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# Seasonality of Surface water Contamination by Heavy Metals in the Lower Enyong Creek, S.E. Nigeria)

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**ABSTRACT**

Surface water samples from three locations in the Lower Enyong Creek, S.E. Nigeria were sampled over six months i.e June to October(wet season) and November in dry season for heavy metals such as Cd, Mn, Fe, Cu, Ni, Pb, Zn, Cr) using Atomic absorption spectroscopic method. Some specific physicochemical characteristics, such as temperature, hardness, alkalinity, salinity, TDS, TSS, pH and conductivity which are known to influence the interactions and dynamics of trace metal loadsin water bodies were also determined. The result of the analysis indicates significant monthly variation of these parameters for the six months. Monthly summary statistics revealed a few seasonal patterns that echoed the hydrologic regime. During the short dry season in August–September period, all the sampled stream channels had lower levels of Cd, Ni, Zn, Cu Cr, Pb and Fe. Total hardness and conductivity levels exhibited patterns similar to heavy metals, but dissolved oxygen did not.Significant correlation ($p<0.05$) however exists between some of the metals.The concentrations of most heavy metals are low, but Zn content is higher than the WHO standard for surface water which indicates significant contamination by Zn in the water body.



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## 1. INTRODUCTION

According to Garbarino et al (1985) and Durube et al(,2007), Heavy metals are chemical elements with specific gravity that is at least four to five times the specific gravity of water at the same temperature and pressure.. These metals such as Pb, Cu, Cd, Cr,, Zn, Fe, and Ni are among the most common environmental pollutants in the river systems. The hydrologic cycle clearly shows that contaminants in air, soil or on land ultimately end up in the river systems. However, the land-phase components of the hydrologic cycle viz; surface run-off, infiltration, sub-surface flow, percolation, and leaching of rocks and regolith may affect their concentration within any drainage basin.In addition,fertilizer application on farmlands, sewage, industrial wastes and petroleum exploration and exploitation are well known causes of surface water pollution. Hence, heavy metals belong to the group of elements whose hydro-geochemistry cycles have been greatly accelerated by man. Anthropogenic metals emission into the atmosphere such as Pb, Cu, Zn, Cd and Cr are 1:3 orders of magnitude higher than natural fluxes. As a consequence these elements are expected to become increasingly accumulated in river systems.

The activity of trace metals in river systems and their impact on life vary depending upon the metal species. Of major importance in this regard is the ability of metals to associate with other dissolved and suspended components. Most significant among these associations is the interaction between metals and organic compounds in water and sediment. These organic species, which may originate naturally from process such as vegetative decay or result from pollution through organic discharge from municipal and industrial sources, have a remarkable affinity and capacity to bind metals (Signer, 1974). We do know that once these particles are incorporated into the fluvial ecosystem, they quickly become absorbed into the food web leading to mutations, change in tissue matter, biochemistry, behavior, reproduction and suppress growth in aquatic life as well as disease which can be harmful to humans.

According to Salati and Moor, (2009), the persistence and non-bio-degradability of heavy metals may result in their bioaccumulation and bio-magnification in the fluvial environment and thus they are also known as 'chemical time bombs'. Often, natural and human disturbances release pollutants to the overlying water, where pelagic (water column) organisms can be exposed. In a recent study, Ogri et al, {2011), observed that the concentration of most metals in river system vary significantly between seasons, although differences in geology may influence the types and concentrations of the metals.

Arising from the foregoing, Enyong Creek, which may have resulted from the Imo River capturing its head waters at a point near Umuahia in SE. Nigeria (Udo, 1970) was chosen for detailed study of seasonal variation in metals loads. The river system is underlain by a wide variety of rocks including cretaceous shale and sandstone. The river is also subjected to organic pollution load arising from the effluent discharge from cassava processing mills .near the river bank.This study becomes imperative because the basin is very rich in nutrients and as a result mothers numerous fishery resources. This work is aimed at assessing the seasonal variation in concentration of some heavy metals (Cd, Cr, Cu, Zn, Pb, Ni and Fe) in surface water in three locations within the lower Enyong Creek.

## 2. MATERIAL AND METHODS

### The Study Area

The investigated area is enclosed between latitudes 5°11′to 5°28′ N and longitudes 7°51′and 7°59′E(Figure 1 It was delineated from toposheet No: Ikot Ekpene 322 NE on 1:50,000 scale.. Geologically, the area under study is underlain by a wide range of diverse geological formations ranging from Asu River Formations e.g the Abakiliki Anticlinorium to the recent alluvium in the south. The Asu River Group underlies most areas in the northern part of the study area e.g its intensely fractured outcrops at Uburu. The Asu River Group, which is Albian in age is sub-divided into three formations, comprising essentially of over 200m bluish grey to olive brown shales and sandy shales, fine-grained micacceous and calcareous sandstones and some limestones (Offordile, 2002). The area is well represented by structurally controlled ridges, denudational hills e.g the 150m high Obotme conical hill, steep-sided valleys, saddle and col at Obot Ito Ikpo, extensive wetlands and alluvial plains forming soil covers of silty clay, sandy and heavily weathered loamy and alluvium. The area enjoys tropical climate and the temperature ranges from 26 to 32° C. The fluctuations in temperature are fairly uniform in character, except during the dry months when the rise in temperature is higher than it is during the long wet period (eight months-March to October) and the level of humidity is high (84%) due to close proximity to the main Cross River Channel.

