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## **Analyses of Selected Heavy Metals and Mineral Elements in Pollution Prone Aquatic Environments of North-Western Region of Nigeria**

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### **ABSTRACT**

Pollution by heavy metals deserves a special attention because of their high toxicities and persistence in aquatic environment, especially with respect to such ecosystems that receive chronic inputs of these metals. Physicochemical properties such as pH, Dissolved Oxygen (DO) and Biochemical Oxygen Demand (BOD) that can influence the availability of the metals in aquatic environment were investigated. Water, sediment and floodplain samples were digested by standard laboratory methods. Metal analyses on water, sediment and flood plain samples were carried out by Atomic Absorption Spectrophotometry (AAS). On the whole, the pH of water, sediment and floodplain samples were in the range of neutrality to a little alkalinity (6.52-7.70). The Dissolved Oxygen (DO) for the two seasons were significantly ( $p > 0.05$ ) low in all the study sites. Biochemical Oxygen Demand (BOD) for Rivers Bunsuru and Gagare were also significantly ( $p > 0.05$ ) low when compared with WHO standard of  $7.0 \text{ mg L}^{-1}$ . Rima River and Goronyo Dam had BOD ( $p < 0.05$ ) on the high side. Except for Rima River, all other rivers had Cu concentrations significantly ( $p < 0.05$ ) high. Lead (Pb) concentrations during the rainy season sampling from River Rima and Goronyo Dam were present above the WHO acceptable limit of  $2.0 \mu\text{g g}^{-1}$ . Other mineral elements and Cd were however within the WHO limits. Significant levels of Pb in water, sediment and floodplain samples mean possible Pb toxicity to aquatic organisms and by implication man through food chain. Presence of Cd even at WHO acceptable limit is at the potential risk of bioaccumulation.

**Key words:** Heavy metals, bioaccumulation, toxicity, mineral elements, physicochemical

### **INTRODUCTION**

Heavy metals originate within the earth where they may be harmless until released by human interference. As the levels of metals rise in the air, water and sediments, they also rise within human bodies contributing to chronic diseases, learning disorders, cancer and premature aging (Keen *et al.*, 1981). Once in the body, they compete with and displace the essential minerals such as zinc, copper, manganese and calcium and bind their receptor sites causing diffuse symptoms by affecting nerves, hormones, digestion and immune function. In general, heavy metals produce their toxicities by forming complexes or ligands with other organic compounds. These modified biological molecules lose their ability to function properly, resulting in malfunction or death of the affected cell (Mouvet, 1984). The most important common groups involved in ligand formation are oxygen, sulphur and nitrogen. When metals bind to these groups they inactivate important enzyme

systems, or affect protein structure. The degree to which a system, organ, tissue or cell is affected by a heavy metal toxin depends on the toxin itself and the individual's degree of exposure. The metals affect an individual in such a way that its respective accumulation within the body leads to a decline in mental, cognitive and physical health of the individual (Lauwreys, 1979). The toxicity is frequently the result of long-term low-level exposure to heavy metal toxin that is present in the environments; air, water and food. The symptoms are difficult to be associated with their cause, because they are very similar to symptoms of other health conditions. Sediment integrates contaminants over time and is in constant flux with the overlying water column. The analysis of heavy metals in the sediments permits detection of pollutants that may either be absent or in low concentration. The distribution of metals in sediments will also provide a record of a spatial or temporal history in a particular region or ecosystem. The occurrence of elevated level of heavy metal in the sediment can be a good indicator of man-induced pollution and high levels can often be attributed to anthropogenic influences rather than natural enrichment of sediment by geological weathering (Lord and Thompson, 1988). Once heavy metals are discharged into estuaries and coastal waters, they rapidly become associated with particulates and are incorporated in bottom sediments (Hanson *et al.*, 1993). The accumulation of metals from underlying water to the sediment is dependent on a number of environmental factors such pH, ionic strength, anthropogenic input and concentration of organic and inorganic ligands and the available surface area for absorption. During rainy season, the runoff (containing the toxic metal) from the mining sites and the processing points could get into the waterways and ultimately to the rivers and cause biotoxicity to aquatic animals and man through food chain. Oxygen gas makes about 21% of the total atmospheric gases and some of this oxygen is dissolved in the body of water. Photosynthesis by microscopic plants living in the water body produces oxygen that is also dissolved in water. Biochemical Oxygen Demand (BOD) is defined as the amount of oxygen utilized when the organic matter in a given volume of water is degraded biologically (Sawyer *et al.*, 2003). It is a measure of the productivity of water that has high energy value, is said to be starved of oxygen, it needs more oxygen to completely degrade the organic life in it and have tendency of mobilizing heavy metals. Many chemical processes in the sediments can change and redistribute the heavy metals between the solid phase and the dissolved phase but most of the metal contaminants are immobilized through sedimentation (Long *et al.*, 1995). Heavy metals become toxic when they are not mobilized by the body and accumulated in the soft tissues. The toxicity of heavy metals to man may occur through food, water, air or absorption through the skin (occupational exposure). It was in Zamfara State (which is part of the study area) that lead poisoning of children took place May, 2010. During rainy season, the runoff (containing toxic metals) from mining sites and processing points could get into the waterways and ultimately to the rivers in Zamfara and the neighbouring states of Sokoto and Katsina thereby causing biotoxicity to aquatic animals and man through food chain. Knowledge and frequent monitoring of the levels of metals in the aquatic environments of the study area will help in policy formation and quick response to any changes to avoid a repeat of lead poisoning which was termed by the WHO as the world's catastrophe in the modern history.

