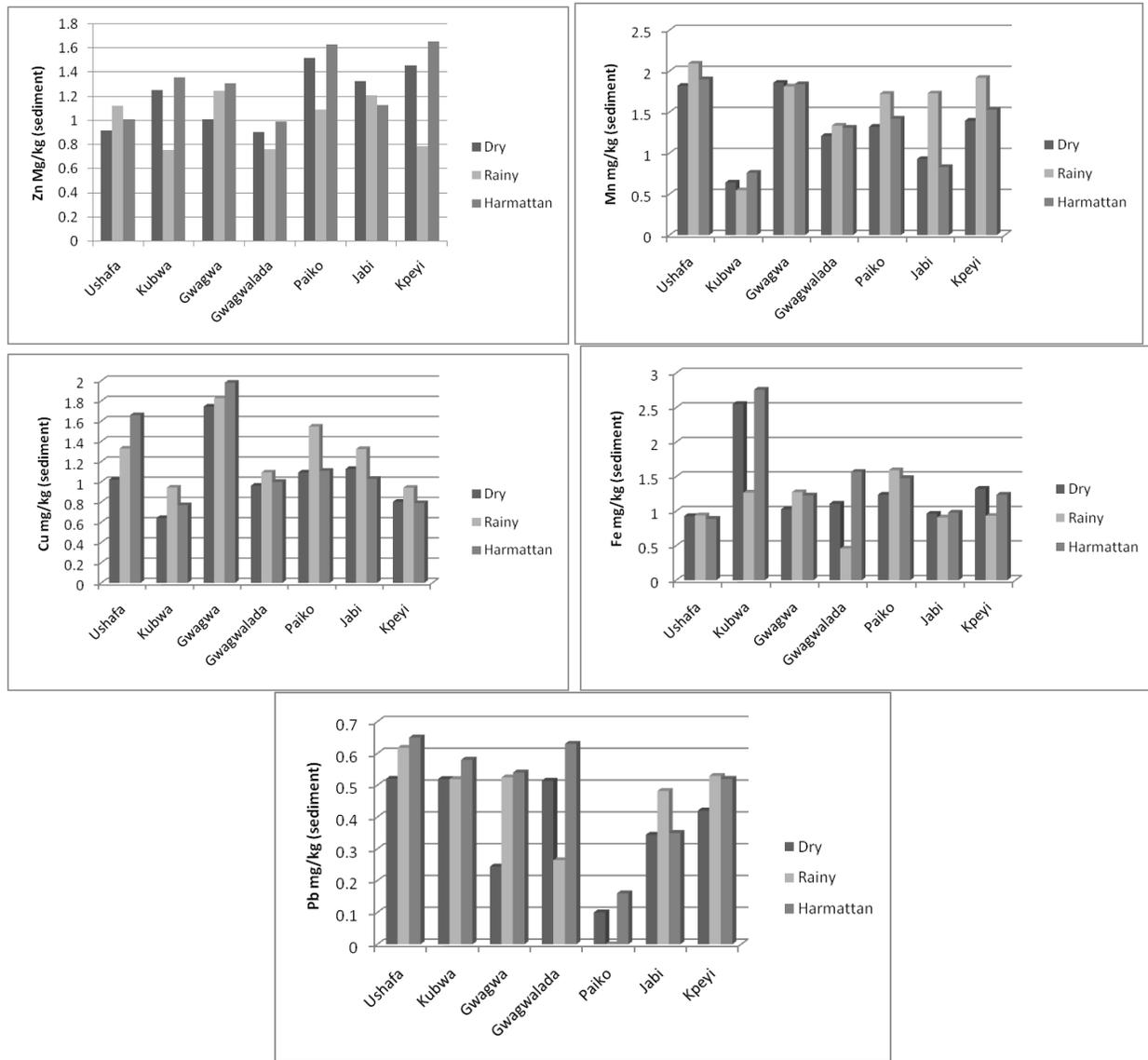
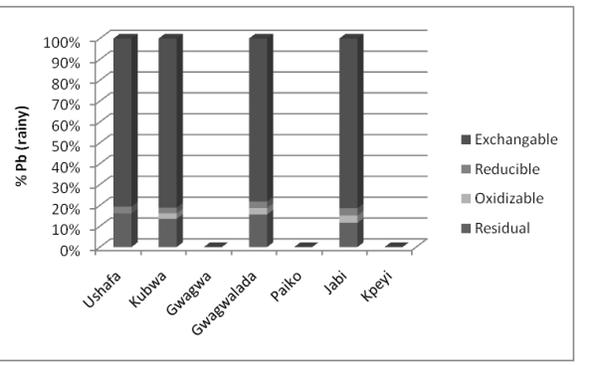
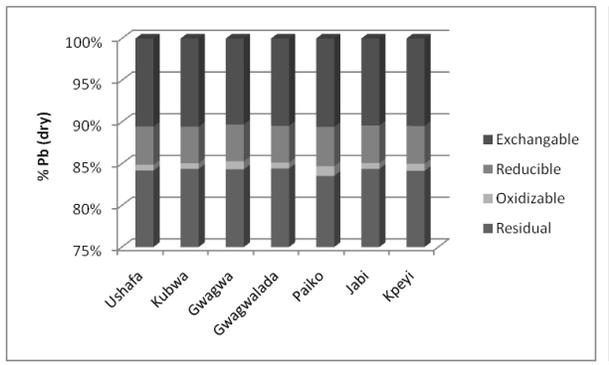
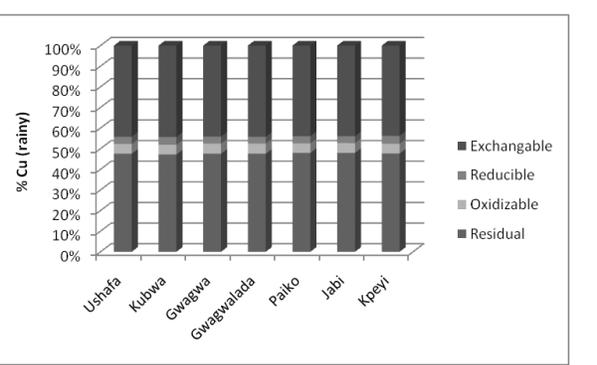
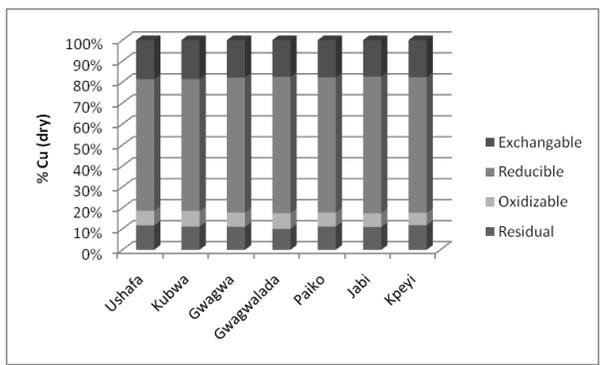
