Post Flooding Assessment of the Heavy Metal Pollution of Water and Fish of Rivers Niger and Benue in Lokoja, Nigeria

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Abstract **-** The study reports the water quality and heavy metal concentrations in *Clarias gariepinus*, *Oreochromis niloticus* and *Synodontis nigrita* obtained from rivers Niger and Benue in Lokoja, Nigeria following the 2012 flooding in Nigeria. The chemical oxygen demand, dissolved oxygen, turbidity and biological oxygen demand of the water ranged: 98.25-141.73 mg/L, 2.26-14.39 mg/L, 5.33-23.13 NTU, 5.56-15.59 mg/L respectively in 2013. Cd, Co, Cr, Cu, Pb and Zn in the water ranged from 0.0082-0.0276, 0.0042-0.0279, 0.0480-0.1391, 0.0979-1.8037, 0.0003-0.0047 and 0.7671-2.8510 mg/L respectively. There was significant difference in the metal levels of the rivers and by sampling periods ($P < 0.05$). The bio-accumulation of Cd, Co, Cr, Cu and Pb by the fish follows the ranking: bone > brain > flesh. Cd and Pb accumulated in the order *O. niloticus* > *C. gariepinus* > S. *nigrita*. The results indicate pollution of the rivers, so enforcement of environmental laws is imperative.

Keywords--- Bio-accumulation, Fish, Flooding, Rivers

I. Introduction

THE most often polluted of the environmental phases is the aquatic systems, which include the water, sediments, fishes and other faunas. This is because contaminants in the air, soil or on land ultimately end up in the aquatic systems [1]. Physicochemical characteristics of water are important parameters as they may directly or indirectly affect its quality and consequently its suitability for the distribution and production of fish and other aquatic animals [2]. Fish may absorb dissolved elements and heavy metals from surrounding water and food, which may accumulate in various tissues in significant amounts and elicit toxicological effects at critical targets [3]. Also, fish may accumulate significant concentrations of metals in water even if those metals are below the limit of detection in routine water samples [4].

Flooding was experienced in towns along River Niger and River Benue in 2012. The concomitant effects among a plethora of others could be the reports by fish marketers that quantity of fish in Lokoja market has dropped drastically compared to past years.

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Enokela and Salifu (2012) reported the pH, turbidity, DO and BOD of River Niger water in Lokoja, Nigeria to be 7.42, 42.75.60 NTU, 8.73 mg/L and 2.24 mg/L respectively for River Niger; with Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} found within the tolerable limit set by WHO [5]. The metal concentration in the water of River Niger in Lokoja was in the sequence Mn > Zn > Cu > Cr > Ni > Cd > Pb [6]. On the other hand, water from River Benue at Makurdi, Nigeria recorded pH (5.00 - 9.00), TDS (6.81 - 521.33 mg/L), turbidity (3.00 - 258 NTU), conductivity (9.90 - 1071.00 µS/cm) and copper (0.00 - 1.45 mg/L) and the ranking for heavy metals was Cd < Cu < Zn < Mn < Pb < Cr < Fe [7], [8].

Tukura *et al.* (2005) stated that except for chromium, metal levels in water were higher than in *Clarias gariepinus* and *Tilapia zilli* and that zinc and lead bio-accumulate most in the gills of the fish species studied [9]. Heavy metals accumulate more in the visceral tissues (liver, kidney, intestines etc) than in other organs and least in the muscles of *Tilapia* and shrimps [10].

This work is aimed at furnishing scientific data on the quality of the water and fish from River Niger and River Benue in Lokoja, Nigeria, since these rivers supply bulk of fish for commercial purpose and serve as source of water for municipal and industrial utilization.

II. Materials And Methods

A. Study Area

The study area is located in Lokoja, the capital of Kogi State, Nigeria lying between latitude 7°49'N to 7° 8.89'N and longitude 6°44'E to 6°5.85'E. The annual rainfall of the area is between 1016 mm and 1524 mm. The rainy season lasts from April to October [11]. River Niger and River Benue meet in Lokoja.

B. Sampling

Water samples were collected from nine sampling points (A – I) as indicated in Fig. 1, each 500.00 metres apart. The sampling was carried out four times: March, June, September and December 2013.

C. Water Pretreatment

About 2000.00 cm^3 of water sample was collected in triplicates at the centre of the river for each sampling point using an improvised sampler into plastic gallons earlier washed with 1.00M nitric acid and rinsed with deionised water.

For analysis of heavy metals, the samples were acidified with 20.00 cm^3 of 2.00M HNO_3 in order to keep the required specie and slow down biological activity in the water [12].

D. Fish Sampling and Pre-Treatment

Fish samples of approximately equal size [*Clarias gariepinus* (Catfish), *Oreochromis niloticus* (Tilapia fish) and *Synodontis nigrita*] were purchased from fishermen at the bank of the rivers at each period of sampling. The samples were stored under ice bag before analysis.