## **MATERIALS AND METHODS**

**Study area:** The Goronyo Dam is located near Keta Village, some 25 km east of Goronyo town and 90 km away from Sokoto town, North-Western part of Nigeria in West Africa. The construction of earth-fill dam was completed across the Rima River in 1984 and has Gagare, Bunsuru and Maradi rivers as the main tributaries. The river Gagare has its source in Zamfara State from KauraNamoda through Moriki to BirninYero. River Bunsuru on the other hand has its source in Katsina state and comes from Zurmi through Bafarawa. Both rivers (Gagare and Bunsuru) have

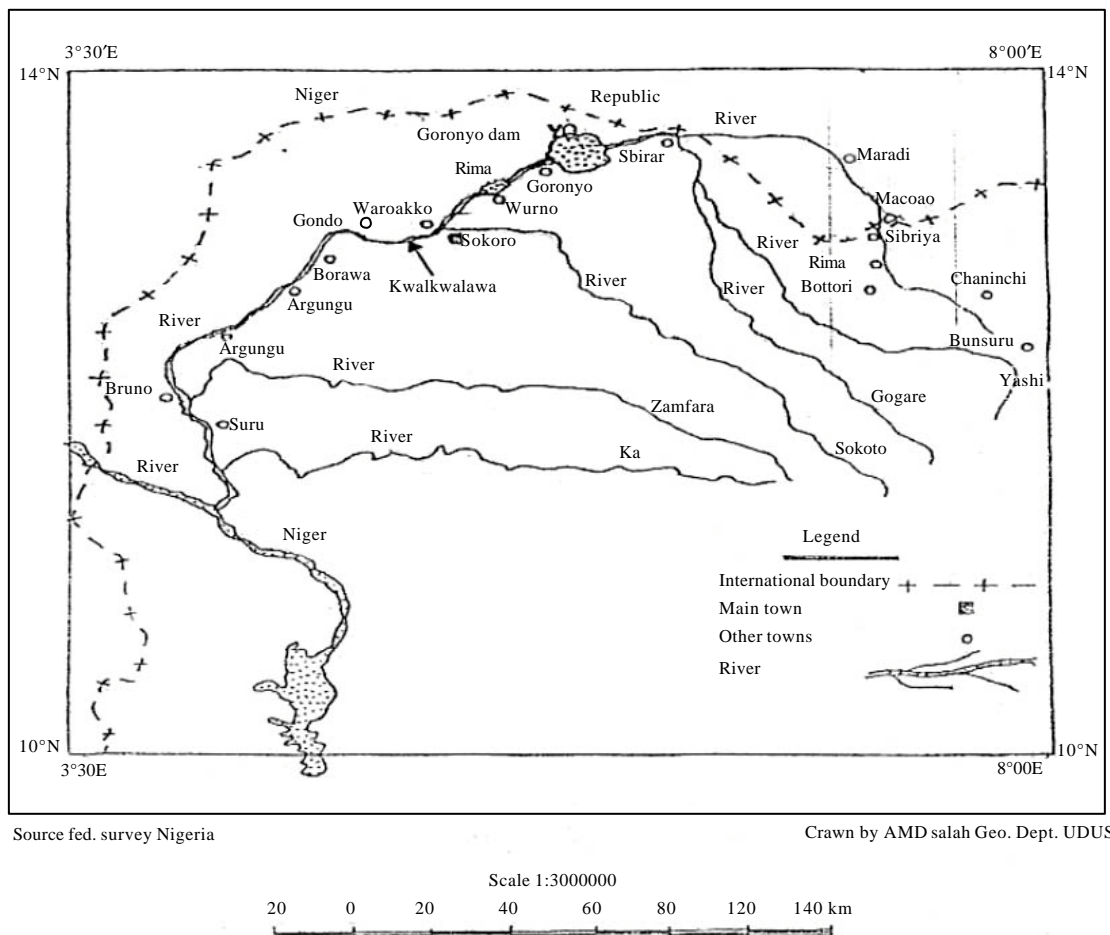


Fig. 1: Goronyo dam, its two tributaires and Rima river

their confluence at Attalawa. The dam is made up of three embankments (main dam, secondary dam and saddle dam) with a reservoir area of 200 km<sup>2</sup> and capacity of 942 Mm<sup>3</sup> at 286 m above sea level (M.A.S.L.) full storage. The dam supplies raw water to Sokoto State Water Board, Stream Bank (Fadama) irrigation through lifting, Wurno and Falalia irrigation schemes and fishing activities. Some of the crops grown by these schemes are rice, cassava, vegetables and garlic. River Rima is an overflow of Goronyo Dam. The lead poisoning of children in Zamfara state of Nigeria is a concern to the Government of Nigeria and the whole world. The miners are still at the sites, continuing with the mining and new sites are being identified in some other parts of Nigeria (Fig. 1).

**Chemicals and reagents:** All chemicals and reagents used for this study were of the analytical grade.

**Sample materials**

**Collection of water samples:** Water samples were collected according to the method of Allen *et al.* (1974) in pre-cleaned 1 L plastic bottles with screwed caps. The sample bottle was

plunged neck downwards about 15 cm below the water surface and about 60 cm from the side of the local fisherman's boat. Samples were stored in the laboratory at room temperature on top of cupboards until required for use.

**Collection of sediment and floodplain samples:** Sediment and floodplain samples were collected by selecting fifteen sites per river and thirty sites for Goronyo Dam (about fifty meters apart). For each site, six bottom sediment and floodplain samples were taken using a soil auger. About 2000 g sediment sample was harvested from each site. The composite sample was prepared by mixing the samples thoroughly and allowed to dry in the laboratory. The samples were mesarated with porcelain mortar and pestle, sieved through a 2 mm brass sieve and stored till ready for use (Allen *et al.*, 1974).

### **Preliminary tests**

**Determination of sediment and floodplain pH:** The method of Allen *et al.