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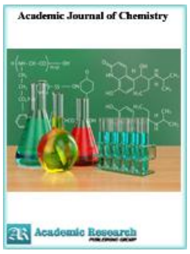

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Post Flood Analysis of Heavy Metal Level in River Benue along Makurdi Metropolis, Nigeria

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Abstract: River water was sampled across various segments of the River within Makurdi town to ascertain the anthropogenic contribution of heavy metal contents, a day after the torrential flood of 2012, and analysed using Atomic Absorption Spectrophotometric techniques. The mean concentration (mg/L) of the metals in sample sites were determined to be; Fe (0.46±0.1), Pb (0.03±0.01), Mn (0.002±0.002), Cr (0.02±0.01), Cd (0.001±0.001) and Zn (0.004±0.001). The results were compared with standards of WHO and EU recommended values for drinking water quality. It was found that Mn, Cr, Cd and Zn were below the WHO/EU limits while Fe and Pb were above recommended value. Statistical analysis shows that there is no significant difference observed for Fe, Mn, Cd and Zn between sites. However, Pb and Cr showed significant differences between sites. This shows that the metals are distributed at different points as a result of human activities, coupled with the impact of flood in their transport and solubility.

Keywords: AAS; Anthropogenic; Distribution; Flood; Heavy metals; River Benue.

1. Introduction

The major sources of environmental pollution are weathering of rocks and natural events such as earthquakes and floods [1]. Flood is a natural phenomenon and it occurs usually when rivers or water bodies overflow their banks due to large volume of water intake either directly from rainfall or from non-point sources. It may have significant negative impacts but can also provide positive environmental benefits. Amongst such benefit is that it helps in the spread organic material, nutrients and sediments. This may in turns replenish water resources naturally and trigger life processes such as migration and seed disposal. Generally, Rivers are dominant pathway for metals transport [2]. Investigation of heavy metal concentrations in sediment deposits on the River Tar floodplain was carried out by Pease, *et al.* [3]. They reported that the concentration of heavy metals were lower than might be expected for a flood of the magnitude. When municipal, industrial, and agricultural wastes enter into water, biological and chemical contaminants including heavy metals also find their way into the water [4]. Today's communities are seriously faced with problems of contaminants from human activities. This is largely due to the industrial and production of a variety of chemicals, followed by increased consumption of some unwanted pollutants by man [4]. Heavy metals entering the aquatic ecosystem originate from different sources such as decay of plants and vegetation, atmospheric particulates, discharge of domestic and municipal wastes [5]. These metals become significant pollutants of concern in many aquatic ecosystems and because of their toxicity and accumulation in aquatic organisms [6, 7]. With increasing industrialization, more metals are entering into the environment and stay permanently because they cannot be degraded in the environment [8]. Metals like lead, cadmium, mercury and arsenic are among the most toxic metals which accumulate in food chains and have a cumulative effect [9]. Therefore, heavy metals are sensitive indicators for monitoring changes in the water environment. The overall behaviour of heavy metals in an aquatic environment is strongly influenced by the associations of metals with various geochemical phases in sediments [10]. However, to assess the environmental impact of contaminated sediments, information on total concentrations is not sufficient and particular interest is the fraction of the total heavy metal content that may take part in further biological processes [10]. River Benue counts the second largest river in Nigeria which provides the neighbouring communities with the major source of water supplies along its course [11]. It passes through Makurdi metropolis, dividing it into two distinct areas designated as South and North- Banks. Benue State is quite open to untreated municipal sewage, agrochemical runoff, abattoir wastewater and leachates of solid wastes around it [12]. The aim of this study was to assess the level of metal loading into river Benue after torrential flood.