E. Determination of Physicochemical Parameters of Water

Turbidity was determined by using a turbidimeter [13].

Total dissolved solids was carried out by the method of AOAC (1998) [14].

The pH of the water sample was also determined *in-situ* with the aid of a HANNA portable pH meter [13].

Electrical conductivity was carried out by a using a conductivity meter [13].

Hardness of the water was measured by the method adopted by Clesceri *et al*. (1998) [15].

Dissolved oxygen and chemical oxygen demand was measured using the method of AOAC (1998) [14]. Biological oxygen demand (BOD) was determined using (APHA, 1992) [13].

F. Digestion of Samples

The digestion of water sample was done using concentrated HNO_3 [13].

The oven dried (60^oC) organs (bones, flesh, and brain) of each fish sample were separately digested using concentrated HNO_3 [16].

G. Atomic Absorption Spectrophotometry Measurements

The amounts of Cd, Co, Cr, Cu, Pb and Zn in the diluted solutions were determined using atomic absorption spectrophotometer (Varian AA240FS) at the Multi-user Laboratory, Ahmadu Bello University, Zaria, Nigeria. All measurements were taken in triplicate, the quality assurance for the analyses was conducted through the spiking method, and mean % recovery for the analyses determined.

H. Statistical Analysis

Analysis of Variance (ANOVA) was used to explain the discrepancies in the levels of heavy metals in the water and organs of the fish (Duncan Multiple Range Test at $P < 0.05$). Pearson Correlation Coefficient was used to determine degree of linear relationship between the physicochemical parameters and heavy metals in the two rivers [17].

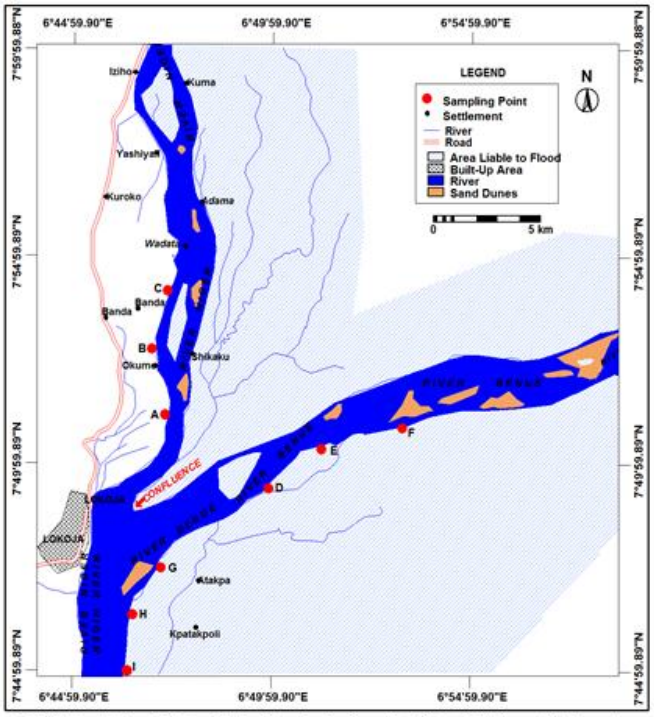


Fig. 3.2 : An Abstract of Lokoja Map Showing the Sampling Sites for Water and Sediment

Source: Modified from Topographic Map of Lokoja Sheet 247 N.E and N.W.

Fig 1 Sampling points for water in River Niger and River Benue

III. Results And Discussion

A. Physicochemical Properties of Water Samples from River Niger, River Benue and the Confluence Point

The biological oxygen demand (BOD) of the water in River Niger had mean values of 9.23 ± 0.56, 7.01 ± 1.31, 15.59 ± 1.13 and 5.56 ± 1.106 mg/L for the month of March, June, September and December, 2013 respectively. For River Benue the mean were 7.82 ± 0.36, 10.34 ± 2.88, 6.69 ± 0.87 and 5.99 ± 0.75 mg/L respectively. The highest BOD values were recorded in September and least in December 2013. In March, June and September 2013 the rivers and the confluence have BOD above the maximum limit set by WHO (6.00 mg/L).

The result obtained for chemical oxygen demand (COD) content of the rivers is in the order River Niger > confluence > River Benue for the month of March 2013. The least COD values were found in the December samples while the March samples recorded the highest values. This indicates that the rivers had high influx of organic compounds and in comparison with the permissible limit set by WHO (10.00 mg/L), all the rivers had COD above the threshold value. However, this study reveals higher values compared to those reported by Osibanjo *et al.* (2011) [18] and Olatunde and Oladele (2012) [19] in their researches in River Ona and River Niger (23.54 - 95.32 and 18.52 - 22.46 mg L^{-1}) respectively.