* (1974) was employed to determine pH values of the samples. The 0.01 M CaCl<sub>2</sub> was used because it gives more accurate result and minimises the effects of differences in electrolyte concentrations caused by salt accumulation or chemical fertilizer application.

**Determination of pH in CaCl<sub>2</sub>:** The 0.01 M CaCl<sub>2</sub> suspension was prepared by mixing 10 g sediment or floodplain sample in 20 mL of 0.01 M CaCl<sub>2</sub> solution. The suspension was allowed to stand for 30 min with occasional stirring with a glass rod. It was decanted and the pH was measured by inserting the electrode into the decanted suspension and reading out the pH. The result was read as "Sediment or floodplain pH in 0.01 M CaCl<sub>2</sub>" (Clark, 1993).

**Determination of sediment and floodplain pH in water:** The 20 g of air-dried, sieved sediment or floodplain sample was weighed into a 50 mL beaker. About 20 mL of distilled deionized water was added and the solution was allowed to stand for 30 min with occasional stirring using a glass rod. The solution was decanted and the electrode of the pH meter was inserted into partly settled suspension and the pH was measured. The pH was reported as sediment or floodplain pH in water (Black, 1985).

**Determination of water pH:** The 20 mL of unfiltered water sample was taken in a beaker. The electrode of the pH meter was inserted into the buffer solution to calibrate it, after which it was inserted into the sample and the pH was recorded.

**Determination of Dissolved Oxygen (DO):** The iodometric titrimetric method known to be most precise and reliable was adopted (Higgins and Burns, 1975). The 244 mL of the water sample was placed in a 250 mL dissolved oxygen bottle. The 2 mL each of manganese sulphate and alkali-iodide solutions were added. The stopper was carefully replaced to prevent further dissolution of oxygen in it. The bottle was vigorously shaken. The precipitate was allowed to settle, leaving a clear supernatant. About 4 mL dilute H<sub>2</sub>SO<sub>4</sub> was added and mixed again till the precipitate dissolved. About 100 mL of the sample was taken into a conical flask and titrated with 0.0125 M sodium thiosulphate solution using starch solution as indicator. The titter value was recorded as DO.

**Determination of Biochemical Oxygen Demand (BOD):** The water sample was thoroughly aerated, seeded with 2 mL domestic water and a screw capped incubator bottle was filled with it to

the brim. Dissolved oxygen determination was carried out on 50 mL of the sample. The bottle was sealed and incubated in the dark cupboard for five days. Dissolved oxygen determination was carried out on the incubated sample. The BOD is the difference between the final and the initial DO levels (Higgins and Burns, 1975).