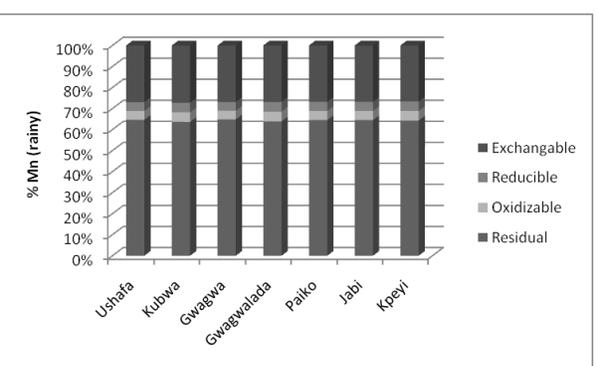
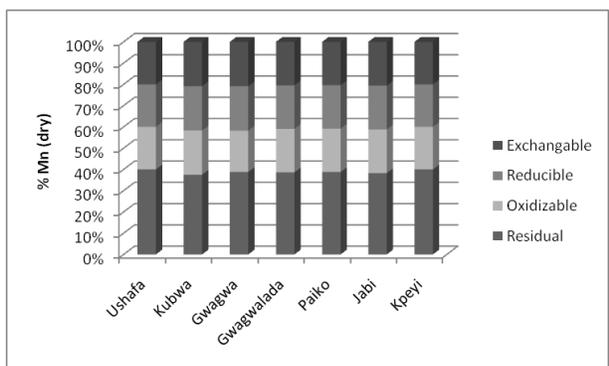
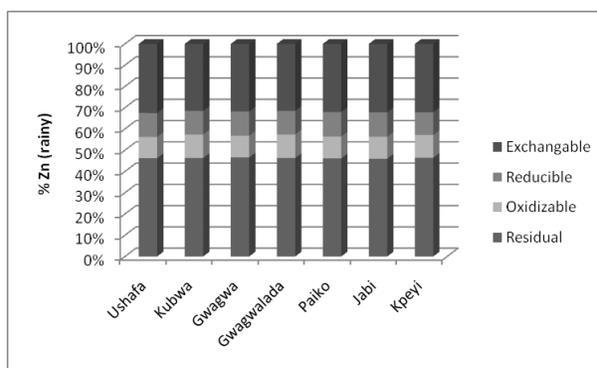
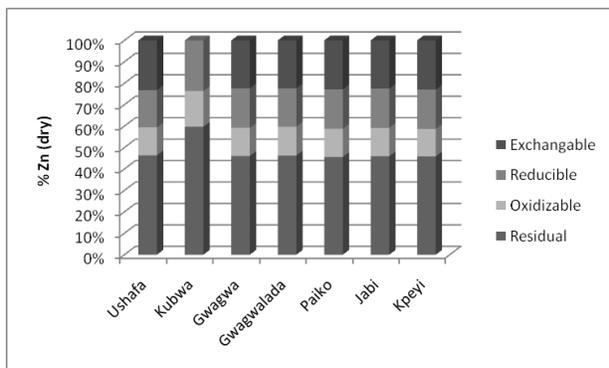