In the months of March, June and September, the water from the three sampling sites had electrical conductivity above the international standard set by WHO (100 µS/cm). From the study, the concentration of dissolved oxygen (DO) of water from the two rivers and the confluence point follow the ranking September > December > June > March 2013. An inverse relationship was noticed between COD and DO. The DO values were lower than the minimum value of 15.00 mg/L

set by WHO. Values below 3.00 mg/L recorded in the March 2013 samples are considered critical DO value [20]. The trend of COD and DO in the study conforms with those reported by other researchers [18], [19], [21], [22].

The water from the confluence had mean hardness of 173.31 ± 11.30, 160.57 ± 49.43, 228.69 ± 16.62 and 53.63 ± 6.04 mg/L for March, June, September and December respectively. While the pH of the water samples ranged from 6.77 - 8.075. However, the work indicated that the highest total dissolved solids (TDS) was 721.61 ± 16.15 in River Niger and the least in the confluence point was 476.98 ± 23.98 mg/L. No regular pattern was recorded in the results of turbidity across the rivers with respect to sampling period. However, the turbidity values were above the acceptable limit set by WHO (5.00 NTU).

B. Heavy Metals in Water Samples of River Niger, River Benue and the Confluence Point in Lokoja

The spiking procedure indicated that the mean percentage recovery for the metals ranged from 81.9 ± 0.15 to 94.9 ± 0.40.

The results reveals that the level of Cd in the water obtained from River Niger during the months of March, June, September and December ranged from 0.016 - 0.034, 0.011 - 0.026, 0.014 - 0.031 and 0.003 - 0.015 mg/L and with corresponding means of 0.022 ± 0.007, 0.0168 ± 0.005, 0.019 ± 0.006 and 0.009 mg/L respectively. The concentrations of cadmium in the water samples indicated that in March 2013, there was a significant different in cadmium concentration of River Niger compared to the other sampling sites (River Benue and the confluence point) at $P < 0.05$. On the other hand, the level of Cd in water obtained in September and December 2013 showed a significant different between the two rivers and the confluence at $P < 0.05$. River Benue is more polluted with Cd than the other sampling sites. The rivers recorded Cd values above the acceptable limit for rivers.

River Niger had the highest level of Co being 0.016 ± 0.003 mg/L and the highest for River Benue which was 0.018 ± 0.008 mg/L were both in the March samples. The level of Co varied significantly between the three sampling sites at all the sampling periods.

Cr concentrations in the water follow the ranking River Niger > River Benue > Confluence. Higher values of Cr in the water were recorded in March and the lowest values were recorded in December 2013. Cr concentration in the water of the three sampling sites was above the recommended value by WHO (0.0500 mg/L) in March, June and September.

The water from the confluence point had Cu values 1.384 ± 0.398, 1.056 ± 0.340, 0.904 ± 0.182 and 0.938 ± 0.339 mg/L for March, June, September and December 2013 respectively.

The values of Pb obtained for the water were far below the WHO value (0.01 mg/L).However, there was significant difference in the levels of Pb in the two rivers and the confluence ($P < 0.005$). On the contrary Apeh and Ekenta (2012) reported mean Pb of 0.03 ± 0.02 mg/L for water obtained from River Benue [8].

The level of Zn in the water samples were generally below the WHO recommended value (4.0000 mg/L). There was significant difference between the Zn concentrations obtained in the water samples during the four sampling periods at $P < 0.05$.

As shown in Table 1 for the water samples collected in March 2013, BOD had high positive correlations with COD (0.909), turbidity (0.817), TDS (0.739), hardness (0.509) and lead (0.663); while strong negative correlation was observed with DO (-0.884), pH (-0.731) and Cu (-0.525) respectively. Similarly, the conductivity of the water samples recorded strong positive linear relationship with turbidity (0.559), TDS (0.508) and Pb (0.523) and strong negative relationship with DO (-0.779) and pH (-0.902) respectively. The only strong correlation recorded among the metals was between Pb and Cu (-0.551) which was an inverse relationship.

TABLE 1
PEARSON CORRELATION MATRICES OF PHYSICOCHEMICAL PARAMETERS WITH HEAVY METALS IN WATER SAMPLE (MARCH SAMPLE)