### **Sample digestion**

**Water sample:** Unfiltered water samples were thoroughly mixed. 50 mL were transferred to refluxing flasks. 10 mL of freshly prepared HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> in ratio 1:1 (v/v) was added to each flask. The solutions were placed in the fume cupboard for 2 h till the volumes were reduced to 20 mL. The heating was continued till clear solutions were obtained. All the samples were cooled and filtered through Whatmann's No. 1 filter paper and the volumes made up to 100 mL with distilled deionized water. The samples were placed in pre-cleaned polythene bottle and sealed until for analyses (Rose *et al.*, 1999).

### **Sediment and floodplains**

**Perchloric acid digestion (Wet oxidation):** The 2.0 g of air-dried and sieved sediment or floodplain samples were weighed into reflux flasks which were previously washed and rinsed with 10% HNO<sub>3</sub>. About 5 mL of HClO<sub>4</sub>, 10 mL of both HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> were added under fume cupboard. The contents of the flasks were mixed and heated gently until dense white fumes appeared. The solution was cooled and 50 mL of distilled deionized water added. It was then filtered through Whatmann No. 1 filter paper and the volume made up to 100 mL (Smith and Schrenk, 1972).

**Estimation of metals:** Atomic Absorption Spectrophotometer (Philips model PU 9100) was used for the estimation of Pb, Cd, Cr, Ni, Fe, Mg, Ca, Cu, Na and K as described in Unican Atomic Absorption data book by Whiteside (1979), in the Pye Unican Atomic Absorption Spectrophotometry. The specific cathode lamps were selected accordingly, since each has its characteristic wavelength. The instrument was calibrated with standard known concentration and the values were recorded. Absorbance is directly proportional to the concentration of the metal ion present in the sample and it was recorded through the instrument.

## **RESULTS AND DISCUSSION**

For earliest times, streams, rivers and seas have been a natural place to discard sewage and even industrial wastes. Toxic metallic wastes in the aquatic environment result from many industrial sources involving the processing of ores, metals and metallic compounds. There is no information available on the concentrations of these metals in various locations where the samples were collected. Such urgent information is needed in view of lead poisoning of both young and adults in Zamfara state of Nigeria by the year 2010.

The physicochemical analyses of water and sediment samples from the four study areas (Table 1) were carried out to ascertain the mobility and retention of heavy metals. The pH in water (1:1) v:v and pH in 0.01 M CaCl<sub>2</sub> for sediment samples during the rainy season in all locations were above 7 (Table 1). The pH above 7 means that the bicarbonate and carbonate anions reinforce the tendency towards alkalinity in areas where there is low rainfall (semi-arid) such as the study sites and probably because of the kind of the parent materials from which the sediments were formed. Same applied to floodplain samples. Most natural waters have Dissolved Oxygen (DO) of 3 mg L<sup>-1</sup>. Except for river Gagare with value of 1.0 mg L<sup>-1</sup> during the dry season analyses, the

Table 1: Physicochemical properties of water samples collected from the sites

Location	Water (pH)	Sediment pH in water	Sediment pH in 0.01 M CaCl <sub>2</sub>	Floodplain pH in water	Floodplain pH in 0.01 M CaCl <sub>2</sub>	Dissolved Oxygen (DO) (mg g <sup>-1</sup> )	Biochemical Oxygen Demand (BOD) (mg g <sup>-1</sup> )							
River Bunsuru	7.10±0.50	6.92±0.41	6.79±0.33	7.14±0.45	6.93±0.39	7.40±0.71	7.25±0.26	6.88±0.32	6.78±0.41	0.90±0.11	1.70±0.12	6.40±0.16	3.20±0.01	
River Gagare	6.90±0.16	7.75±0.34	7.15±0.22	7.12±0.17	6.96±0.19	6.90±0.13	7.01±0.27	7.02±0.24	6.90±0.33	1.0±0.010	1.20±0.15	6.70±0.29	4.20±0.31	
River Rima	6.87±0.14	7.10±0.22	6.82±0.10	6.57±0.21	7.18±0.52	7.10±0.31	7.32±0.42	7.18±0.46	7.16±0.51	7.05±0.24	0.90±0.12	1.10±0.10	7.10±0.38	3.30±0.21
Goronyo Dam	6.52±0.02	7.20±0.01	6.95±0.10	6.68±0.02	7.05±0.24	7.01±0.01	7.11±0.10	6.90±0.30	7.24±0.12	7.11±0.10	0.60±0.02	1.90±0.12	7.50±0.11	3.00±0.01

