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Evaluation of some Heavy Metals Concentration in River Argungu

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ABSTRACT
Pollution of inland water ways is largely as a result of human activities along the river banks. Some heavy metals concentrations of River Argungu were evaluated due to its close proximity to the town. The study lasted for 12 months (March, 2014-February, 2015) using Energy Dispersive X-ray Fluorescence (ED-XRF) Analysis. Nickel and copper were highest during the month of July with mean values of 1.02±0.02 and 1.81±0.23 mg L^{-1}, respectively, lead and chromium were highest during the month of September with mean values of 13.12±0.18 and 0.14±0.05 mg L^{-1}, respectively. The Mean±SD of eight heavy metals assessed indicated that, nickel, iron, lead and cadmium detected were observed to be higher than the permissible limit (nickel 0.02, iron 0.30, lead 0.01 and cadmium 0.003 mg L^{-1}) throughout the study period. Zinc was however, lower than the permissible limit of World Health Organization (WHO) throughout the period of the study. Most of the highest concentrations of heavy metals observed were at the onset and during the rainy season. The high concentrations of some heavy metals observed in the river could be as a result of human activities mostly concentrated at the river banks and run-off during the rainy season. This study infers that, some fish species could be threaten as a result of the high concentrations of most of the heavy metals, thus the need for an efficient and sustainable fisheries management to control human activities along the river bank.

Key words: Water samples, analysis, composition, X-ray, concentration

INTRODUCTION
Heavy metals are elements that exhibits metallic properties they are of high density and toxicity. They may include transition metals, metalloids, lanthanides and actinides. Heavy metals are naturally present and form part of the lithosphere. They are often get into the environment through volcanism, soil erosion, dissolution of water-soluble salts and weathering of rocks (Fergusson, 1990), but often, the presence of large quantity of heavy metals in the environment is largely due to human activities (Obaroh *et al*., 2014). Though living organisms require trace amount of some heavy metals such as zinc, cobalt, strontium and copper for normal growth and metabolism, excess quantity of these metals can pose a threat to the living organisms. Studies have pointed to the modification and loss of aquatic habitat as the primary factor threatening the conservation of freshwater fishes and its communities (Allen and Flecker, 1993; Hewitt *et al*., 2008).

Dumping of wastes into rivers and run-off from roads during the rainy season contributes largely to water pollution. Used chemical containers are most often carelessly dumped into the river, all these can cause serious damage to the aquatic environment and subsequent hazards to human health. Water being the most abundant and important solvent is needed for the existence of all living organism. Heavy metal pollution in aquatic environment and subsequent uptake in the food chain by aquatic organism and man can result in morphological abnormalities, neurophysiological disturbances, genetic alteration of the cell (mutation), teratogenesis and carcinogenesis. Heavy metals can affect enzymatic and hormonal activities as well as growth rate and increase mortality (Bubb and Lester, 1991).

High concentration of heavy metals in water could be toxic to the aquatic organism as a result this could decline the fish population in the water body (Ezeronye and Ubalua 2005). Their accumulation in aquatic food web is also a potential threat to public health. Heavy metals are of high priority pollutants because of their relatively high toxic effects and accumulation in the environment. The pollution of aquatic environment by heavy metals and successive uptake in the aquatic food chain poses hazard to human population. Aquatic environment has been reported to be grossly affected by increase in human activities (Obaroh *et al*., 2012). The concentrations of some heavy metals observed in Nigerian water bodies such as lead, copper, zinc, nickel, chromium, cadmium and iron had been reported to be well above acceptable and permissible levels (Olayinka and Alo, 2004; Essoka and Umaru, 2006).

River Argungu located along Argungu town is well known for its annual fishing festival, though there is restriction on fishing activities in the river, human activities such as dumping of refuse, washing and small cottage block making industry are on the increase along the river bank and no work was observed to have been reported on the heavy metal concentrations of River Argungu, thus the need for this study, to assess the heavy metal concentrations of water from different locations in the river.

MATERIALS AND METHODS

Study area: Argungu is located on latitude 12.75°N longitude 4.54°E. As shown in Fig. 1, the river source is near Funtua in the south of Katsina State, some 275 km in straight line from Sokoto, it flow North-West through Gusau in Zamfara State. Further downstream the river enters Sokoto State where it passes by Sokoto town and is joined by River Rima, then turning south and flowing through Argungu to Birnin Kebbi, Kebbi State, Nigeria. About 120 km south of Birnin Kebbi, it reaches its confluence with the River Niger (Akane and Jurgen, 2005).

Water sampling: Water samples were collected monthly for a total period of twelve months between (March, 2014-February, 2015). Water samples for chemical analysis were collected at 30 cm depth with a distance of 1 m away from the shore (APHA., 1998) using glass jars (100 mL). Water samples collected were preserved by adding 1.0 M of concentration HNO_3 and stored in refrigerator in preparation for chemical analysis at the Agriculture Physical laboratory of Usmanu Danfodiyo University Sokoto, Nigeria.