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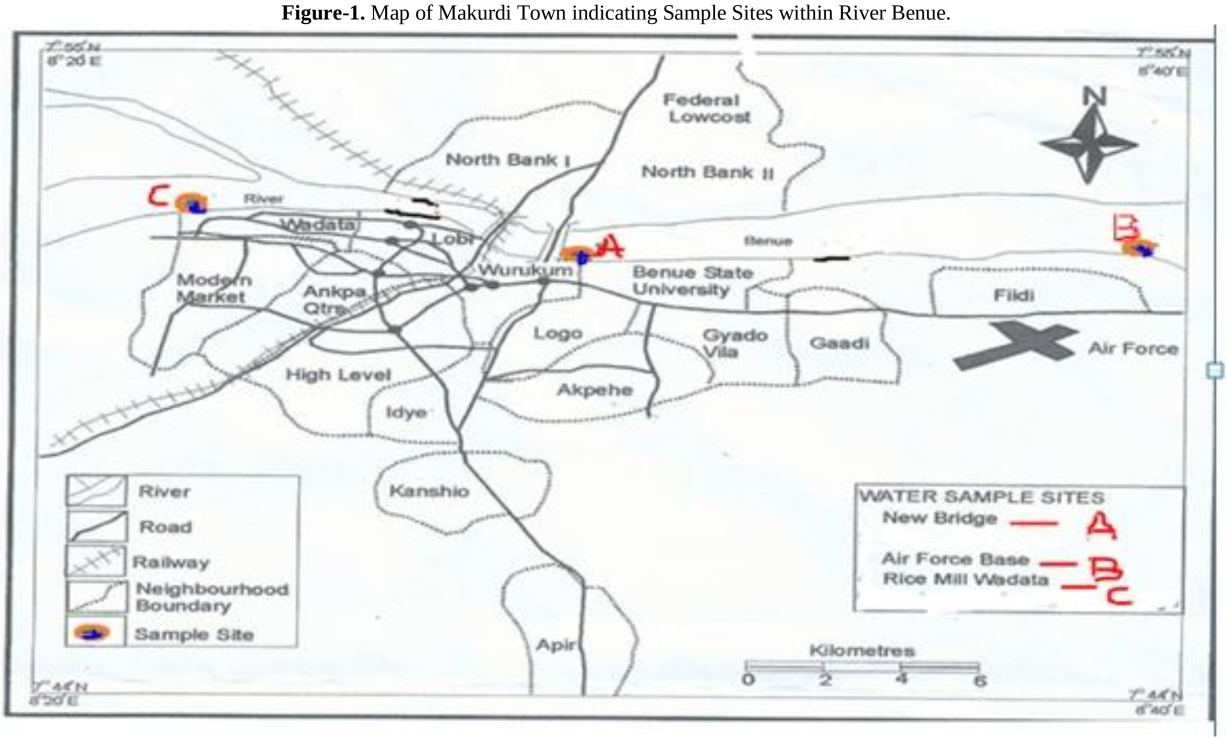
2. Materials and Methods

Sampling Area: Three sampling points of interest along the course of River Benue designated as sites New Bridge (A), Nigerian Air Force Base (B) and Wadata open Market (C) were chosen within Makurdi town as indicated in Figure 1. The main activities carried out in the designated sites include fishing, washing, Abattoir, open waste dumpsites, sand and gravel extraction business, farming of crops in their seasons and through irrigation where pesticides and organic manure are used intermittently, as well as effluents from Zoological garden and Benue State University Teaching Hospital.

Figure-1. Map of Makurdi Town indicating Sample Sites within River Benue.



Source: Ministry of Lands and Survey, Makurdi

Collection of Samples and Storage: Plastic containers (2 L) were used for water sampling from the shore of the river banks in December 2012, after a notable flood in Makurdi. Duplicate samples were obtained from each sample point and homogenized. The standard method described by AOAC. (Association of Official Analytical Chemists) [13] was adopted with any modification to keep the metal ions in solution and kept in refrigerator.

Digestion Process: Digestion was carried out by the method described by Eneji, *et al.* [14] without modification. Some quantity of water sample (200 mL) was measured and 5.0 mL of concentrated HNO_3 (73 % w/w) was added, shaken and heated at about 110 ^{0}C in a conical flask until the water reduces to 10 mL. Another 5 mL of Conc. HNO_3 was added and further concentrated to solubilise particulate matter content until it became clear. The sample was allowed to cool; thereafter, a little quantity of distilled water was added and filtered through a filter paper. The filtrate was made up to volume in a 100 mL volumetric flask then transferred to plastic sample bottle and covered for AAS analysis.