+: December-April, ++: July-October. The samples were collected in the dry season after the rain has ceased and when the rain is at its peak. The high Biochemical Oxygen Demand (BOD) as seen in River Rima and Goronyo Dam means the water samples have tendency of mobilizing heavy metals

other three locations had values below  $1 \text{ mg L}^{-1}$ , i.e.,  $0.9 \text{ mg L}^{-1}$  for both (Rivers Bunsuru and Gagare) and  $0.6 \text{ mg L}^{-1}$  for Goronyo Dam. The Biochemical Oxygen Demand (BOD) of the water samples (Table 1) in the rainy season was low for all the study areas. When the biochemical oxygen demand concentration falls below  $5 \text{ mg L}^{-1}$ , fish species intolerant of low oxygen levels become stressed. The lower the oxygen value in aquatic environment, the greater the stress. For the rainy season samples, BOD of Rivers Bunsuru and Gagare ( $6.40$  and  $6.70 \text{ mg L}^{-1}$ , respectively) still fell below the WHO standard of  $7.0 \text{ mg L}^{-1}$ . River Rima and Goronyo Dam had higher values  $7.10$  and  $7.50 \text{ mg L}^{-1}$ , respectively. According to Wallace (2000), water that has high BOD has tendency of remobilizing heavy metals.

The concentration of the analysed metals and mineral elements (Pb, Cd, Ni, Fe, Mg, Cr, Cu, Ca, Na and K) in the bottom sediment, water and floodplain samples of all the study areas are presented in Table 2. Leads (Pb) concentration in sediment and floodplain samples ( $3.71 \pm 0.27$  and  $2.17 \pm 0.33 \mu\text{g g}^{-1}$ , respectively) of River Bunsuru (Table 2) have been found to be significantly high ( $p < 0.05$ ) during the rainy season sampling, while Cu values were consistently high for the two seasons. Apart from the levels of Pb obtained in rainy season, some measurable concentrations were observed in sediment, water and floodplain samples of dry season. In accordance with the fact that Pb plays no biological or physiological role, its presence in sediments at whatever concentration poses a threat to fishes in aquatic environment because of the bottom feeding habits of the aquatic organisms.

In contrast to River Bunsuru, sediment sample of River Gagare (Table 2) had low Pb and Cd levels and high Cu levels during the two seasonal samplings. Same case applies to River Rima (Table 2). Goronyo Dam (Table 2) which receives water from Rivers Bunsuru and Gagare had significant levels ( $p < 0.05$ ) of Cu in all samples and for both seasons. Because the discharge of heavy metals into rivers by domestic and industrial activities causes their rapid association with particulates and incorporation into bottom sediments, high levels are observed in sediment samples compared with the water samples. Their continuous presence in sediments and water means bioavailability to fish tissues and subsequent biotoxicity. There were no regular patterns of the seasonal variations in the concentration of metals in sediment, water and floodplain samples. Aquatic organisms like fish species accumulate metals in their tissues many times than present in sediment and water. Man, being at the top of tropic level of food chain is at the risk of Pb and Cu poisoning. Copper (Cu) is a powerful oxidant causing inflammation and free radical damage to tissues. It's binding to ceruloplasmin and metallothionein leads to impairment of adrenal and liver function. The free Cu builds up and interferes with conversion of thyroid hormone at cellular level. This inhibits glucocorticoid production thereby causing hypoglycaemia and increases aldosterone production that enhances brain activity. Cu toxicity causes a decrease in  $\text{Na}^+/\text{K}^+$ ATPase activity that leads to a decrease in whole body  $[\text{Na}^+]$ . Cu exposure can also induce stress and could be responsible for regulation of genes involved in protein synthesis, proteolysis and ATP production. Though Cu is necessary for the synthesis of haemoglobin (Cu is a constituent of ALA synthase needed for haem biosynthesis), abnormal levels are deposited in liver and lenticular nucleus of brain. This may lead to hepatic necrosis and brain necrosis. Cu deposition in kidney causes renal damage that leads to increased excretion of amino acids, glucose, peptides and haemoglobin in urine.

In terms of seasonal variation of metals, some dry season values were consistently higher than rainy season values or vice versa. The reasons for lack of seasonal variations are not clear but may be attributed to high variability over large areas of samplings and restriction of number of samples.



Table 2: Level of metals in sediments, water and floodplain in River Bunsuru, River Gagare, River Rima and Goronyo Dam