Figure 2: Seasonal variation for total metal concentration in sediment at the sampling

Table 6: Guideline levels of metals in sediment described in the literature

	Zn (mg/kg)	Mn (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Fe (mg/kg)	Cr (mg/kg)
<b>ATSDR</b>							
<b>GMMC</b>	1.00	1.00		0.02	0.90		0.20
<b>EPA</b>	9.80	9.30	2.80	0.583	3.70	1.88	3.63
<b>NOAA</b>	3.80	4.00	2.50	0.10-0.30	1.70	0.18	1.30
<b>Present study</b>							
<b>Dry season</b>	0.91-1.52	0.64-1.86	0.64-1.74	BD	0.10-0.52	0.93-1.33	0.23-0.86
<b>Rainy season</b>	0.76 – 1.25	0.55-2.09	0.94–1.83	0.08-0.11	0.26–0.62	0.26–1.06	0.77–1.62
<b>Harmattan</b>	0.24 – 0.62	0.11 – 0.70	0.01 – 0.48	BD	0.01 – 0.16	0.23– 0.87	0.18

GMMC: Geometric mean maximum concentration



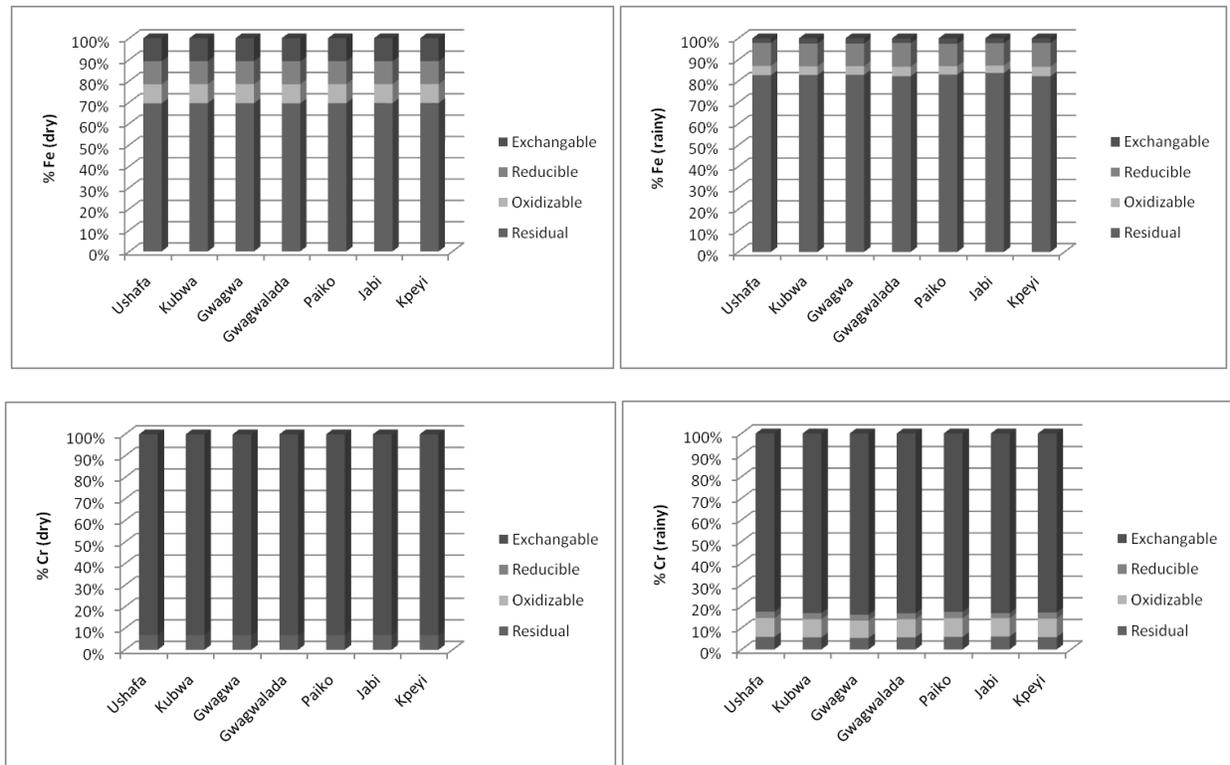


Figure 3: Distribution of heavy metals in sediment; determined by BCR procedure sites

**4.4 Metal concentrations in fish tissues**

The metal concentrations in muscle, gill and liver of *synodontis membranaceus* (catfish) and *oreochromis niloticus* (tilapia) are shown in Table 7. McGeer et al (2003) observed that the level of metal concentrations found in tissues of fishes is directly related to the exposure concentrations in river water and sediment.

**Table 7:** Average metal concentrations in tissue of *oreochromis niloticus* (tilapia) and *synodontis 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)
<b>Tilapia</b>	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
	<b>Total</b>	<b>0.63</b>	<b>0.43</b>	<b>0.68</b>	<b>BD</b>	<b>BD</b>	<b>1.68</b>	<b>0.56</b>
<b>Catfish</b>	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
	<b>Total</b>	<b>0.20</b>	<b>0.41</b>	<b>0.50</b>	<b>BD</b>	<b>BD</b>	<b>2.06</b>	<b>BD</b>