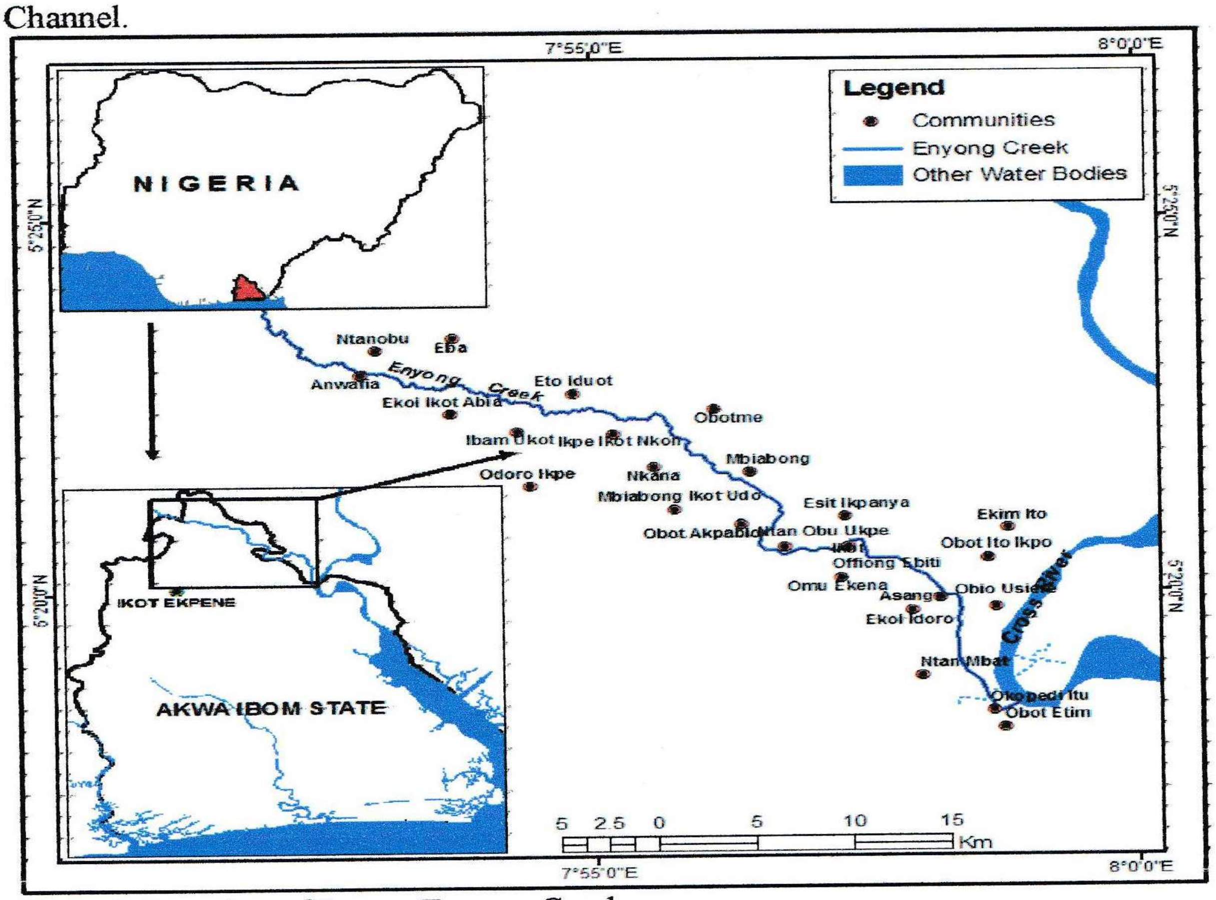


Figure1 :Location of Lower Enyong Creek

The details of annual and monthly rainfall for Umudike (the closest station to the basin indicates that rainfall ranges from 1511mm in 1983 to 2572mm 1996 with a mean annual of2156mm, c.v.=44.4% recorded between 1972 and 2012 (Okutinyang, 2015). The monthly distribution of rainfall is shown in Table 1 and Figure 2 clearly shows eight wet months- March to October, the dry months are November to February. The rainfall pattern is uni-modal, but the little dry season in August may occur in some years.In the humid tropics rainfall is the main input into the river system and hence, Thornthwaite' s water balance was computed using rainfall and evaporation data (Udosen, 2000) to illustrate groundwater movement.

**Table 1: Monthly Rainfall distribution at Umudike(1972-2012)**

| Month | Range in | Mea n | Raindays /month |
|---|---|---|---|
| Jan | 0-78 | 15 | 1 |
| Feb | 0-132 | 38 | 3 |
| Mar | 4-266 | 113 | 7 |
| Apr | 70-357 | 176 | 12 |
| May | 102-445 | 270 | 16 |
| Jun | 101-576 | 288 | 18 |
| Jul | 166-450 | 292 | 21 |
| Aug | 103-535 | 306 | 21 |
| Sep | 206-670 | 341 | 21 |
| Oct | 75-499 | 257 | 16 |
| Nov | 0-212 | 53 | 5 |
| Dec | 0-35 | 7 | 1 |