Parameters	Level of metals ( $\mu\text{g g}^{-1}$ )									
	Pb	Cd	Ni	Fe	Mg	Cr	Cu	Ca	Na	K
<b>River Bunisuru</b>										
<b>Season I</b>										
Sediment	0.37±0.03 <sup>a</sup>	0.14±0.02 <sup>a</sup>	0.20±0.02 <sup>a</sup>	41.63±3.17 <sup>a</sup>	27.36±2.70 <sup>a</sup>	0.39±0.09 <sup>a</sup>	4.43±0.09 <sup>a</sup>	232.82±21.95 <sup>a</sup>	54.17±3.35 <sup>a</sup>	9.65±1.44 <sup>a</sup>
Water	0.24±0.01 <sup>b</sup>	0.10±0.01 <sup>b</sup>	1.99±0.10 <sup>b</sup>	20.29±1.48 <sup>b</sup>	45.11±4.40 <sup>b</sup>	0.05±0.001 <sup>b</sup>	5.03±0.01 <sup>b</sup>	136.41±8.85 <sup>b</sup>	3.66±0.57 <sup>b</sup>	3.67±0.48 <sup>b</sup>
Floodplain	0.31±0.04 <sup>c</sup>	0.15±0.01 <sup>a</sup>	0.15±0.01 <sup>a</sup>	46.76±2.79 <sup>c</sup>	32.23±2.15 <sup>c</sup>	0.47±0.09 <sup>c</sup>	7.63±0.09 <sup>c</sup>	275.83±18.34 <sup>c</sup>	47.88±3.94 <sup>c</sup>	9.04±1.16 <sup>c</sup>
<b>Season II</b>										
Sediment	3.71±0.27 <sup>a</sup>	0.36±0.06 <sup>a</sup>	0.20±0.06 <sup>a</sup>	42.77±2.12 <sup>a</sup>	62.91±6.49 <sup>a</sup>	1.21±0.21 <sup>a</sup>	4.46±0.08 <sup>a</sup>	205.52±12.17 <sup>a</sup>	11.30±1.06 <sup>a</sup>	15.26±1.31 <sup>a</sup>
Water	0.58±0.11 <sup>b</sup>	0.16±0.04 <sup>b</sup>	0.13±0.06 <sup>b</sup>	24.84±2.22 <sup>b</sup>	37.62±3.35 <sup>b</sup>	0.71±0.09 <sup>b</sup>	6.31±0.07 <sup>b</sup>	235.03±24.71 <sup>b</sup>	3.50±0.27 <sup>b</sup>	3.76±0.30 <sup>b</sup>
Floodplain	2.17±0.33 <sup>c</sup>	0.54±0.12 <sup>c</sup>	0.21±0.04 <sup>a</sup>	45.64±2.73 <sup>c</sup>	43.30±4.46 <sup>c</sup>	0.56±0.13 <sup>c</sup>	6.36±0.09 <sup>c</sup>	192.03±11.82 <sup>c</sup>	6.92±0.97 <sup>c</sup>	3.01±0.30 <sup>c</sup>
<b>River Gagare</b>										
<b>Season I</b>										
Sediment	0.35±0.06 <sup>a</sup>	0.32±0.01 <sup>a</sup>	0.21±0.02 <sup>a</sup>	33.34±5.70 <sup>a</sup>	33.11±3.40 <sup>a</sup>	0.62±0.01 <sup>a</sup>	7.10±0.01 <sup>a</sup>	233.10±8.71 <sup>a</sup>	7.70±1.35 <sup>a</sup>	6.50±1.24 <sup>a</sup>
Water	0.09±0.02 <sup>b</sup>	0.02±0.01 <sup>b</sup>	0.17±0.01 <sup>b</sup>	11.26±0.37 <sup>b</sup>	9.48±0.42 <sup>b</sup>	0.17±0.02 <sup>b</sup>	9.01±0.02 <sup>b</sup>	91.23±4.48 <sup>b</sup>	11.02±0.55 <sup>b</sup>	12.12±0.38 <sup>b</sup>
Floodplain	0.31±0.05 <sup>a</sup>	0.26±0.03 <sup>c</sup>	0.27±0.02 <sup>c</sup>	33.67±4.86 <sup>c</sup>	31.79±3.31 <sup>c</sup>	0.35±0.05 <sup>c</sup>	5.06±0.01 <sup>c</sup>	189.10±10.0 <sup>c</sup>	77.90±1.26 <sup>c</sup>	6.48±0.77 <sup>c</sup>
<b>Season II</b>										
Sediment	0.20±0.04 <sup>a</sup>	0.11±0.05 <sup>a</sup>	0.45±0.14 <sup>a</sup>	17.31±1.58 <sup>a</sup>	94.86±6.80 <sup>a</sup>	1.10±0.11 <sup>a</sup>	10.40±0.05 <sup>a</sup>	162.29±9.42 <sup>a</sup>	5.34±0.23 <sup>a</sup>	9.39±0.50 <sup>a</sup>
Water	0.26±0.11 <sup>b</sup>	0.40±0.06 <sup>b</sup>	0.21±0.50 <sup>b</sup>	2.86±0.46 <sup>b</sup>	73.07±4.89 <sup>b</sup>	0.92±0.13 <sup>b</sup>	8.70±0.06 <sup>b</sup>	69.24±4.46 <sup>b</sup>	7.64±0.23 <sup>b</sup>	7.50±0.35 <sup>b</sup>
Floodplain	0.23±0.06 <sup>a</sup>	0.10±0.04 <sup>a</sup>	0.16±0.03 <sup>a</sup>	10.95±1.90 <sup>a</sup>	79.33±8.82 <sup>c</sup>	1.14±0.69 <sup>c</sup>	5.18±0.06 <sup>c</sup>	86.93±5.67 <sup>c</sup>	5.62±0.25 <sup>a</sup>	6.77±0.27 <sup>c</sup>
