



Research Paper

## Study of Physico-Chemical Parameters and Heavy Metals Distribution on Surface Water Sediments in Okpoka Creek, Portharcourt Rivers State, Nigeria

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### ABSTRACT

The quality of Okpoka creek in Port Harcourt south-south Nigeria was investigated by a field survey during the rainy season. Water and sediment samples were collected from three sites (capturing the activities in a boating/badge operation, a market and residential community) along the river course. Samples were analysed for physicochemical parameters using standard methods. Heavy metals (Zn, Pb, Ni, Cr and Fe) in water and sediment samples were carried out using Atomic Absorption Spectrophotometer (AAS). Descriptive statistics and Pearson correlation were used to analyze data at  $P < 0.05$  and  $0.01$ . Generally, only Chloride (2508.00–9400.00mg/l) recorded elevated values across the sample stations, the other parameters ranged; pH (7.49–7.77), Conductivity (4.00–4.40 $\mu$ S/cm), DO (8.60–14.00mg/l), BOD (2.00–3.80mg/l), Sulphate (53.8–106.50mg/l), Nitrate (0.0049–0.2448mg/l) and Phosphate (0.0612–0.1836mg/l). Heavy metals values ranged Zn (1.3432–7.2696ppm), Pb (0.00–0.07ppm), Ni (0.00–0.141ppm), Cr (0.00–0.056ppm), and Fe (0.056–1.746ppm) with relative abundance in the order Zn>Fe>Ni>Pb>Cr. Heavy metal values from sediment recorded low concentrations, with, Zn (0.34–4.30ppm), Pb (1.33–1.84ppm), Ni (0.059–0.258ppm), Cr (0.00–0.476ppm) and Fe (1.531–1.862ppm) recording significant values in relative order of Zn>Fe>Pb>Cr>Ni. Significant correlations at  $p < 0.05$  were recorded for Zn with Chloride (+1.000\*), also pH recorded significant correlations with Pb (–1.000\*) and Cr (–1.00\*). Water quality index value of 262, 653 and 746 for stations I to III respectively indicated that Okpoka creek is almost always threatened or impaired; conditions usually depart from natural or desirable levels. The heavy metal species and some physical and chemical parameters especially chloride in the Okpoka creek were to a large extent above the WHO limits; and thereby pose a health risk to rural communities who rely heavily on the river primarily as their source of domestic water. The study revealed a need for continuous pollution monitoring and management program of surface water in Rivers state and Nigeria as a whole. It was recommended that relevant authorities beef up the regulation of indiscriminate dumping of domestic waste and untreated industrial effluents into the creek.

**Keywords:** Physico-chemical, Heavy metal, Creek, Sediment, Water quality, Anthropogenic, Industrialisation

Received 08 Dec, 2021; Revised 21 Dec, 2021; Accepted 23 Dec, 2021 © The author(s) 2021.

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### I. INTRODUCTION

Water is a marvellous substance which is essential for life. It is the medium in which all living process occurs and it is an indispensable unit of life. Water covers 70% of the earth's surface. It is a necessity for life, but industrialization and urbanization brought about pollution of water bodies. Anthropogenic activities carried out around water bodies have led to the introduction of substances that cause pollution. Water pollution involves the degradation of water bodies; it is an integrated occurrence that must be taken seriously according to the Environmental Protection Agency (EPA). This includes the discharge of unwanted chemicals, biological and physical materials from man's environment into water bodies.

The quality of any water is governed by its physico-chemical and heavy metal factor. The monitoring of physico-chemical characteristics of water body is vital for both long term and short term evaluation of its quality. Lakes, rivers and streams have important multi-usage components, such as source of drinking water, irrigation, fishery and energy production. Water is a scarce and fading resource and its management can have an impact on the flow and the biological quality of rivers and streams. Expanding human population, industrialization, intensive agricultural practices and discharges of massive amount of waste water into the rivers and streams have resulted in the deterioration of water quality. The impact of these anthropogenic activities has

been so extensive that the water bodies have lost their self-purification capacity to a large extent. Fresh water ecosystem had been used for the investigation and abundance of aquatic organisms. The physical and chemical characteristics of water bodies affect the species composition, abundance, productivity and physiological condition of aquatic organisms (Swingle, 1969; Moses, 1983).