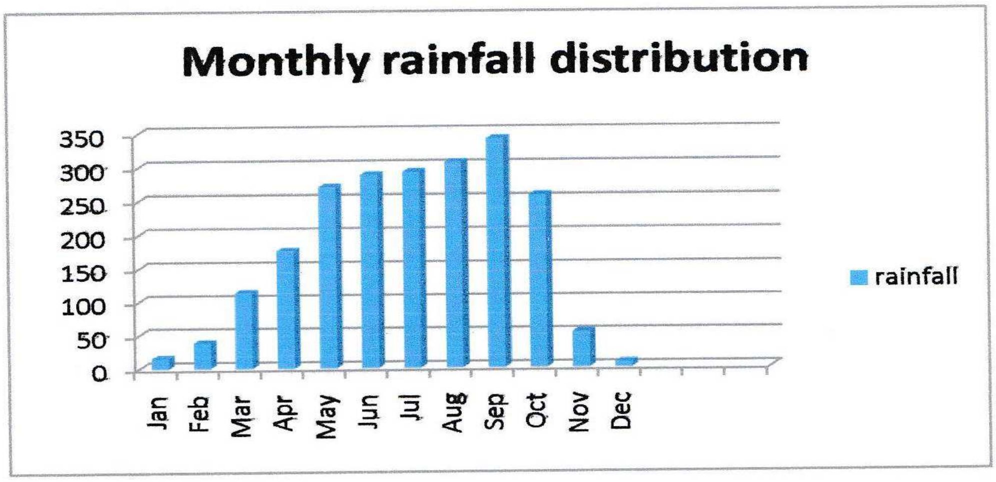


Fig 2: The mean monthly rainfall at Umuahia, (1972-2012)

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The results indicate a runoff coefficient of 0.68 for Uyo, located barely 18kms south of the study area. The implication is that over 60 percent of rainfall is converted to surface runoff, depending on amount and type of vegetation, soil infiltration rates and slope aspects. Furthermore, the computed water balance indicates that ground water contributes significantly to channel flow from June to September (Fig. 3).The demobilized rock minerals and metals may enter the river system from ground water between June and September

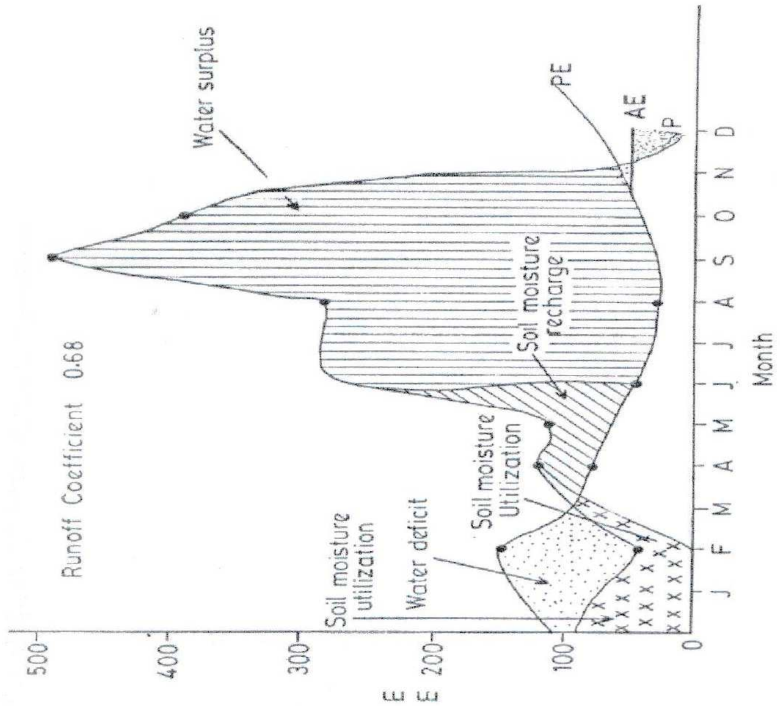



Fig. 3: Water Balance [Uyo ]
Source: Udosen, (2000)

**Materials and methodology**
Sampling was done from the three established sites between June and November, 2014 (heavy metals) and physiochemical properties), Schlosser, 1982; Hanson, 1973; and Bartram and Balance, 1996). The water's chemical analysis was done using standard and analytical methods of water analysis (Bartram and Ballance, 1996; APHA – AWWA – WPCF, 2005; USEPA, 1979). Sampling was done at a specific time intervals (i.e10am). At each sampling location, the surface water samples were collected at the middle of the river and stored in a clean polythene bottles that have been pre-washed with nitric acid and thoroughly rinsed with deionized water (Bartram and Balance, 1996). Non-conservable parameters such as temperature, pH and electrical conductivity were determined, at the time of sampling, in the field (*in situ*). Water samples were collected approximately 15 – 20cm below the water surface with 125cm$^3$ using pre-cleaned and chemically neutral 1 litre plastic vessels for laboratory analysis of other physic-chemical parameters. AAS was employed for trace metals analysis

Statistical analysis: SPSS package was employed in both descriptive analysis and inferential statistics; pair-wise Pearsons Product Moment correlation (PPMC) to establish significant relationship between the physicochemical parameters while factor analysis was employed to collapse the variables and sieve out redundant variables as well as isolate the sources of water pollution.

***Study locatios:***
This study was conducted on three locations along the Enyong Creek viz; stream channels at Ito, Obio Usiere and Okopedi (Fig.1). The geographic co-ordinates are listedinTable2.