<b>River Rima</b>										
<b>Season I</b>										
Sediment	0.54±0.10 <sup>a</sup>	0.20±0.03 <sup>a</sup>	0.28±0.05 <sup>a</sup>	23.91±1.59 <sup>a</sup>	41.70±2.02 <sup>a</sup>	0.16±0.02 <sup>a</sup>	2.16±0.03 <sup>a</sup>	104.84±10.61 <sup>a</sup>	5.45±0.57 <sup>a</sup>	11.26±0.52 <sup>a</sup>
Water	0.27±0.02 <sup>b</sup>	0.23±0.03 <sup>b</sup>	0.33±0.03 <sup>b</sup>	30.41±1.86 <sup>b</sup>	38.60±0.04 <sup>b</sup>	0.18±0.04 <sup>b</sup>	3.14±0.03 <sup>b</sup>	160.90±07.20 <sup>b</sup>	3.20±0.32 <sup>b</sup>	2.85±0.27 <sup>b</sup>
Floodplain	0.79±0.02 <sup>c</sup>	0.15±0.01 <sup>c</sup>	0.25±0.07 <sup>c</sup>	22.55±1.32 <sup>c</sup>	41.05±3.15 <sup>c</sup>	0.51±0.06 <sup>c</sup>	6.37±0.07 <sup>c</sup>	87.31±06.11 <sup>c</sup>	4.89±0.33 <sup>c</sup>	12.51±0.38 <sup>c</sup>
<b>Season II</b>										
Sediment	0.25±0.03 <sup>a</sup>	0.02±0.02 <sup>a</sup>	0.11±0.01 <sup>a</sup>	37.95±5.18 <sup>a</sup>	100.37±4.41 <sup>a</sup>	0.44±0.08 <sup>a</sup>	3.08±0.03 <sup>a</sup>	62.82±05.24 <sup>a</sup>	10.98±2.13 <sup>a</sup>	8.30±1.11 <sup>a</sup>
Water	0.11±0.02 <sup>b</sup>	0.24±0.02 <sup>b</sup>	0.39±0.03 <sup>b</sup>	15.11±2.40 <sup>b</sup>	72.81±2.75 <sup>b</sup>	0.34±0.04 <sup>b</sup>	2.20±0.02 <sup>b</sup>	18.38±02.12 <sup>b</sup>	3.28±0.19 <sup>b</sup>	4.62±0.42 <sup>b</sup>
Floodplain	0.25±0.03 <sup>a</sup>	0.12±0.02 <sup>c</sup>	0.11±0.01 <sup>a</sup>	37.95±5.18 <sup>a</sup>	100.37±4.41 <sup>a</sup>	0.44±0.08 <sup>a</sup>	3.08±0.03 <sup>a</sup>	162.82±05.24 <sup>c</sup>	10.98±2.13 <sup>a</sup>	8.30±1.11 <sup>a</sup>
<b>Goronyo Dam</b>										
<b>Season I</b>										
Sediment	0.35±0.04 <sup>a</sup>	0.18±0.02 <sup>a</sup>	0.18±0.01 <sup>a</sup>	57.43±2.70 <sup>a</sup>	48.30±3.00 <sup>a</sup>	0.91±0.10 <sup>a</sup>	7.14±0.03 <sup>a</sup>	201.63±8.48 <sup>a</sup>	50.48±3.09 <sup>a</sup>	35.21±2.28 <sup>a</sup>
Water	0.26±0.03 <sup>b</sup>	0.05±0.02 <sup>b</sup>	0.29±0.04 <sup>b</sup>	33.08±1.59 <sup>b</sup>	21.37±1.16 <sup>b</sup>	0.14±0.02 <sup>b</sup>	8.08±0.02 <sup>b</sup>	116.47±4.96 <sup>b</sup>	18.58±1.29 <sup>b</sup>	12.58±0.67 <sup>b</sup>
Floodplain	0.21±0.02 <sup>c</sup>	0.13±0.01 <sup>c</sup>	0.26±0.02 <sup>c</sup>	30.29±1.16 <sup>c</sup>	26.83±1.18 <sup>c</sup>	0.49±0.05 <sup>c</sup>	6.17±0.01 <sup>c</sup>	175.64±6.13 <sup>c</sup>	36.70±2.23 <sup>c</sup>	21.43±0.62 <sup>c</sup>
<b>Season II</b>										
Sediment	6.23±0.52 <sup>a</sup>	0.94±0.27 <sup>a</sup>	0.24±0.04 <sup>a</sup>	62.81±3.70 <sup>a</sup>	130.88±5.26 <sup>a</sup>	0.90±0.07 <sup>a</sup>	6.20±0.05 <sup>a</sup>	227.10±23.14 <sup>a</sup>	16.93±2.76 <sup>a</sup>	14.83±1.54 <sup>a</sup>
Water	9.44±0.49 <sup>b</sup>	1.54±0.27 <sup>b</sup>	0.55±0.10 <sup>b</sup>	34.34±1.37 <sup>b</sup>	96.04±5.04 <sup>b</sup>	0.56±0.09 <sup>b</sup>	7.17±0.02 <sup>b</sup>	479.42±16.14 <sup>b</sup>	9.54±0.46 <sup>b</sup>	7.70±0.46 <sup>b</sup>
Floodplain	4.58±0.71 <sup>c</sup>	0.79±0.12 <sup>c</sup>	0.04±0.01 <sup>c</sup>	52.29±4.01 <sup>c</sup>	100.02±8.60 <sup>c</sup>	0.71±0.04 <sup>c</sup>	7.36±0.10 <sup>c</sup>	226.72±5.490 <sup>c</sup>	4.45±0.35 <sup>c</sup>	4.76±0.38 <sup>c</sup>