Analysis: Analysis of heavy metals was carried out at National Research Institute for Chemical Technology (NARICT) Zaria, Kaduna State, Nigeria using Shimadzu AA-6800 Model Atomic Absorption Spectrophotometer (AAS). Standard calibration curves of each element were plotted which was used for determination of unknown samples, Both instrument and sample blanks were prepared to check matrix interference as replicate measurements were also taken to ensure good precision. Actual metal concentration was calculated as follows:

$$Concentration\left(\frac{mg}{L}\right) = \frac{A\ X\ B}{C}$$

Where A = concentration of metals in digested solution (mg/L), B = final volume (mL) of digested solution and C = sample size (mL and g for liquids and solids).

3. Results and Discussion

The mean concentration (mg/L) of heavy metals in each of the sample sites are shown in Table 1, with the highest concentration found in Fe and the lowest in Cd. Fe ranges from 0.36 mg/L in site A to 0.56 mg/L in site C which indicated the highest concentration. Pb ranges between 0.02 to 0.04 mg/L across the sample sites, with the highest value fond in site B and the lowest in site site A. Mn also ranged between 0.002 to 0.01 mg/L, with the highest concentration in site C while its lowest was found in site B. Cr ranged between 0.01 to 0.03 mg/L, with the highest concentration in site C and the lowest in site B. The concentration of Cd ranged between 0.0002 to 0.002 mg/L across the sample sites, the highest value was found in site B while it has its lowest value at site A. Zn was determined to range between 0.004 to 005 mg/L. Similar quantities of Zn were found between sample sites A and C, while site B was slightly lower. Slightly higher metal concentrations were found in site C due to the large volume of human activities exhibited within this site, being a commercially viable market for mostly consumer products in this urban area as wash- off effluents are emptied into the river body directly. Table 2 shows comparison of heavy metals in River Benue before and after the flood. Some metals were higher than the work carried out while others were lower in magnitude than this work. This observation could also be attributed to influx of debris during the flood, large volume of water flowing with some insoluble components dilution factor etc.

Table-1. Mean Concentration (mg/L) of Heavy Metals in each Sample Sites

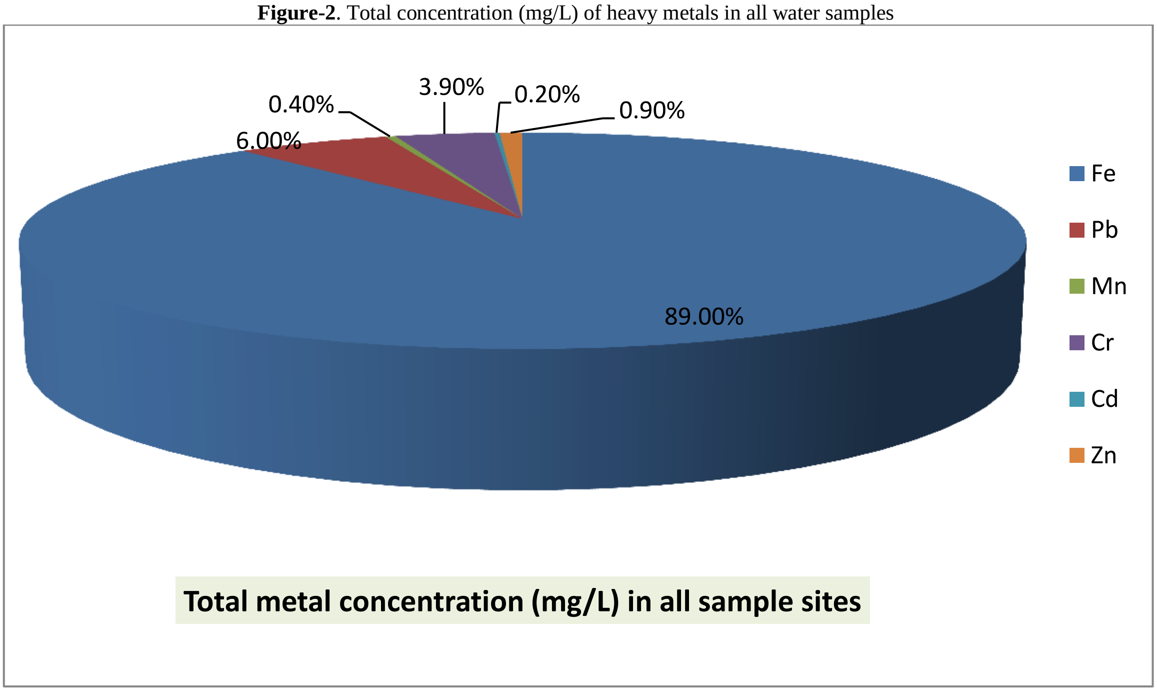
Heavy Metals	Sites		
	A	B	C
Fe	0.36±0.2	0.47±0.1	0.56 ± 0.1
Pb	0.02±0.002	0.04±0.001	0.03±0.01
Mn	0.003±0.002	0.002±0.002	0.01±0.003
Cr	0.02±0.002	0.01±0.001	0.03±0.002
Cd	0.0002±0.0001	0.002±0.001	0.001±0.001
Zn	0.005 ±0.0004	0.004 ±0.001	0.005± 0.001