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 6). Various tissues of fish measured in the two species have no significant values when compared to tolerable values posted in table 6. It is remarkable to note that metals' concentration in tissues of catfish is significantly lower than those in tilapia. 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 (Owolabi, 2008).

Correlations of metal concentrations in fish tissues with sediment fractions were scarce; however, the concentrations of the metals in tilapia tissues were relatively higher than those of catfish; which could be due to benthic nature of tilapia. Within the sediments, different fractionations were established; such as exchangeable, oxidizable, reducible

and residual, which are determining factors of metal bioavailability in the water sediments. There is no notable correlation between the metal concentrations in fishes' tissues and those of the sediments.

## 5. CONCLUSION

The metallic contamination of sediment of River Usuma was investigated in this study. Zn, Mn and Fe, showed the highest concentrations in the sediment. Metal concentrations were compared with quality guidelines values and they were below the tolerable values posted by selected organizations, except Fe that exceeded the values in the sediments. In addition, speciation analysis of sediment was performed providing information of availability of metal. 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 (*oreochromis niloticus*; tilapia and *synodontis 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 sediment from speciation studies were found. It is noteworthy that catfish showed no correlations with fractions of sediment, but catfish did indicating different availability of metals related to the different behaviour of these species.

## 6. ACKNOWLEDGEMENT

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