Concentrations of some heavy metals in water from the river were determined using Energy Dispersive X-Ray Fluorescence (EDXRF) (XRF HORIBA Model, Bruker UK) at the Energy Research Centre of Usmanu Danfodiyo University Sokoto, Nigeria.

Fig. 1: Map Showing the location of Argungu town along river Sokoto

Water sample preparation for XRF analysis: To 100 mL of acidified water sample, 10% of ADPC (Ammonium Pyrrolidine Dithiocarbamate, $C_6H_{12}N_2S_2$) was added and the contents were allowed for 15-20 min. The sample was then filtered using Millipore membrane filter in a filtration unit with the aid of a vacuum pump. The precipitate on filter was then measured. Measurements were performed using an annular 25 m CiCd-109 as the excitation source, which emits Ag-K X-rays (22.1 keV) in which case all elements with characteristic excitation energies were accessible for detection in the samples. The system consists furthermore of a Si (Li) detector, with a resolution of 170 cV for the 5.90 keV line, coupled to a computer controlled ADC card. Quantification was carried out using a modified version of (E-T) method (Kump, 1996; Angeyo *et al*., 1998; Funtua, 1999) and it involves the use of pure target material such as Molybdenum (Mo) to measure the absorption factors in the sample. The Mo target serves as a source of monochromatic X-rays, which are excited through the sample by primary radiation and then penetrate the sample on the way to the detector. In this way, the absorption factor is experimentally determined which the program uses in the quantification of concentration of the elements.

Sensitivity calibration of the system was performed using pure metal foils (Ti, Fe, Co, Ni, Cu, Zr, Nb, Mo, Sn, Ta, Pb) and stable chemical compounds (K_2CO_3, $CaCO_3$, Ce_2O_3, WO_3, ThO_2, U_3O_8). The spectra for the samples were collected for 3000 sec with the Cd-109 source. The concentrations are expressed as milligram per liter.

Statistical analysis: Data obtained from the concentration of heavy metals from river Argungu was subjected to Analysis of Variance (ANOVA) using the Genstat 4.2 Statistical Analysis Software and Duncan Multiple Range Test (DMRT) to test for the differences between monthly concentrations by means separations, respectively.

RESULT AND DISCUSSION

As shown in Table 1, the highest concentration of nickel (Ni) was recorded during the month of July, with a mean value of 1.02±0.02 mg L^{-1}, while the lowest value of 0.20±0.02 mg L^{-1} was recorded in November and February. There was no nickel detected in the months of August, 2014 and January, 2015. The highest concentration of iron (Fe) was observed during the months of August and December, 2014 with mean values of 7.52±0.11 and 7.55±0.33 mg L^{-1}, while the lowest was observed during the month of March, 2014 with a mean value of 1.85±0.94 mg L^{-1} (Table 1). The highest concentration of lead (Pb) was recorded during the month of September, 2014 with a mean value of 13.12±0.18 mg L^{-1}, while the lowest was observed during the month of 0.07±0.12 mg L^{-1}. No lead was detected during the months of October, November and December 2014 and January and February, 2015 (Table 1).

As presented in Table 1, the highest concentration of chromium (Cr) 0.14±0.05 mg L^{-1} was recorded in September, while the lowest similar values of 0.02±0.02 mg L^{-1} were recorded in October 2014 and January 2015. There was no chromium detected from March to June 2014. The highest concentration of copper (Cu) 1.81±0.23 mg L^{-1} was recorded in July, 2014, while the lowest 0.46±0.12 mg L^{-1} was recorded in December. No Cu was detected during the months of December 2014, January and February 2015 (Table 1). The concentration of cadmium was found to be highest during the month of December 2014 with a mean value of 0.67±0.04 mg L^{-1}, while the lowest 0.01±0.01 mg L^{-1} was observed during the month of June 2014. Cadmium was not detected from August to November, 2014 and January to February 2015 (Table 1).

As indicated in Table 1, the concentration of Manganese (Mn) was found to be highest during the month of March, 2014 with a mean value of 1.64±1.09 mg L^{-1}, while the lowest concentration was recorded in August, 2014 with a mean value of 0.02±0.01 mg L^{-1}. The concentration of zinc (Zn) was highest in December, 2014 recording 0.94±0.06 mg L^{-1}, while the lowest concentration of 0.01±0.01 mg L^{-1} was in June, 2014. Zinc was not detected in August, 2014 (Table 1).