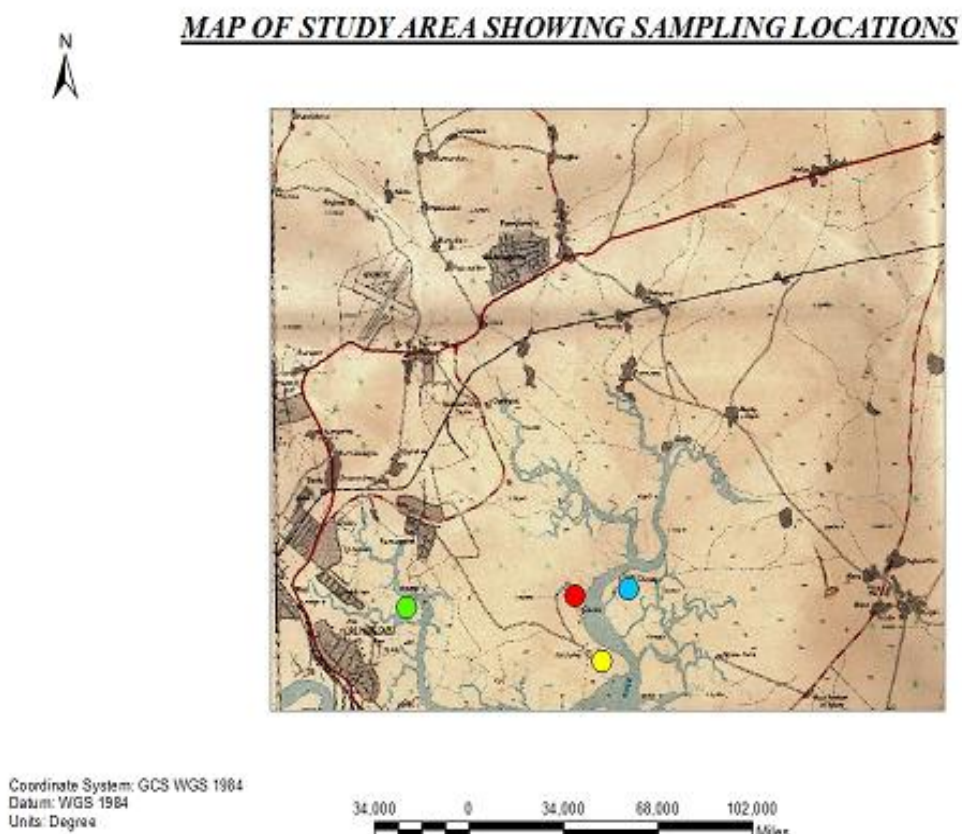
The Okpoka creek is an important river system in the region. It is exceptionally prone to human impacts because of the numerous human activities that are carried out around the Woji creek. This include fishing, boat construction, welding, sand mining, dredging, mangrove cutting, engine boat transportation, effluent disposal, animal slaughter, landfill, open dump site, etc may be potential sources of pollution to the environment. Besides, there are a lot of municipal waste discharges such as human waste, refuse dumps, sewage and septic waste into the creek water.

In Nigeria, studies on the physico-chemical quality of water bodies have been reported extensively. However, less attention has been given to rivers like Okpoka creek, which are scattered all over the country and contain a significant proportion of the nation's aquatic biodiversity. Okpoka creek plays an important role in the lives of the surrounding inhabitants. Fishing, farming, bathing, washing, laundry, dredging, car/motorbike and tricycle washing and other afore-mentioned activities are constantly going on within and around this river. The objective of this present study is therefore to evaluate the physico-chemical parameter and some trace metal content of woji creek, Rivers state, Nigeria.