	COD	DO	Turb	BOD	TDS	Hd	Ct	pH	Cd	Co	Cr	Cu	Pb	Zn
COD	1													
DO	-.947**	1												
Turb	.772**	-.713**	1											
BOD	.909**	-.884**	.817**	1										
TDS	.762**	-.667**	.868**	.739**	1									
Hd	-.592**	.473*	- .346	.509**	- .472*	1								
Ct	.714**	-.779**	.559**	.747	.508**	-.235	1							
pH	-.707**	.735**	-.638**	-.731**	-.563**	.197	-.902**	1						
Cd	-.360	.268	-.104	-.179	-.241	.330	-.169	.087	1					
Co	-.132	-.132	-.282	-.247	-.268	.111	-.029	.062	.141	1				
Cr	.205	-.279	.182	.188	.192	-.026	.207	-.218	-.103	-.227	1			
Cu	-.575**	.599**	-.527**	-.525**	-.507**	-.400*	-.333	.323	.065	-.024	-.264	1		
Pb	.703**	.703**	.748**	.663**	.785**	-.387*	.523**	-.684**	-.044	-.118	.062	-.551**	1	
Zn	.013	.020	.285	.092	.176	-.095	.048	-.172	.529	-.041	-.369	-.126	.367	1

**Correlation is significant at 0.01 level (2-tailed) , * Correlation is significant at 0.05 level (2-tailed)
Turb= Turbidity, Hd= Hardness, Ct= Conductivity

C. Heavy Metal Concentrations (mg/kg) in Organs of Fish from River Niger and River Benue in Lokoja

As presented in Table 2, the maximum Cd concentration was in the bones of the three fish species. The Cd level accumulated in the fish follow the trend *O. niloticus* > *S. nigrita* > *C. gariepinus.* The range obtained for the concentration of cadmium was 1.508 - 1.323, 1.882 - 5082.257 and 1.829 - 2.019 mg/kg in the bones of catfish, tilapia and S. *nigrita* respectively. This result conforms to that of Abraham *et al*. (2012) [23]. All the organs of the fish were polluted with Cd like the work of reference [24].

The result indicated that Co in the organs follow the ranking *C. gariepinus* > *S. nigrita* > *O. niloticus*. The results showed high accumulation of Co in the brain of *C. gariepinus* and *S. nigrita* while *O. niloticus* recorded high values in the bone. The study showed that the trend of the concentration of Cr in the organs is bone > brain > flesh in all the fish species (Table 2). The values of Cr recorded in the organs exceeded the WHO set value of 0.15 mg/kg; therefore this scenario poses a serious threat to consumers of the fish from the study area.

Copper was accumulated more by the bone compared to brain and flesh of the fish species. *O. niloticus* accumulated the highest concentration of Cu. There was no significant variation in Cu level of the organs of the three fish with respect to collection time.

The lead levels ranged from 1.907 ± 0.690 – 2.874 ± 0.916, 2.778 ± 0.689 – 3.532 ± 1.257 and 1.575 ± 0.413 – 2.674 ± 0.925 mg/kg for the bones of *C. gariepinus*, *O. niloticus* and *S. nigrita* respectively. Lead was found to accumulate in the organs of the three species of fish studied, though there was low content of Pb in the water from the study area; this trend is corroborated by the assertion of refence [4]. This implies that the concentration of Pb in aquatic biota is not totally dependent on level in the water. However, the lead in the organs were above the recommended value set by WHO (1993) being 0.5 mg/kg. Following from Table 2, zinc in the organs decreased in the order: bone > brain > flesh. The organs had levels of metals in the order Zn > Cr > Cu > Cd > Pb > Co.

IV. Conclusion

Water samples from the two rivers and their confluence showed critical values of COD, DO, turbidity, BOD, TDS, hardness and conductivity in the months March, June and September 2013; while pH was within the permissible limit during the study period. Cd, Co, Cr and Cu were predominantly above the permissible limits in the water sample while Pb and Zn were below the tolerable limits in all the water samples.

Also, the level of Co and Cr exceeded the threshold limit in all the fish samples irrespective of the organ or fish species. Despite the low values of Pb recorded in the water, all the selected fish species studied accumulated Pb above the critical limit. Conclusively, the results indicated that bioaccumulation of Zn in all the samples of the three species of fishes was low compared to the limits set by WHO (1999). The findings reiterate the need for environmental laws to be strictly enforced in order to maximize the potential of the two rivers.

Table II
Maximum Concentrations Of Some Heavy Metals (Mg/Kg) In Organs Of Three Species Of Fish Collected From River Niger, River Benue And The Confluence Point

Specie	Organ	Cd	Co	Cr	Cu	Pb	Zn
C. gariepinus	Bone	1.508	1.774	3.683	2.424	1.907	5.460
	Brain	1.206	3.159	3.322	1.852	1.564	4.045
	Flesh	0.894	0.800	2.156	1.444	1.284	3.236
O. niloticus	Bone	2.257	2.664	3.603	3,002	2.964	6.013
	Brain	2.076	1.350	2.814	2.572	3.326	4.801
	Flesh	1.072	0.919	1.894	1.751	1.451	3.151
S. nigrita	Bone	2.019	1.687	3.315	2.564	2.674	5.302
	Brain	1.747	2.541	2.793	1.940	2.439	3.822
	Flesh	0.851	0.872	2.294	1.360	1.046	2.781

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