Table 1: Heavy metal concentration of river argungu

	Concentration (mg L^{-1})					
Heavy metals	March	April	May	June	July	August
Nickel	0.88 ± 0.25^{cd}	0.87 ± 0.08^{cd}	0.75 ± 0.32^{c}	0.93 ± 0.07^{cd}	1.02 ± 0.02^{d}	ND
Iron	1.85 ± 0.94^{a}	2.85 ± 0.36^{b}	2.70 ± 0.94^{ab}	3.74 ± 0.31^{c}	5.33 ± 0.49^{d}	7.52 ± 0.11^{e}
Lead	0.17 ± 0.29^{a}	0.10 ± 0.17^{a}	0.07 ± 0.12^{a}	ND	0.80 ± 0.26^{b}	11.41 ± 1.00^{c}
Chromium	ND	ND	ND	ND	0.03 ± 0.02^{ab}	0.03 ± 0.01^{ab}
Copper	1.67 ± 0.02^{d}	1.63 ± 0.02^{d}	1.63 ± 0.02^{d}	1.65 ± 0.10^{d}	1.81 ± 0.23^{d}	1.07 ± 0.15^{c}
Cadmium	0.02 ± 0.01^{abc}	0.03 ± 0.01^{bc}	0.03 ± 0.01^{c}	0.01 ± 0.01^{ab}	0.04 ± 0.01^{c}	ND
Manganese	1.64 ± 1.09^{b}	0.52 ± 0.23^{a}	1.55 ± 1.03^{b}	0.34 ± 0.06^{a}	0.60 ± 0.17^{a}	0.02 ± 0.01^{a}
Zinc	0.03 ± 0.02^{ab}	0.04 ± 0.04^{ab}	0.04 ± 0.02^{ab}	0.01 ± 0.01^{a}	0.33 ± 0.15^{cd}	ND
	Concentration (mg L^{-1})					
Heavy metals	September	October	November	December	January	February
Nickel	0.33 ± 0.04^{b}	0.30 ± 0.08^{b}	0.20 ± 0.02^{ab}	0.35 ± 0.02^{b}	ND	0.20 ± 0.02^{ab}
Iron	6.13 ± 0.13^{d}	1.89 ± 0.11^{a}	5.56 ± 0.50^{d}	7.55 ± 0.33^{e}	5.52 ± 0.48^{d}	4.15 ± 0.36^{c}
Lead	13.12 ± 0.18^{d}	ND	ND	ND	ND	ND
Chromium	0.14 ± 0.05^{c}	0.02 ± 0.02^{a}	0.08 ± 0.02^{b}	0.03 ± 0.02^{ab}	0.02 ± 0.02^{a}	0.13 ± 0.06^{c}
Copper	0.47 ± 0.15^{b}	0.50 ± 0.17^{b}	0.46 ± 0.12^{b}	ND	ND	ND
Cadmium	ND	ND	ND	0.67 ± 0.04^{d}	ND	ND
Manganese	0.19 ± 0.01^{a}	0.05 ± 0.01^{a}	0.16 ± 0.02^{a}	0.22 ± 0.03^{a}	0.08 ± 0.01^{a}	0.24 ± 0.05^{a}
Zinc	0.32 ± 0.10^{cd}	0.21 ± 0.19^{bcd}	0.04±0.01ab	0.94±0.06e	0.14 ± 0.22^{abc}	0.32 ± 0.05^{cd}

ND: Not detected, Values with different superscripts are significantly difference ($p\geq0.05$)

Nickel, iron, lead, chromium were observed to be higher than the permissible limit (Ni 0.02 mg L^{-1}, Fe 0.30 mg L^{-1} and Pb 0.01 mg L^{-1}) throughout the study period, (WHO/UNICEF, 2010) water pollution is most often due to human activities (Hammer, 1986). The Major ones are indiscriminate disposal of industrial, municipal and domestic wastes in water channels, rivers, streams and lakes (Kahlown and Majeed, 2003), for example an estimated 2 million t of sewage and other effluents are discharged into the world water every day (Azizullah *et al*., 2011).

The high concentrations of some of the heavy metals observed during this study could be as a result of human activities observed to be concentrated around the river banks, human activities observed along the river bank include, washing of household wares and vehicles, dumping of refuse and small cottage block making industry. Human activities have been reported to be a contributing factor to high increase in heavy metal concentration of rivers (Obaroh *et al*., 2012). The major source of nickel has been reported to be leaching from metals in contact with the water, it is used mainly in the production of stainless steels, electroplating, as catalyst in nickel-cadmium batteries and in certain pigment and electronics (IARC., 1990). Cadmium and lead have been reported to be present in children's toys at a level that is above the regulatory standard (Finch *et al*., 2015), all of these sources are what constitute the household waste. There were monthly variations, these could be due to the different seasons, higher concentration of most of the heavy metals were observed at the onset and during the raining season this could be attributed to the run-off. The different locations at which water samples were collected could also be a source of variation. Earlier report by Ogedengbe and Oke (2011) also reported that, cement dusts were observed to be rich in heavy metals concentrations.

CONCLUSION

Toxic heavy metals are found naturally in the earth but they become concentrated as a result of human activities. Most of the high concentrations of heavy metals observed were at the onset and during the rainy season periods as earlier stated, these high concentrations could also be attributed to run-off during the rainy season in addition to leaching from household utensils and toys mostly dumped in the river. All the heavy metals analyzed except zinc were observed to be above the acceptable limit as stipulated by WHO, thus posing a threat to the aquatic organisms.

Industrial and public education programs are required on awareness of health risks associated with heavy metals polluted waters. Conclusively, dumping of refuse and illegal desilting should be prohibited and the block making industries along the river banks should be relocated.

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