## **II. METHODOLOGY**

### **Study Area**

Okpoka creek is located in Port Harcourt Local Government Area of Rivers state and lies between longitude  $5^{\circ}60'E - 6^{\circ}60'E$  and latitude  $6^{\circ}06'N - 6^{\circ}70'N$ . The creek is one of the tributaries of the upper Bonny estuary, brackish and tidal in nature with fresh waters intrusion from the surrounding inland waters and flood during the wet season. The Bonny River Estuary lies on the south-eastern edge of  $7^{\circ}14'$  East and latitudes  $4^{\circ}34'$  North with an estimated area of  $206\text{km}^2$  and extends 7km offshore to a depth of about 7.5 meters (Scott, 1966, Alalibo, 1988). Along the shores of the River are located; the Port Harcourt Trans Amadi Industrial layout, several establishments, markets, the main Port Harcourt zoological garden and several communities. The communities are Azuabie, Okujagu-Ama, Okuru-Ama, Abuloma, Oginibga, Obu-Ama and Kalio-Ama. Artisanal fishers mainly exploit the fisheries resources. The study area features a tropical monsoon climate with lengthy and heavy rainy season and very short dry season. Only the months of December and January truly qualifies as dry season months in the city. The harmattan which climatically influences many cities in West Africa is less pronounced. Its heaviest precipitation occurs during September with an average of 370mm of rainfall. December on average is the driest month of the year with an average rainfall of 20mm. Temperatures throughout the year is relatively constant showing little variations. Average temperatures are typically between  $25^{\circ}\text{C} - 28^{\circ}\text{C}$  (Abu and Egeronu, 2004). Anthropogenic activities in the study area include agricultural, commercial, industrial, automobile/boat and ship building, Proliferation of both human and solid waste dumps.



**Fig 1: Study area showing sampling points**

**Sampling**

The sampling site was selected based on the positions on the site of waste and metal components, discharge and easy accessibility. Three sampling stations were established at 500m apart from eastern by-pass through the Amadi axis on foot along the creek banks from the Rumukalagbo to the Nkpogu axis through the Abuloma jetty. Station 1 (Woji), Station 2 (Azuebie), Station 3 (Abuloma). Water and sediment samples were collected at each location during the rainy season of early April.

**Station 1:** Slaughter/Azuabie: This is located at the Port Harcourt main abattoir waterfront. The bank fringing the Azuabie/abattoir is bare; no visible plants except toilet houses, residential houses, animal pens, boats and badge construction, while at the opposite side there are few mangrove and Nypa palm. Human activities here include slaughtering of animals, marketing, fishing and boat building.

**Station 2:** It is about 500m away from station 1 and the major activity here includes sand mining/dredging and boat building.

**Station 3:** This is situated at Abuloma. There are human activities going on in this area. The shore line fringes have mainly Nypa palm. The area is shallow and at low tide. The greater part of the bottom mud flat is exposed. Activities here include sand dredging, boat/badge construction, oil and non-oil industrial activity and jetty operations.

**Sample Analysis:** River water and sediment samples were analysed for pH and heavy metal concentrations according to standard methods (APHA, 2012). Possible metal-metal, metal-pH relationships were investigated using the Pearson correlation coefficient to determine significant levels (95% confidence). The relations below were used to estimate the Water Quality index (WQI) of the water body;

$$Wi = \frac{wi}{\sum n wi} \dots\dots\dots (1)$$

Where, **Wi** is the relative weight, **wi** is the weight of each parameter and n is the number of parameters.

$$qi = (Ci / Si ) * 100.....(2)$$

Where *qi* is the quality rating, *Ci* is the concentration of each chemical parameter in each water sample in mg/L and *Si* is the drinking water standard for each chemical parameter in mg/L according to the World Health Organisation (WHO, 2008).

$$Sli = Wi.qi..... (3)$$

Finally, WQI was computed for the sample by using the following formula:

$$WQI = \sum Sli ..... (4)$$

The computed WQI values are classified into five types; <50 is class I with ‘Excellent water quality’, 50-100 is class II with ‘Good water quality’, 100-200 is class III with ‘poor water quality’, 200-300 is class IV with ‘very poor water quality’ and >300 class V with ‘unsuitable water’. Al-Hadithi (2012).

### III. RESULT AND DISCUSSION

#### Variations of Physico-Chemical Properties of Okpoka Creek

The mean pH values across the three locations (Woji, Azuabie and Abuloma) show close to neutral values (7.49 –7.77) (Fig 2). The pH values measured in the three locations were within permissible limit of 6.5–8.5 (Egborge, 1994). Studies in the other creeks and estuaries within the Niger Delta region reveal alkaline pH Opute (1990), USEPA (1990). The close to neutral pH could be due to the large volumes of fresh water emptying into the creek from adding swamp forest streams and municipal drains (Chindah *et al.*, 2004).