Season I: December- April, Season II: July-October, <sup>a</sup>Means on the same column, with same superscripts are not significantly different ( $p>0.05$ )  
<sup>b</sup> <sup>c</sup>Means on the same column, with different superscripts differ significantly ( $p=0.05$ ), Except the sediment and floodplain samples of season II with lead (Pb) levels above the WHO permissible limits, all other metals and mineral elements are within the tolerable limits. Copper (Cu) in River Gagare in all samples and for the two seasons are above the WHO limits. All metals and mineral elements for all seasons in River Rima are within the permissible limits. Lead (Pb) in Goronyo Dam season II samples are present above the WHO permissible limits, while copper (Cu) in all samples for both seasons are also above the limits of WHO

In case of sediment samples, their heterogenous nature (a critical determinant) of their heavy metal content is such that heavy metal content can vary even within the scale of millimeters (Tucker *et al.*, 2003).

Rima River (Table 2) had all the investigated metals except Cu level of the floodplain sample within the limits of WHO. However, the low Pb and Cd levels that appeared in all the samples could accumulate to toxic levels with time.

Goronyo Dam (Table 2) samples (sediment, water and floodplain) recorded highest values of Pb  $6.33\pm0.52 \mu\text{g g}^{-1}$ ,  $9.44\pm0.49 \mu\text{g L}^{-1}$  and  $4.58\pm0.71 \mu\text{g g}^{-1}$ , respectively during the rainy

season sampling and a corresponding high Cd and Cu levels for sediment and floodplain samples of dry season. This may be attributed to the fact that the Dam is receiving water from different sources. The processing of ore by individual miners has left a measurable quantity of lead in the environment which gets into the rivers during heavy rain fall. Most samples with high Pb levels also had high Cu levels. Again, for those heavy metals that were found in high concentrations in the rainy season, the increase in flux of water may lead to the introduction of extra heavy metals that may have been held in stagnant drainages during the dry season.

The observed variation in concentrations of the metals can be explained on the basis that various activities involve the utilization of compounds that contain heavy metals (especially the artisan gold mining in Zamfara State where River Gagare has its source) as raw materials and component which dictates the constituent of the residuals. Elevated concentration of heavy metals in aquatic environment is a good indicator of man-induced pollution (Davies *et al.*, 1991). Because the discharge of heavy metals into rivers by domestic and industrial activities cause their rapid association with particulates and incorporation in bottom sediments, high levels were observed in all the sediment samples analysed compared with water samples (Table 2). The continuous presence of lead (Pb) in sediment, water and floodplain samples means their potential bioavailability to fish tissues and subsequent biotoxicity. Aquatic organisms like fish species accumulate metals in their tissues many times than present in sediments and water. This bioaccumulation can be a rich source of lead (Pb) and other metals to man.

## CONCLUSION

It was in Zamfara State (part of the study area) that lead poisoning of adult and children took place in the year 2010. Over 400 children under age five died as a result of what Human Rights Watch considers the worst lead poisoning epidemic in modern history. Thousands of children in North-Western Nigeria are in urgent need of treatment for lead poisoning. Dozens of villages in North-Western Zamfara State remain contaminated, two years after the problem was first discovered. And because human system is very sensitive to lead (Pb) and no Pb level is safe, (especially for fetuses and young children whose blood brain barrier is still at the process of formation), a concerted effort is needed to reduce the exposure to lead and other toxic metals.

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