Table-2. Comparison of heavy metals Level (mg/L) in River Benue before and after the flood

Fe	Pb	Mn	Cr	Cd	Zn	Reference
0.46	0.03	0.002	0.02	0.001	0.004	This work
0.751	0.207	0.181	0.381	0.052	0.0787	[14]
0.011	0.125	0.038	0.005	0.001	0.007	[15]
0.09	0.05	0.04	0.02	0.03	1.5	[16]
0.30	0.05	0.05	0.05	0.005	5.0	[17]

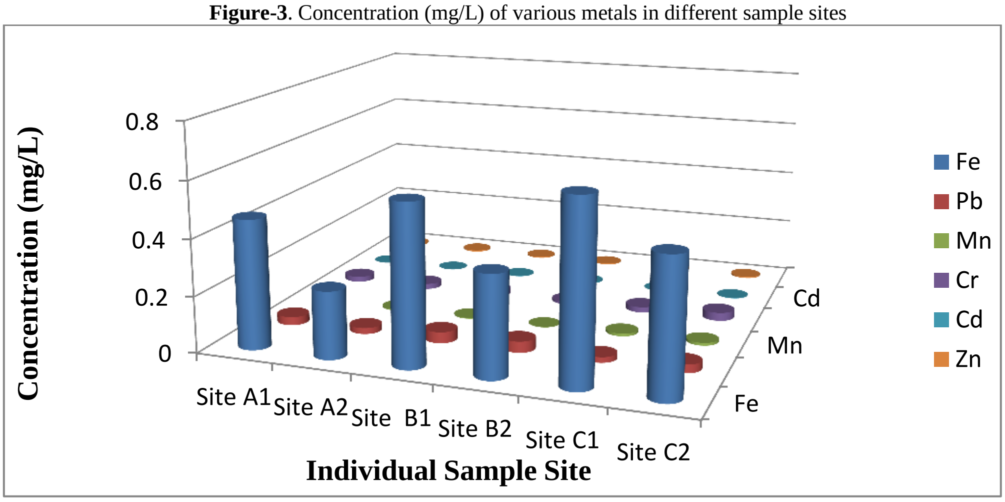
The total concentration (mg/L) of each metal analysed in all the water samples across the three sample sites is represented in Figure 2**.** Iron has a much larger cumulative concentration in comparison to all other metals except that reported by [Nnamonu, *et al.* [15], 16]. This could be due to anthropogenic interactions that engenders deposition of iron such as influx of iron scraps and welding activities from auto mechanic workshops upstream the sample sites, run off from water work equipment and effluents from Wadata market surrounding parks (garage), corrugated iron sheets, retailers' metallic containers from the river shore and syringe needles and surgical utilities emanating from the Benue State Teaching Hospital which are main contributors to metal loads in terms of iron. The variation in concentration was as a result of differences in metal distribution and dilution at various distances. Due to large volume of moving water in the river and differences in metal ion solubility. The **c**oncentration of replicate metals samples in the respective sites are given in Figure 3**,** in which Fe successively indicated higher concentrations where as Cd decreases steadily within each metal group across the sites.