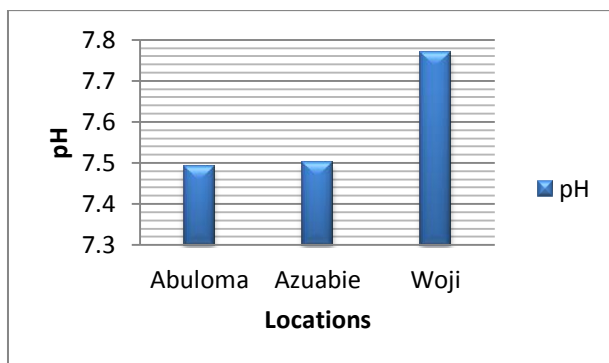


Figure 2: Variation of pH in Okpoka Creek

Dissolved oxygen (DO) of the Okpoka creek is high and above permissible limit of 4-10 mg/l (Fig 3). Similar trend was recorded by Saad (1978). Lower DO was reported by Egborge (1994). The increase in DO levels (8.6-14mg/l) may have resulted from high currents which promotes turbulence and leads to greater dissolution of oxygen (Akhionbare, 2009). The lower Woji DO values compared to Abuloma and Azuabie could be attributed to the floods and municipal drains depositing wastes (organic, inorganic, debris) into the creek thereby leading to increased failing and degradation as was observed. Waste deposition especially organic leads to oxygen depletion (Egborge, 1994). Microbial reduction of nitrate to nitrite and sulphate to sulphide which is an indication of the utilization of organic and inorganic compounds from wastes.

BOD showed high negative correlation with Nitrate (-0.886), Iron (-0.899) and high positive correlation with phosphate (0.527) while there was low correlation with lead (0.064) chromium (0.064) and sulphate (-0.206) (Table 1). The trend of BOD at the sampling stations was different from the observed DO. According to Moore and Moore (1976) the BOD ranking (1–2mg/l = clean water, 2–4 = fairly clean, 5 = doubtful, 10 = bad and polluted but okpoka creek falls at fairly clean category. The high DO values and lower BOD mean values indicate the clearing effect of the tide which serves as a rapid conductant for the steroids. BOD was within permissible range 2.0–3.8 mg/l variation at the different locations though the values are normal but it was higher than the report of Nweke (2000) and falomo (1998) as well as in Elechi creek as well as that of chinda (2004), Ajayi and osibanjo (1984) in new Calabar River (Fig 3).

Sulphate and chloride were the nutrients that recorded high values, sulphate (53.8–106.5), chloride (2508–9400) (Fig 3). (Paveena *et al.*, 2007) recorded similar trend. Nutrients are needed by plants and animals for growth and reproduction. However when these nutrients enter the water ways in excess from point and non-point sources the results are eutrophication from algal bloom which prevents sunlight penetration, endangering aquatic life and oxygen depletion due to death of algae.

Table 1: Relationships between variables in waters of Okpoka creek

	pH	EC	DO	BOD	Sulphate	Nitrate	Phosphate	Chloride	Zn	Pb	Ni	Cr	Fe
pH	1												
EC	-0.294	1											
DO	0.996	0.373	1										
BOD	-0.047	0.941	0.037	1									
Sulphate	0.987	0.137	0.970	0.206	1								
Nitrate	0.504	0.677	0.430	0.886	0.636	1							
Phosphate	0.824	0.784	0.869	0.527	0.723	-0.074	1						
Chloride	0.897	0.159	0.857	0.484	0.956	0.834	0.489	1					
Zn	0.898	0.156	0.858	0.481	0.957	0.832	0.491	1.000**	1				
Pb	1.000*	0.277	0.995	0.064	-0.990	-0.519	-0.814	-0.904	0.906	1			
Ni	1.000*	0.277	0.995	0.064	-0.990	-0.519	-0.814	-0.904	0.906	1.000*	1		
Cr	1.000*	0.277	0.995	0.064	-0.990	-0.519	-0.814	-0.904	0.906	1.000*	1.000*	1	
Fe	0.478	0.699	0.403	0.899	0.613	1.000*	-0.103	0.818	0.818	0.816	-0.494	0.494	1