**Table 2:** Sampling Villages and location.

| Village | Location | |
|---|---|---|
| Ito | 5°19.227'N | 007°56.291'E |
| Obio Usiere | 5° 15.693'N | 007°56.970"E |
| Okopedi –Itu | 5°12.144'N | 007o58.913'E |

**Results and Discussion**

Descriptive statistics of physicochemical parameters (temperature, pH, salinity, dissolve oxygen, total suspended solids(TSS) total dissolved solids(TDS), hardness, alkalinity, Na, $NO_3$,Ca,Mg, K, ammonium and conductivityinsurface water studied at Ito, Obio Usiere and Okopedi during dry and wet season are presented in Table 3.The pH was slightly acidic in a range5.55-6.46, 5.58- 6.34 and5.62-7.08 and corresponding mean values of 6.09±0.4, 6.39±0.44 and 6.3±0.59 for Ito, Obio Usiere and Okopedi respectively. The range in pH values is peculiar to Nigeria. The moderately acidic pH condition affects metal speciation and may enhance metals' solubility and possible leaching into the water column

Table 3: Changes in Physicochemical parameters at different locations/sub-catchments in lower Enyong Creek.

| **Physicochemical parameters** | **Min-max (Mean ±SD ) ITO** | **Min-max (Mean ±SD ) OBIO USIERE** | **Min-max (Mean ±SD ) OKOPEDI** |
|---|---|---|---|
| DO | 2.85-3.88 | 2.88-3.71 | 0.90-8.4 |
| | (3.25±0.4) | (3.24±0.37) | (3.67±2.77) |
| Temperature | 28.1-30.6 | 28.3-31.2 | 27-29.5 |
| | (28.3±0.1.24) | (29.38±1.02) | (28.38±0.99) |
| pH | 5.55-6.49 | 5.58-6.83 | 5.62-7.08 |

| | | | |
|---|---|---|---|
| | (6.09±0.6) | (6.39±0.44) | (6.3±0.59) |
| Conductivity | 4.14-61.3 | 5-42.5 | 16.9-89.2 |
| | (28.5±19.4) | (28.55±3.12) | (39.3±65.8) |
| Salinity | 0.07-0.60 | 0.07-0.80 | 0.08-0.50 |
| | (0.33±0.4) | (0.26±0.17) | (0.22±0.15) |
| TSS | *0.00-0.007* | 0.0-0.004 | 0.0-0.04 |
| | *(0.013*±0.002) | (0.002±0.053) | (0.01±0.08) |
| TDS | 7.00-16.72 | 2.0-19.72 | 2.0-11.0 |
| | (10.45±1.3) | (9.15±1.9) | (7.4±2.83) |
| Hardness | 4.96-6.72 | 5.2-10.2 | 5.6-14.6 |
| | (5.27±0.6) | (46.62±70.03) | (7.9 ±3.4) |
| alkalinity | 5.50-175 | 5.4-180 | 5.6-200 |
| | (102.8±5.9) | (90.68±59.15) | (99.4 ± 63.5) |
| Nitrate | 1.32-3.01 | 1.37-3.26 | 1.37-3.46 |
| | (1.96±0.49) | (2.02±0.74) | (1.36 ± 1.2) |
| BOD | 0.10-0.46 | 0.15-0.9 | 0.55-6.3 |
| | (0.3±0.16) | (1.40±0.98) | (1.98±2.17) |

*Source:* Analyzed from Field Data, 2014

Water temperature, which is influenced by latitudinal location, season, air circulation, turbidity, amongst others ranged between 27 and 31.2°C for all the stations. The temperature of natural inland waters in the tropics generally varies from 25°C to 35°C (Alabaster and Llyod, (1980). However, temperature range is critical, as it affects physical, chemical and biological processes in water bodies and consequently leading to alteration of concentration of dissolved oxygen. Hence, water temperature can strongly influence the feeding patterns, growth rates and breeding seasons of fish and shell fishes (Ezekiel et al, 2011). DO levels in the lower Enyong Creek ranged from 2.85 to 3.88 (3.25±0.4); 2.88-3.71, (3.24±0.37) and 0.90-8.4 (3.67±2.77) for Ito, Obio Usiere and Okopedi respectively

The concentration of DO in the lower Enyong Creek is affected by organic wastes and other nutrient inputs from sewage, agro-based cottage industries as well as agricultural and urban runoff, all of which can lead to a decrease in oxygen levels Concentrations of DO in unpolluted waters are usually about 8-10 mg $L^{-1}$ (Joseph and Jacob, 2010) and streams with a high DO concentration (greater than 8 mg $L^{-1}$) are considered healthy and are able to support a significant diversity of aquatic organisms. The dry months (November to February are usually the most critical time for DO levels because stream flows tend to lessen and water temperatures tend to increase. In general, DO levels of less than 3 mg $L^{-1}$ are stressful to most aquatic organisms (http://www.dnr.mo.gov/env/esp/waterquality-parameters.htm). Table 3 shows that few of the water samples exhibited DO values less than 3 mg $L^{-1}$. As a result, the water at these sites will not maintain most aquatic organisms. The monthly DO (mg $L^{-1}$) values were as follows: June (3.00-3.88), July (3.11-3.91), August (3.25-3.28), September (3.68-8.4), October (2.04-2.76), November (0.9-2.88)- Table 4..

