Journal of Energy, Environmental & Chemical Engineering
2017; 2(1): 6-9
http://www.sciencepublishinggroup.com/j/jeece
doi: 10.11648/j.jeece.20170201.12

Concentration of Heavy Metals in Fish (*Synodontis clarias*) of Benin River, Delta State, Nigeria

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To cite this article:
Isaac Adewale Omole. Concentration of Heavy Metals in Fish (*Synodontis clarias*) of Benin River, Delta State, Nigeria. *Journal of Energy, Environmental & Chemical Engineering.* Vol. 2, No. 1, 2017, pp. 6-9. doi: 10.11648/j.jeece.20170201.12

Received: October 27, 2016; **Accepted**: February 10, 2017; **Published**: March 2, 2017

Abstract: The concentrations of four heavy metals [Lead (Pb), Aluminium (Al), Nickel (Ni) and Chromium (Cr)] in *Synodontis clarias* sampled in July, August and September (2014) at two locations along the Benin River, Delta State, were investigated by means of the atomic absorption spectrophotometer technique. A total of 24 samples of *S. clarias* with an average weight of 189g and length of 23cm were collected from the two locations along the river. Results showed that the total mean concentration values of metals recorded in *S. clarias* was: Pb (1.507mg/kg), Al (5.170mg/kg), Ni (2.380mg/kg) and Cr (0.075mg/kg). ANOVA showed significant differences ($p<0.05$) between the concentrations of each metal in *S. clarias* of Benin River at Koko during the different months of sampling. However, the concentration of Pb was not significantly different ($p>0.05$) in July compared to September, and July compared to August. Metal concentrations in the fish were generally within the acceptable limits set by Food and Agriculture Organisation (FAO) and World Health Organisation (WHO) in fish and fishery products, except for Nickel which exceeded the FAO recommended 0.5-0.6mg/kg limit. However, the concentrations of the heavy metals in water were much higher than recommended safe limits for human consumption thereby posing a direct health challenge to the people of the Koko community who depend on the water for domestic uses. There is an urgent need to check the sources of pollution in the area to forestall any imminent danger.

Keywords: Atomic Absorption Spectrophotometer, Heavy Metals, *Synodontis clarias*, Benin River

1. Introduction

The 20th century has witnessed a lot of concern over the relationship between man and his environment. The escalating contamination of the environment by toxic substances is of growing concern in Nigeria and worldwide [1]. The concern about heavy metals stems from their persistence in the environment as they are not easily degraded either through biological or chemical means unlike most organic pollutants [2]. Among animal species, fishes are the inhabitants that cannot escape from the detrimental effects of these pollutants. Fishes are at the apex of the aquatic food chain and can bioaccumulate some of these substances into their tissues [3]. As a consequence, fish are often used as indicators of heavy metals contamination in the aquatic ecosystem because they occupy high trophic levels and are important food source [4].

Rivers are used as a source of drinking water for humans and considered as a sink for waste. Undoubtedly, a riverine aquatic environment suffers the consequences of domestic and industrial activities occurring in its watershed [5]. In Nigeria, environmental management practices are inefficient due to poor infrastructure and lack of environmental protection awareness [6]. As a result of the ineffectiveness of purification systems, waste water may become seriously dangerous, leading to the accumulation of toxic products in the receiving waster bodies with potentially serious consequences on the ecosystem [7].

The Benin River is of great importance to inhabitants in the many villages through which it flows. The inhabitants of surrounding villages rely mainly on the river for their domestic water supply, fishing, sand mining and inter-village transportation. The river also receives effluents from many industries including ASCA oil, Optima, Total Asphalt blending plant, sawmills and abattoirs along the river bank.

This study aims to determine the heavy metals concentration in the Benin River with special focus on Koko community which is a major fishing community along the stretch of the river.

2. Materials and Methods

2.1. Study Location

The Benin River is located on latitude 6°00'N and longitude 5°28'E. It is approximately 93 km long with average width of 3.0km and 1.4km in its downstream and upstream sections respectively. The area is characterized by tropical equatorial climate with mean annual temperature of 32.8°C and annual rainfall of 2673.8mm. The forest is rich in timber trees, palm trees, as well as fruit trees. Human activities within and around this river include dredging, logging, fishing, boating, watercraft maintenance, saw milling, transportation, laundering, bathing and swimming. The area is also subjected to oil spillage and industrial wastes discharge as a result of the oil prospecting and exploitation in the Niger Delta region of Nigeria.