\*correlation significant at P<0.01, \*\*correlation significant at P<0.05, DO=Dissolved Oxygen, EC=Electrical Conductivity

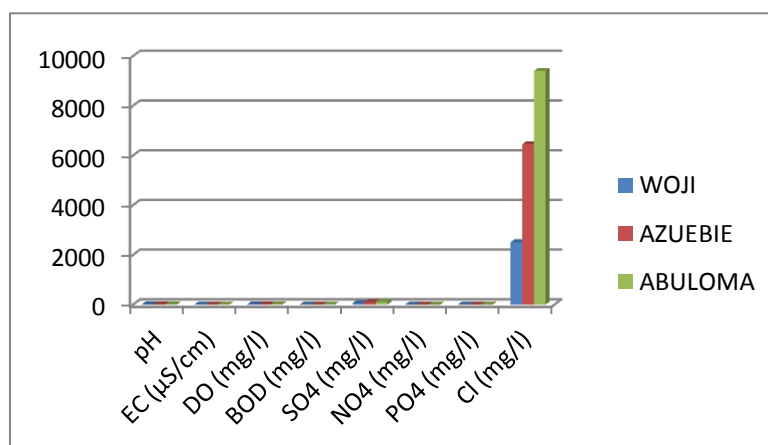


Figure 3: Levels of physico-chemical variables in Okpoka creek

### Relationship Among Physico-Chemical Parameters

pH had a high positive correlation with DO (0.996), Sulphate (0.987), Phosphate (0.824), chloride (0.897) and Zinc (0.898), it also recorded significant negative correlation with Pb, Ni and Cr (1.000\*) (Table 1). These strong correlations mean that the source of these pollutants in water is not only the input from a particular source but also from other anthropogenic activities within the watershed.

Dissolved oxygen recorded high positive correlation with Sulphate (0.970), Chloride (0.857), Phosphate (0.869), zinc (0.858), and high negative correlation with lead (-0.995), Chromium (-0.995) as well as low correlation with BOD (0.037).

Sulphate recorded high positive correlation with Chloride (0.956), Zinc (0.957) Nitrate (0.636), Phosphate (0.723), Iron (0.613) and negative correlation with lead (-0.990), chromium (-0.990) (Table 1).

### Variation of Heavy Metals in Okpoka Creek

Figure 4 depicts the variations in heavy metal values. Zinc recorded the highest levels ranged from 1.343–7.269mg/kg and had high correlation with Cr (0.906) and Iron (0.816). The high zinc and Iron levels could be attributed to bunkering, industrial effluent and domestic waste disposal (Table 1).



Heavy metals are among the most common environmental pollutants, and their occurrence in wastes and biota indicate the presence of natural or anthropogenic source. Creeks and rivers are dominant pathways for metals transport (Miller *et al.*, 2003) and heavy metals become significant pollutants of these waste bodies. The increase in residue levels of heavy metal content in water, sediment and biota, will result in decreased productivity and increase in health risk in case of human beings (Kazi *et al.*, 2009). The behaviour of metals in natural water is a function of the substrate sediment composition, the suspended sediment composition and water chemistry. During their transport the heavy metal undergoes changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena (Dassenakisi *et al.*, 2009) which effect their behaviour and bio-availability.