Table 4: Seasonal Variation of DO (in mg/l) in the lower Enyong Creek

| Location | June | July | August | September | October | November |
|---|---|---|---|---|---|---|
| Ito | 3.88 | 3.11 | 3.25 | 3.48 | 2.95 | 2.88 |
| Obio Usiere | 3.01 | 3.21 | 3.71 | 3.68 | 2.96 | 2.88 |
| Okopedi | 3.00 | 3.91 | 3.78 | 8.4 | 2.04 | 0.9 |

The mean values of salinity decreases downstream viz; 0.33±0.4, 0.26±0.17 and 0.22±0.015 recorded at Ito, Obio Usiere and Okopedi respectively (Table 3). Usually, salinity of surface water does not vary significantly along the coast due to the effects of tidal movements, waves and wind. Enyong Creek is neither influenced by tides nor waves andsalinity values range from 0.07to 0.80 mg/lfor allthe sample sites while the seasonalvariation shows higher values in dry season (in this case November) asillustrated in table 5.This is contingent on low flow of water, decrease in water level, high rates of evaporation and salt water intrusion from the main Cross River channel

Table 5 :Seasonal Variation of Salinity in the lower Enyong Creek

| Lotion | June | July | August | September | October | November |
|---|---|---|---|---|---|---|
| Ito | 0.30 | 0.09 | 0.07 | 0.40 | 0.50 | 0.60 |
| Obio Usiere | 0.20 | 0.08 | 0.07 | 0.20 | 0.20 | 0.80 |
| Okopedi | 0.20 | 0.10 | 0.08 | 0.20 | 0.22 | 0.50 |

In a related study, Dan et al (2014) established significant correlation between salinity and heavy metals in the dry season (Dan, et al, 2014). They concluded that metals ions may have become immobile by the salt ions resulting in decrease in the levels of heavy metals in the surface water during dry season

Comparison of the overall distributions of water quality characteristics reveals differences between the three streams (Table 3and Figs. 4-7). Data for each stream shows that mean TSS wasfive to ten times higher between July and October at Okopedi-(downstream) than in Ito and Obio Usiere (Table 6) while TDS levels in were higher in June than any other month.TDS also exhibited spatial variation and tended to increase in the upstream sample sites (Ito and Obio Usiere),as shown in Fig.4

Table 6: Seasonal variation of TSS in the lower Enyong Creek

| Location | June | July | August | September | October | November |
|---|---|---|---|---|---|---|
| Ito | 0.00 | 0.00 | 0.07 | 0.003 | 0.001 | 0.003 |
| Obio usiere | 0.00 | 0.00 | 0.002 | 0.004 | 0.002 | 0.002 |
| Okopedi | 0.00 | 0.00 | 0.04 | 0.002 | 0.023 | 0.002 |

Table 7:Seasonal Variation of TDS in the lower Enyong Creek

| Location | June | July | August | September | October | November |
|---|---|---|---|---|---|---|
| Ito | 16.72 | 9.00 | 7.00 | 9.00 | 10.00 | 11.00 |
| Obiousiere | 19.72 | 2.00 | 7.00 | 7.00 | 9.20 | 10.00 |
| Okopedi | 11.00 | 2.00 | 6.00 | 7.00 | 8.20 | 10.00 |