2.2. Sample Collection and Analysis

Fresh *S. clarias* samples (average weight, 189g and total length, 23cm) were procured from fishermen at the landing site. In the laboratory, total body length was determined using a measuring board and recorded to the nearest 0.1cm while weight was determined using a top loader (Mettler, P. E. 230) and recorded to the nearest 0.1g respectively. The fish samples were oven-dried to constant weight at 90°C for 48 hours. The dried samples were ground into powder using a porcelain mortar and pestle and stored at a temperature of -10°C. Water samples were collected in plastic bottles and acidified in the laboratory to pH 1.5 using 10% HNO_3. All the samples were stored at a temperature of -4°C.

A method described by [8] was employed in digesting the fish samples. 2g of the milled fish sample was measured into a 250ml conical flask. 20ml of nitric acid and perchloric acid (3:1) were added to the sample. The mixture was heated (200°C - 250°C) over an electric plate under a hood until the sample became a clear solution. The solution was allowed to cool before adding 5ml of 20% hydrochloric acid (HCl). The digest was filtered into a 100ml volumetric flask using Whatman No.1 filter paper and made up to the 100ml mark with distilled water.

Water digestion was carried out according to the method described by [9]. 2ml of water sample was digested using 15ml concentrated nitric acid (HNO_3) in a 250ml conical flask. The mixture was heated over an electric hot plate at a temperature of between 200°C and 250°C under a hood until the volume was reduced to 5ml. The digest was stored the same way as with the fish digest.

The metals were analysed using an atomic absorption spectrophotometer (AAS) (Solar 969 Unicam series) while statistical analysis was done using the computer software (Genstat Version 8.1, 2005). One-way analysis of variance (ANOVA) was used in all cases to test for significant differences between means at 5% probability level. Significant treatment means were separated using the New Duncan's Multiple Range Test in a CRD model.

3. Results

Results obtained during this study (Figure 1) showed that the mean Pb value recorded in *S. clarias* was 1.507mg/kg with a higher Pb concentration (1.518mg/kg) recorded in fish caught at Station 2 than in those from Station 1 (1.497mg/kg), although there was no significant difference ($p>0.05$) between the two locations. The mean Al concentration recorded in *S. clarias* during the study period was 5.170mg/kg. A significant difference was recorded between concentrations from Stations 2 (5.278mg/kg) and 1 (5.062mg/kg). The total mean Ni concentration recorded in *S. clarias* during the study was 2.380mg/kg. Station 2 recorded a higher mean Ni concentration (2.408mg/kg) than Station 1 (2.352mg/kg) but there was no significant difference with ANOVA. The total mean concentration of Cr recorded during the study was 0.075mg/kg. Station 2 recorded a slightly higher Cr value (0.076mg/kg) than Station 1 (0.074mg/kg); the concentrations were not significantly different.

Heavy metals concentration in water of Benin River during the study period is shown in Figure 2. The mean concentration of Pb recorded in water of Benin River during the study was 0.187mg/l. The Pb concentration was higher at Station 1 (0.208mg/l) than at Station 2 (0.165mg/l) although no significant difference was recorded. A mean concentration of 2.863mg/l was recorded for Al in water, with a significantly higher concentration at station 2 (3.185mg/l) than at station 1 which had a concentration of 2.542mg/l. The mean Ni concentration recorded in water was 0.628mg/l. Station 2 had a higher concentration (0.640mg/l) than Station 1 (0.615mg/l); the difference was not significant. The mean concentration for Cr in water of Benin River during this study was 0.056mg/l. Station 1 had a higher concentration value (0.058mg/l) than Station 2 (0.054mg/l). The concentration did not vary significantly for Cr between the sampling stations.

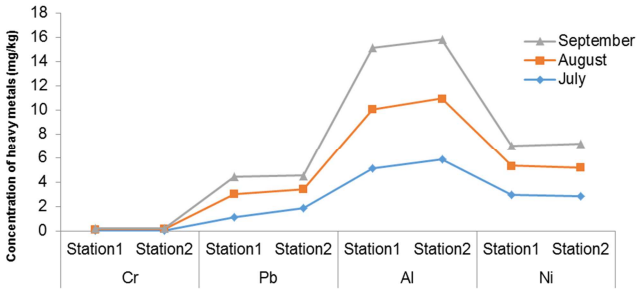

Figure 1. *Concentration of heavy metals in fish.*

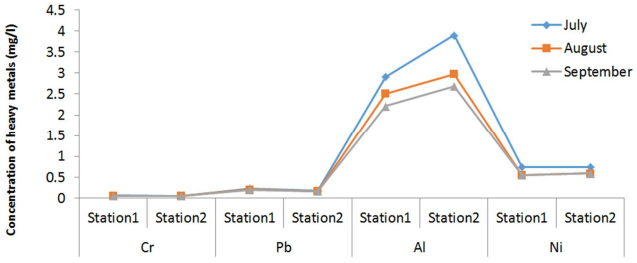

Figure 2. *Concentration of heavy metals in water.*

4. Discussion

The results of this study confirmed the presence of the selected heavy metals in the water and fish of Benin River at Koko. Heavy metals are non-biodegradable natural resources but their levels have increased due to domestic, industrial, mining and agricultural activities [10, 11]. If the concentration levels of these elements increased beyond the level required, they can act in either acutely or chronically toxic manner [12].