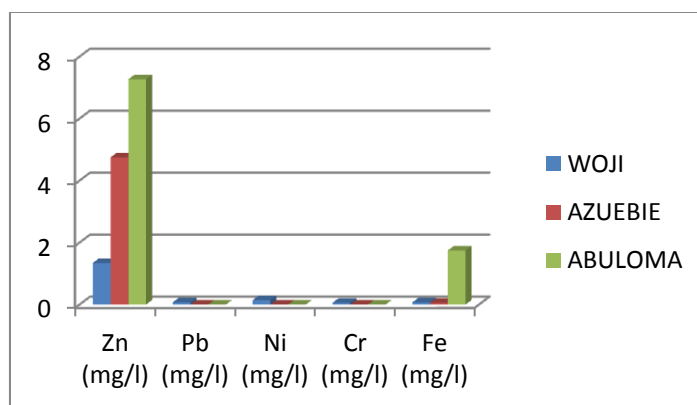


Figure 4: Levels of Metals in waters of Okpoka creek

#### Variation of Heavy Metals in Creek Sediment

River sediments serves as a depository for most heavy metals, they act as reservoirs or sinks for heavy metals and other pollutants and have much greater heavy metals than river water (Akhionbare, 2009). This study expectedly recorded heavy metal values in sediment above that in water. (Fig 5) with Fe (1.53–1.86), Pb (1.33–1.84) and Zn (0.34–4.30) recording the highest value in relative abundance of Fe>Pb>Zn>Cr>Ni. The inputs from the wastewater and other anthropogenic activities like mechanical workshop could have caused this elevated level. The high heavy metals levels could be attributed to dredging, boating, badge construction, fishing, bathing, Jetty operation, water transportation, domestic waste disposal, effluent and runoff discharge from RIVOC, Halliburton, Schlumberger, Coca-cola and Port Harcourt 200, bunkering, abattoir and market waste excreta disposal.

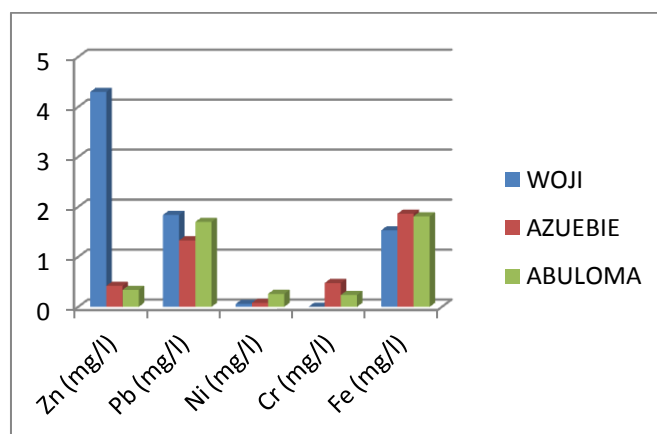


Figure 5: Levels of Metals in sediment of Okpoka creek

Heavy metals can accumulate in the upper sediment. Such accumulation takes place by biological and geochemical mechanisms, and cause significant environmental concentration such as toxic to sediment dwelling organism and fish, resulting to decrease survival, reduced growth or impaired reduction and lowered species diversity (Mucha *et al.*, 2003; Praveen *et al.*, 2007). Sediments can come from soil erosion or from the decomposition of plants and animals, United States Environmental Protection Agency (USEPA, 2002). The capacity of sediments to concentrate trace levels of most of the metals make them useful indicators for monitoring purposes and for detecting sources of pollution in the aquatic system. These heavy metals are

sensitive indicators for monitoring changes in the water environment. Also the experimental data obtained based on analysis of sediment cores helps to provide a historical record of the heavy metal burdens.

In natural water, fish are often exposed to chromium (Cr) waste and demonstrate cumulative deleterious effects as a function of time. (Steinhagen *et al.*, 2004) examined the effect of Cr and Carp (Cyprinus carpio) derived from immune cells. The result demonstrated that at concentrations between 2 and 200 µg/L Cr, the metal induced cytotoxicity and decreased the activation of mitogen-induced lymphocytes, as well as phagocyte functions. Neutrophils showed changes in cell shape together with reduced nitric oxide and reactive oxygen production at concentrations much lower than the cytotoxic effects. The altered lymphocyte and entropic found reflect the decreased resistance to pathogens observed in fishes under chronic challenge.