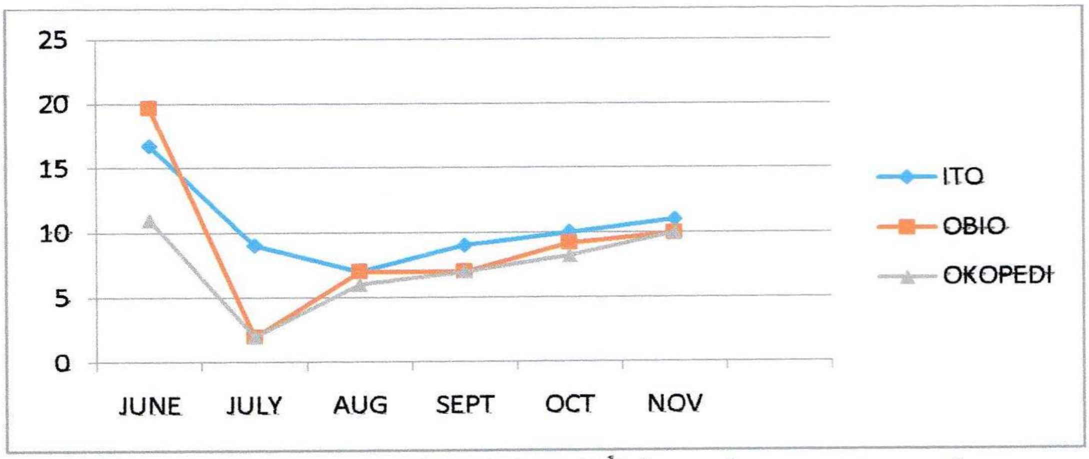



Fig.4 Seasonal Variations of TDS (mg $L^{-1}$) in surface water samples

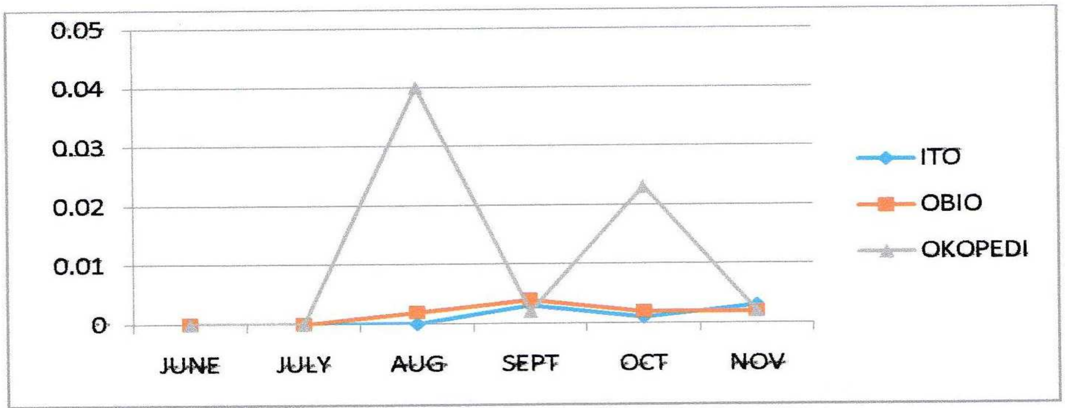
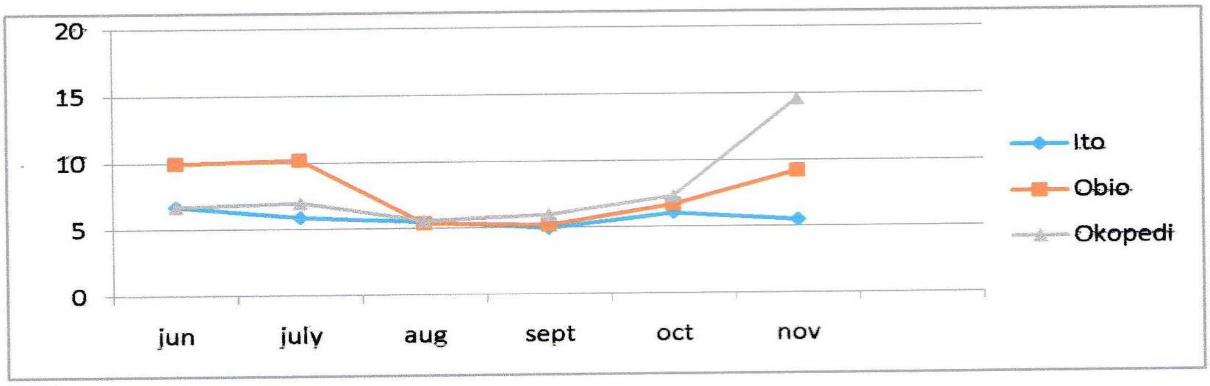
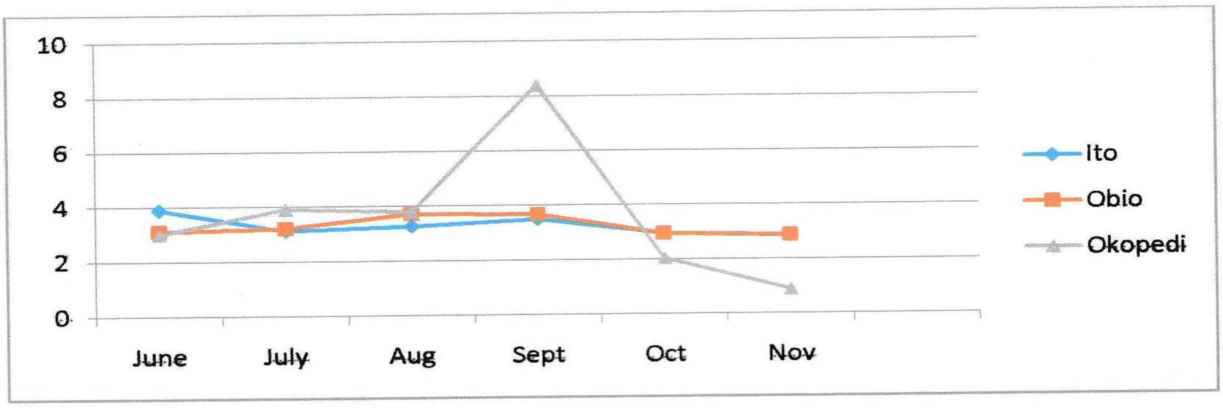



Fig. 5 Seasonal Variations of TSS (mg $L^{-1}$) in surface water samples

The three streams displayed similar distributions of nitrate, sulphate, potassium, magnesium, calcium and ammonium Table 3. Others have noted the linkages between flashy hydrology and elevated levels of nutrients in streams (Pionke et al., 2000; Norton and Fisher, 2000). Enyong Creek is not characterized by this hydrograph and the longitudinal differences in chemical water quality may reflect land use along the study reaches