Figure-2. Total concentration (mg/L) of heavy metals in all water samples



The student t-test was used to compare iron with all the elements between sites at p = 0.05 and it shows that there is no significant difference between distribution of Fe, Mn, Cd and Zn. However, significant difference was observed between sites A and C for Pb and Cr but no difference between sites A and B for the same elements. This means that there is variation in activities leading to deposition of these metals at different points. Akaahan, *et al.* [17] reported the levels (mg/L) of 0.42, 0.39, 0.35, 1.58, 0.19 and 0.04 for Pb, Ni, Cu, Cr, Cd and Al in river Benue, respectively. These values were above the WHO drinking water quality standard except for Cu. The concentration of Cd in river Benue during the study period varied from 0.09 to 0.30 mg/L with a mean concentration of 0.19 mg/L. However, [14] reported that the levels of most of the parameters determined, with the exception of Cd, Cr and Pb were, generally, within acceptable limits for drinking water and concluded that the River Benue is only moderately contaminated with regard to heavy metals. This present study corroborated with [14] values except for Fe and Pb which were above WHO limits. This could be attributed to dilution factor by water as a result of flood resulting to low metals concentration. Due to the turbulence created by increase of flow, some sediments and heavy metals inside them are displaced and carried away from the river bed. As Summer starts, the rise in temperature and evaporation and the end of the rain period cause the rise in heavy metals concentration in water and finally in sediments because metal ions transfer from water to sediment [4].

Figure-3. Concentration (mg/L) of various metals in different sample sites



Fe: The mean concentration (mg/L) of Fe in sites **A, B** and **C** were 0.36±0.2, 0.47±0.1 and 0.56±0.1, respectively. The total mean concentration (mg/L) of Fe across all the sample sites was determined to be 0.46±0.1, which is above both the WHO acceptable limit and that of National Agency for Food, Drug administration and control (NAFDAC) for drinking water (0.3 and 0.2 mg/L), respectively. Thus, Fe has the overall highest concentration among all the metal samples determined. A similar trend was observed by Nnamonu, *et al.* [15] when Fe was found to have the highest concentration among other metals determined in same water body using similar method of analysis. Results obtained from heavy metal analysis in river Benue using AAS method showed that Fe was within the WHO 1991 maximum permissible level [18].

Pb: Lead (mg/L) was determined to be 0.02 ± 0.002, 0.04 ± 0.001, 0.03 ± 0.01for sample sites **A, B**, and **C**, respectively. The total mean concentration of Pb in all the sample sites was 0.03 ± 0.01, this means that it was higher in all the sites in magnitude than the limit of 0.01 mg/L set by WHO for drinking water. Site **B** has slightly higher presence of lead than sites **A** and **C**. This was similar to Akaahan, *et al.* [17] who found out that the levels of Pb (mg/L) obtained in same river Benue for two seasons was 0.42, which was also reported to be above the WHO drinking water quality standard. According to Eneji, *et al.* [14], who used the same method of analyses in river Benue, lead was also reported to be above the acceptable limit for drinking water. Adamu and Nganje [18] also found that concentration of Pb (0.02-0.10 mg/L) obtained from a similar work in river Benue was more than the WHO 1991 maximum permissible limit. Possible sources of lead include its use in batteries, solder, paints, ammunition, devices to shield against x-rays and most consumer electronic items. Lead-based paint and leaded fuel. It also has an attendant health consequences such as restlessness, poor attention, muscle tremor span, headaches, hallucinations, irritability and loss of memory, gastrointestinal symptoms. Other health challenges associated with lead toxicity include tiredness, sleeplessness, irritability, headaches, joint pain etc [15-20].

Mn: The concentration (mg/L) of manganese was determined to be 0.003 ± 0.002, 0.002 ± 0.002 and 0.01±0.001 in sites **A, B** and **C**, respectively; while the total mean concentration of manganese was 0.002 ± 0.002. This indicates that Mn level was much lower than the acceptable limit (0.5 mg/L) for drinking water as set by WHO and that by European Union (0.05 mg/L), meaning that the water in terms of Mn is not contaminated as at this period. Manganese (0.06-2.0 mg/L) was however, determined to be higher than the 1991 maximum acceptable limit set by WHO as reported by Adamu and Nganje [18].