Nickel (Ni) and nickel compounds have many industrial and commercial uses and the progress of industrialization in the biota, particularly in the phytoplankton or their aquatic plants which are sensitive bio-indicators of water pollution. It can be deposited in the sediment by such process as precipitation, complexation and adsorption on clay particles and via uptake by biota (Haber, 2000). Levels of precipitation and Ni of 0.9Mg/M<sup>2</sup>/year over long periods were found to be dangerous for biological systems of fresh water catchments (Coogan, 1989). In rivers, nickel is transported mainly as a precipitated coating on particles and in association with organic matter. Recent studies have suggested an increase in cancer in refinery areas where exposure to water-solution nickel salts occurs (Clarkson, 1998). Nickel has been shown to be immunotoxic, altering the activity of all specific types involved in the immunological response, resulting in contact dermatitis or asthma (Coogan, 1989). Human exposure to highly polluted environment had the potential to produce a variety of pathological effects. Among them are skin allergies, lung fibroses, cancer of the respiratory tract and iatrogenic nickel poisoning (Kasprzak *et al.*, 2003). While no reproductive effect has been associated with nickel exposure to humans, several studies on laboratory animals have demonstrated fetotoxicity (Donskoy, 1986).

Lead (Pb) is not essential for plants, and excessive amount can cause growth inhibition as well as reduced photosynthesis, mitosis and water absorption. The decline of some European Spruce Forest has been attributed to excessive concentrations of atmospheric Pb (Backhaw and Backhaus, 1986). Lead is toxic to all phyla of aquatic biota, though effects are modified significantly by various biological and abiotic processes. Wastes from Pb mining activities have severally reduced or eliminated populations of fish and aquatic invertebrates, either directly through lethal toxicity or indirectly through toxicity to prey species. Health advisories warning anglers against eating Pb-contaminated fish have been posted in Missouri (Schmitt and Finger, 1987).

### Water Quality Index

**Table 2: Water Quality Index value for Station I**

Parameters	wi	Wi	Qi	Sli
pH	4	0.114	103.60	11.81
BOD	4	0.114	60.00	6.84
DO	5	0.151	66.15	9.98
Sulphate	4	0.114	21.20	2.42
Nitrate	3	0.085	0.0124	0.0011
Chloride	5	0.151	1003.20	151.48
Phosphate	4	0.114	612.00	69.77
Zn	3	0.085	44.77	3.81
Pb	3	0.085	70.00	5.95
		$\sum wi=35$	$\sum Sli=262.06$	

**WQI = 262**

**Table 3: Water Quality Index value for station 2**

Parameters	wi	Wi	Qi	Sli
pH	4	0.114	100.00	11.41
BOD	4	0.114	76.00	8.66
DO	5	0.151	107.69	16.26
Sulphate	4	0.114	39.36	4.49

Nitrate	3	0.085	0.0275	0.0023
Chloride	5	0.151	2580.00	389.58
Phosphate	4	0.114	1836.00	209.30
Zn	3	0.085	158.33	13.45
Pb	3	0.085	-	-
$\Sigma w_i=35$				$\Sigma S_{li}=653.15$

WQI = 653

**Table 4: Water Quality Index value for station 3**

Parameters	wi	Wi	Qi	Sli
pH	4	0.114	99.86	11.38
BOD	4	0.114	40.00	4.56
DO	5	0.151	103.07	15.56
Sulphate	4	0.114	42.60	4.85
Nitrate	3	0.085	0.6125	0.052
Chloride	5	0.151	3760.00	567.76
Phosphate	4	0.114	1070.00	121.98
Zn	3	0.085	242.33	20.59
Pb	3	0.085	-	-
$\Sigma w_i=35$				$\Sigma S_{li}=746.73$

WQI = 746

The computed WQI values for three (3) stations in the watershed ranges from 262 to 746 as shown in Tables 2–4 and therefore, can be categorized as types IV and V which is “Unsuitable water”. The high value of WQI at these stations has been found to be mainly due to the higher values of Phosphate, Sulphate and Chloride. Where it was found that there is a very high correlation coefficient between them (Table 1)

#### IV. CONCLUSION

The Okpoka creek as a result of the numerous anthropogenic activities will have its visual image thwarted leading to poor aesthetics value. The result of the laboratory analysis shows that the quality of the creek and its sediments has declined which has far reaching implications in waste resources utilization. Odour level will increase probably to a nuisance stage owing to the level of biological wastes been discharged into the creek. Oxygen depletion may also set in with time as DO and BOD continues to fluctuate along the creek. The considerable level of zinc and iron in the creek as well as lead, Nickel and chromium is likely to lead to heavy metal poisoning. Abuloma end of the creek is more susceptible to eutrophication and algal bloom which can lead to fish kill especially during the dry season. This station also recorded the worst water quality.

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