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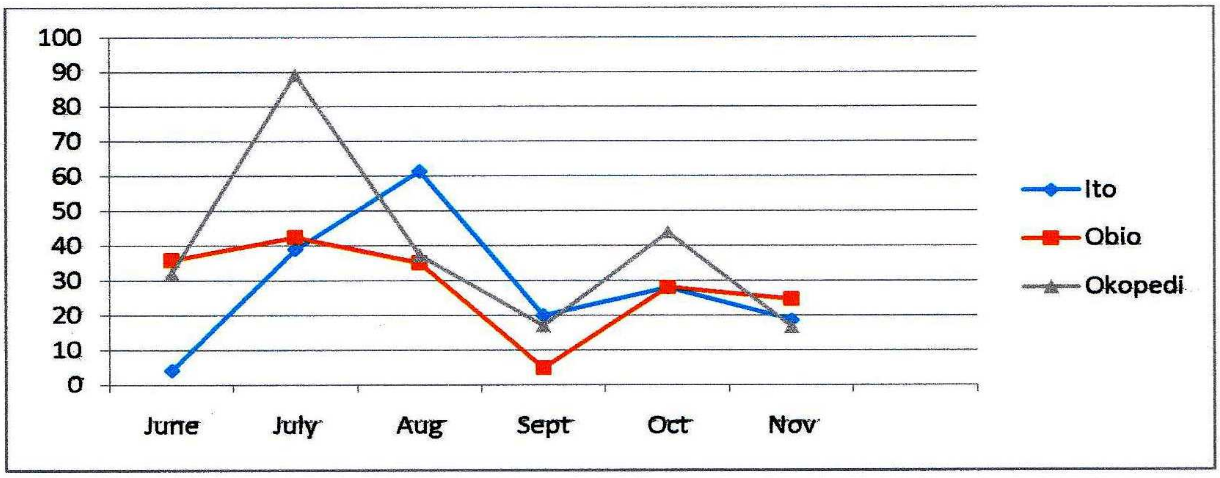


Fig 6: Monthly Variation in Total Hardness (A), dissolved oxygen(B),Conductivity (C) and pH (D)

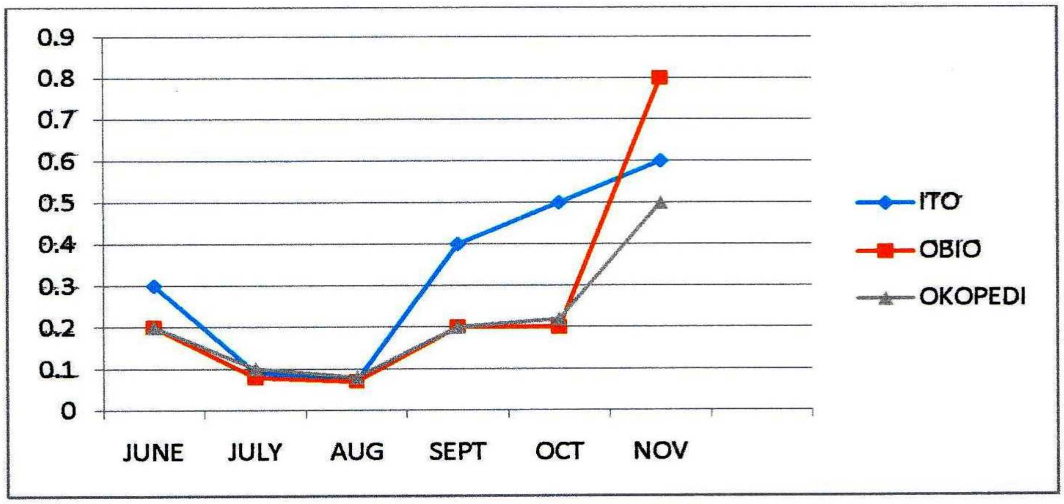


Fig. 7: Seasonal Variations of Salinity (mg $L^{-1}$) in surface water samples

**It** is observed from table 8 that the concentration of each metal in the surface watergenerally increases from station I to I1I. It is difficult to make an overall assessment of the degree of the contamination of surface water by heavy metals because of the variations in the concentration of heavy metals within locations.As can be seen from table 8, metal levels in the three stations exist in the order of Zn (0.14-1.9) > Fe (0.13 -1.5) > Cu (0.04 -0.9) > Ni (0.02-0.14) >Cr (0.01-0.42) > Pb (0.01-0.81) > Cd (0.01-0.2),measured in mg/l of which were generally lower than those reported for Lagos lagoon (Okoye, 1991) and Niger Delta coastal waters (Kakulu et al, 1988). However, similar trend in some heavy metals distribution was obtained in other similar studies. The high concentrations of Zn in the surface water have no identifiable point source discharge rather than non-point source discharge of wastes/effluents and lithological or crustal origin. There is no doubt that wastes generated due to human activities are discharged on land or stream in and around the study area were transported by surface run-off to the water body by rain. Thus, contribution from run-off in this regard may be significant as evident in Table 8. On the other hand, the relatively low metal level recorded in the study may be attributed to the preponderance of rural settlements in Enyong watershed.