Cr: The mean concentrations (mg/L) in sites **A, B** and **C** were found to be 0.02 ± 0.002, 0.01 ± 0.001 and 0.03 ± 0.002; while the total mean concentration was 0.02 ± 0.01. These values were less than WHO acceptable limits for drinking water, indicating no danger in terms of chromium content for this period of time. Although, it was determined to fall within acceptable limit from the same river [14, 19] which could be due to seasonal variation of metal contents. Higher concentration of Cr (0.62 mg/L) was found in an urban river in pre-monsoon than that in monsoon (0.54 mg/L) and post-monsoon (0.59 mg/L) water samples collected before 2009. The chromium concentration was much higher than the standard level for drinking water (0.05 mg/L) proposed through Environment Conservation Rules (ECR) of 1997 [21, 22], but was lower than that of the present study in river Benue.

Cd: The concentrations (mg/L) of Cd as distributed across sites **A, B** and **C** were 0.0002 ± 0.0001, 0.002 ± 0.001 and 0.001 ± 0.001, respectively; while the total concentration (mg/L) is 0.001±0.001. Cd has the lowest concentration in all the respective sample sites followed by manganese except in site B where they are the same. Cd concentrations both for individual site and total content were below WHO limit of 0.003 and EU limit of 0.005 mg/L, respectively also showing no immediate threat to human life but has to be carefully monitored. [15] determined that Cd also has the lowest concentration value among other metals of interest in a research carried out in same river Benue. Mohiuddin, *et al.* [22] determined the content of cadmium to be 0.16 mg/L in summer and 0.22 mg/L in winter, respectively, which were reported to be much higher than the drinking water standard value (0.005 mg/L). The lower level of Cd during summer than in winter may have resulted from dilution effect of rise in water level in summer. He suggested that, seasonal industrial discharges may also have direct effect on these variations, as some metals in water are higher in summer and some others in winter. He however, does not observe any significant seasonal variation in Zn level (0.26 mg/L in summer and 0.22 mg/L in winter) and the values were lower than the drinking water standard (5 mg/L). [22] however, concluded that considering the Toxicity reference values (TRV) proposed by USEPA [23] almost all the heavy metals were much greater than the limit for safe fresh water, also Cr, Pb, Cd values exceeded one hundred times the toxicity reference value.

Zn: The concentration (mg/L) of zinc in sample sites **A, B** and **C** were 0.01 ± 0.0004, 0.004 ± 0.001 and 0.01 ± 0.001, while the total mean concentration (mg/L) was 0.004 ± 0.001. These were all below WHO acceptable limit of 3 mg/L. Zinc is an essential trace metal for both retarded growth, loss of taste and hypogonadism, leading to decreased fertility [24]. Zn toxicity is rare, but at concentrations in water up to 40 mg/kg, may induce toxicity, characterized by symptoms of irritability, muscular stiffness and pain, loss of appetite, and nausea [25]. The highest concen-tration of Zn (3.45 mg/kg) was seen in the gill of *Tilapia zilli*, while the lowest value of 0.06 mg/kg was measured in the flesh of *Clarias angullaris.* The FAO maximum guideline for Zn is 30 mg/kg [26]. Thus, the concentrations of Zn in the fish samples were within the FAO guideline. This finding was however at variance with [27] who found that the concentrations of Cr and Cd were above the WHO limits while Pb was below WHO acceptable limit for rivers for river Benue, though taken in Lokoja axis, Kogi state. This difference could result from different rates/frequency of waste dissipation, especially through dumpsites as well as dilution factor.

4. Conclusion

There is variation in the heavy metal concentration across the different sites indicating a corresponding variation in the activities leading to deposition of these metals at different points due to different rates of metal ion mobility or transportation and difference in solubility. We found that Mn, Cr, Cd and Zn were below the standard WHO and EU limits. However, Fe and Pb were above the recommended values. Statistical analysis using t-test at 0.05 propability (95 %) confidence limit shows that there is no significant difference observed for Fe, Mn, Cd and Zn between sampling sites. However, Pb and Cr showed significant differences between sites. This shows that the metals were distributed at different points as a result of human activities, such as farming, slaughtering effluence, dumpsites, auto-mechanic and marketing interference.

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