Results obtained indicated higher heavy metals concentrations in fish than those recorded in water, which agrees with the observation of [13] that fish accumulates heavy metals directly from water and diet. The mean concentration of heavy metals in recorded fish and water in decreasing order was: Al > Ni > Pb > Cr.

The high Pb concentration recorded in the study area may be attributed to the wastes generated by the nearby industries (Optima and Total) and the activities of motorized water crafts, since water is the dominant means of transportation in the area. The mean Pb concentration recorded in this study was lower than the recommended level [14]. It was also lower than the value reported by [15] in *Clarias anguillaris* (4.067mg/kg) from River Niger probably due to the rate by which natural and anthropogenic wastes are continuously being discharged into the River Niger. The recorded Pb concentration for water was lower than the Pb value (1.656mg/l) reported by [16] in lower Cross River but exceeded the guideline for potable drinking-water [17].

Table 1. *Mean Concentration (mg/kg) of Heavy Metals in Synodontis clarias of Benin River.*

Heavy Metals	Months	Station A	Station B	FAO Standard
Lead	July	1.135	1.915	
	August	1.910	1.525	2.0
	September	1.445	1.115	
Aluminium	July	5.140	5.895	
	August	4.970	5.060	1.0
	September	5.075	4.880	
Nickel	July	2.995	2.485	
	August	2.360	2.360	0.5–0.6
	September	1.700	2.020	
Chromium	July	0.085	0.088	
	August	0.072	0.074	1.0
	September	0.065	0.065	

Table 2. *Mean Concentration (mg/l) of Heavy Metals in the water of Benin River.*

Heavy Metals	Months	Station A	Station B	WHO Standard
Lead	July	0.230	0.170	
	August	0.205	0.165	0.01
	September	0.190	0.160	
Aluminium	July	2.910	3.900	
	August	2.505	2.975	0.2
	September	2.410	2.680	
Nickel	July	0.745	0.740	
	August	0.550	0.590	0.07
	September	0.550	0.590	
Chromium	July	0.060	0.057	
	August	0.057	0.053	0.05
	September	0.057	0.053	

Aluminium is released into the environment mainly by natural processes such as melting of the ores [18]. The high level of Al recorded at Station 2 may be attributed to the presence of structural installations and buildings on water at the station whose metallic properties gradually leach into the river. The concentration value for this study was lower than the Al value (7.79mg/l) recorded by [19] in Bindare stream. The recorded value was above the safe limit (0.2mg/l) recommended by [17] for potable water.

Nickel is one of the prominent trace metals in petroleum hence the relatively high level recorded in this study. The Ni concentration recorded in fish during this study was higher than higher than the value (0.468mg/kg) recorded by [20] in *Synodontis clarias* from Taylor Creek but lower than value recorded by [15] in *Clarias anguillaris* (18.500mg/kg) in River Niger. The recorded Ni value for water was higher than the Ni value (0.06mg/l) reported by [21] in water of Benin River. The mean concentration of Ni recorded for fish and water during this study was above the safe limits set by [14, 17].

Chromium reaches water bodies primarily from the discharge of industrial wastes and disposal of products containing the metal [22]. The presence of Cr in soaps and detergents used for washing and bathing coupled with petroleum products being discharged into the river could be responsible for the high Cr level in the water. The recorded concentration of Cr was lower than the value recorded by [15] in *Clarias anguillaris* (2.233mg/kg) of River Niger. The value was within recommended limits by [23]. The recorded concentration of Cr in water during this study was higher than the value (0.02mg/l) reported by [24] for creeks around the Kokori-Erhoike Petroleum Flow Station in Delta State. The recorded value was also above the guideline (0.05mg/l) for Cr in drinking-water recommended by [17].

5. Conclusion

The concentration levels of heavy metals, particularly Cr and Pb, portend danger to the inhabitants of the study area, who depend on the surface water in the region for drinking and domestic uses. The consequence of this is that the ignorant inhabitants make use of this heavily contaminated water to their detriment. Nickel is a hazardous heavy metal with the propensity to cause cancer of the lung and nasal cavity and the high level recorded in fish is a cause for concern. Increased urbanization and industrialization result in more wastes being generated with the river being a main recipient of effluents in the area. Based on the findings of this study, it can be concluded that Benin River at Koko is highly polluted with respect to heavy metals which makes the water unfit for drinking.

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