Table: 8 Changes in Trace metals loads of different locations/sub-catchments in lower Enyong Creek.

| **Trace metals** | **Min- max (mean ±SD ) ITO** | **Min- max (mean ±SD ) OBIO USIERE** | **Min- max (mean ±SD ) OKOPEDI** |
|---|---|---|---|
| Cu | 0.026-0.889 | 0.006-0.9 | 0.009-0.856 |
| | (0.275±0.04) | (0.3058±0.04) | (0.298±0.117) |
| Fe | 0.186-1.125 | 0.132-1.583 | 0.17-1.51 |
| | (0.697±0.06 ) | (0.638±0.142) | (0.638±0.242) |
| Zn | 0.143-1.535 | 0.199-1.921 | 0.146-1.76 |
| | (0.962±0.684) | (1.143±0.728) | (1.092±0.734) |
| Pb | 0.005-0.083 | 0.002-0.1 | 0.001-0.081 |
| | (0.0377±0.007) | (0.044±0.012) | (0.0037±0.0012) |
| Cr | 0.021-0.415 | 0.011-0.348 | 0.014-0.0352 |
| | (0.147±0.104) | (0.1093±0.014) | (0.109±0.014) |
| Cd | 0.005-0.112 (0.027±0.004) | 0.002-0.202 (0.038±0.009) | 0.001-0.13 (0.048±0.027) |
| Ni | 0.021-0.643 | 0.019-0.437 | 0.022-0.411 |
| | (0.261±0.025) | (0.188±0.111) | (0.197±0.023) |

*Source:* Analyzed from Field Data, 2014

Monthly summary statistics revealed a few seasonal patterns that echoed the hydrologic regime. During the short dry season inAugust–September period, all the sampled stream channels had lower levels of Cd, Ni, Zn, Cu Cr, Pb and Fe. Total hardness and conductivity levels exhibited patterns similar to heavy metals, but dissolved oxygen did not. DO levels rose during the drier August break in the downstream channel, while hardness values were

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much higher during beginning of the four dry months in November, possibly reflecting periods of lower groundwater inflows for each stream, particularly downstream.. Salinity levels were elevated by about a factor of three during the drier months of November through April

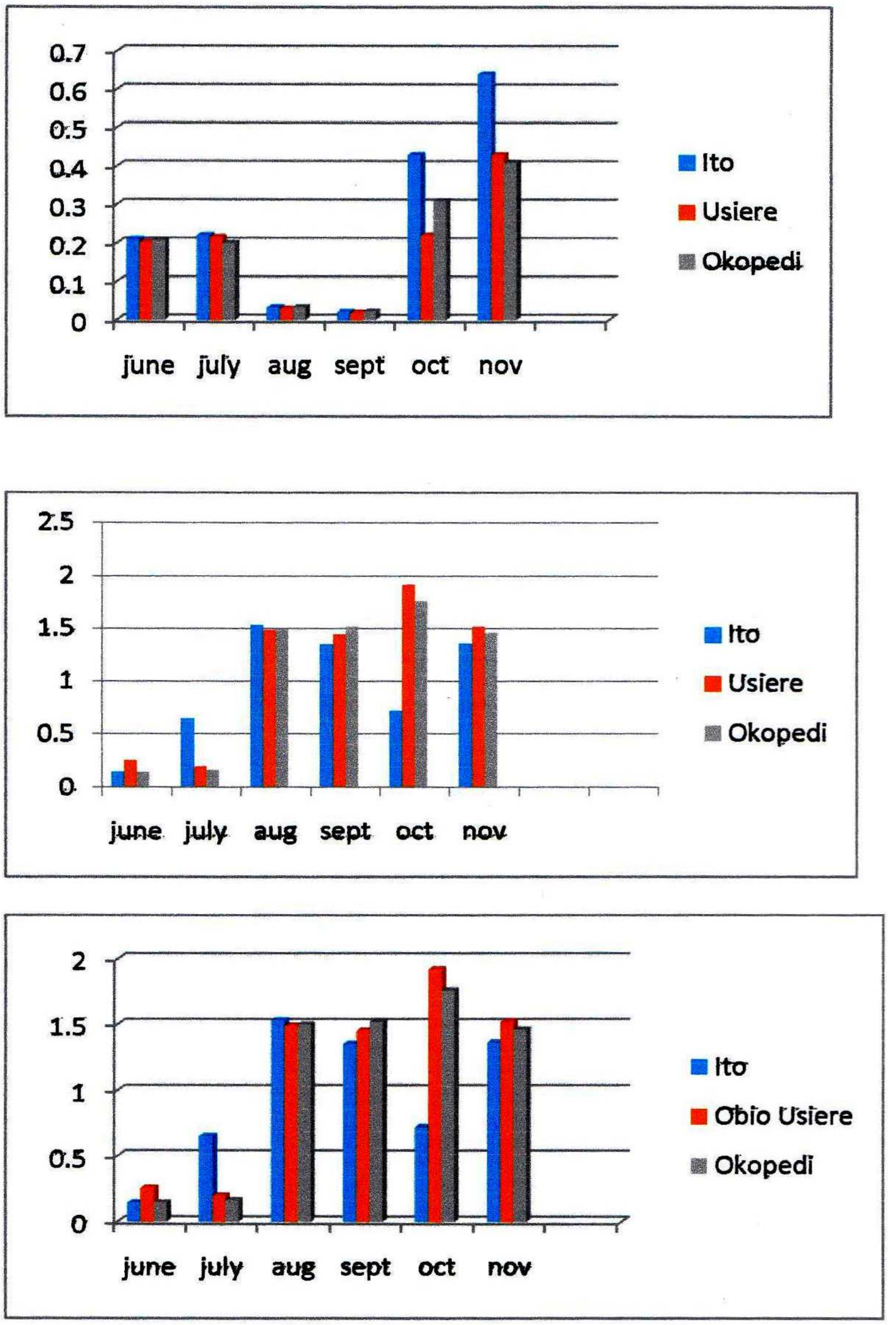


**Fig. 8: Seasonal variation in Cd (A), Fe (B) and Cu(C) in the Lower Enyong Creek**