Scientia Africana, Vol. 15 (No. 1), June 2016. Pp 151-157
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LEVELS OF HEAVY METALS, TOTAL HYDROCARBON AND ORGANIC CARBON CONTENTS OF SEDIMENTS FROM IKPOBA (EDO) AND ETHIOPE (DELTA) RIVERS OF NIGERIA.

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Received: 21-01-16
Accepted:29-04-16

ABSTRACT

The sediment samples of River Ethiope and Ikpoba River were collected and extracted using n-hexane (BDH, England) and the resulting extracts were read at 460nm with a spectrophotometer. The heavy metal analysis was carried out by using atomic absorption spectroscopy. The organic carbon was determined by titrimetric method. The results show that the organic carbon contents were 0.53mg/kg (Ikpoba river) and 0.40mg/kg (Ethiope river). THC contents were 6.50mg/kg (Ikpoba river) and 42.10mg/kg (Ethiope river). The organic contents were very low in both river sediments. The low Organic contents could be attributed to the constant flow of the rivers. Generally, higher hydrocarbon concentrations are often recorded in stations that have oil formations than those without oil formations. Some of the results obtained for the heavy metals analysis were higher than the WHO standards. The THC analysis from Ikpoba river sediment was lower compared to WHO standards, while the THC in Ethiope river sediment was higher than the WHO standard. Overall, the parameters analysed were detected in both river sediments, but in varied concentrations.

Key words: Heavy metals, Total hydrocarbon, Organic carbon.

INTRODUCTION

Organic matter in rivers and sediments is widely distributed over the earth surface occurring in almost all terrestrial and aquatic environments (Schnitzer, 1978). Soils and sediments contain a large variety of organic materials ranging from simple sugars and carbohydrates to the more complex proteins, fats, waxes, and organic acids. Important characteristics of the organic matter include their ability to form water-soluble and water insoluble complexes with metal ions and hydrous oxides, interact with clay minerals and bind particles together, sorbs and desorbs both naturally-occurring and anthropogenically introduced organic compounds. Naturally occurring organic carbon in river sediments is a key component in a number of chemical, physical and biological processes. It contributes significantly to acidity of natural waters through organic acids (Hernes and Benner, 2002). Biological activity through light absorption, carbon metabolism and water chemistry through the complexation and mobilization of metals and organic pollutants. By forming organic complexes, total organic carbon (TOC) can influence nutrient availability and control the solubility and toxicity of contaminants (Cho *et al*., 1999). In general, TOC consists of dissolved organic carbon (DOC) and Particulate organic carbon (POC). Dissolved organic carbon is known to be a strong complexing agent for many metals such as iron, copper, aluminum, zinc and mercury. Dissolved organic carbon can also increase the weathering rate of minerals and increase the solubility and thus the mobility and transport of many metals and organic contaminants (Kim and Ahn, 2005). The specific effects of organic compounds will vary depending on the type of compound concerned. In general organic contaminants tend to accumulate in an ecosystem, causing long-term toxicity (Chiew *et al*., 1997).Polycyclic aromatic hydrocarbon (PAHs) are a major concern because they are carcinogenic (Stein *et al*., 2006), hydrophobic environmentally persistent and potentially toxic (Depree and Ahrens, 2005). The environmental effects that they have are similar to those of metals in that they have the potential to impact on marine life and the presence in the food chain, possibly ultimately impacting on humans (Chapman, 1989).

Natural processes and human activities have resulted in elevated content of TOC in soils, sediments and streams. These include diverse inputs from rain fall, steam flow, inappropriate animal waste applications and disposals, forest clearing cuttings, agricultural practices and changes in land uses (Como *et al*., 2007). Recent studies on Ikpoba River reveals that the River is the ultimate recipient for municipal waste and industrial effluents in Benin City (Osa-iguehide et al.,2016) while Ethiope River which passes across Towns and Villages in Delta State have been reported to be a source of municipal waste dump and other polluting substances (Osakue and Peretiemo-Clarke, 2013). There is need for constant assessment of the river or river sediments around our habitable environment in order to ascertain any level of pollution to man or the aquatic environment. Arising from the above, the research is set to examine the total hydrocarbon and organic carbon concentrations of Rivers Ikpoba (Edo State) and Ethiope (Delta State), in view of the fact these rivers act as sources of water consumption for the inhabitants of the areas and both locations have municipal and industrial pollution tendencies respectively.

MATERIALS AND METHODS

Collection and Treatment of Sediment Sample

Sediment samples were collected from the sediments of Ikpoba and Ethiope River respectively using a scoop and stored in sample bottles at ambient temperature (28-31°C).

The study sites are located at Ikpoba River in Ikpoba-Okha Local Government Area of Edo State (as control site due to its low or limited exposure to crude oil spillage), with coordinates N 06^0 21^1 03.3^{11} and E 005 $38^1 50.9^{11}$for the first sampled point and N $06^0 21^1$ $05.2^{11}$and 005^0 38^1 $50.9^{11}$for the second sampled point and Ethiope River in Sapele Delta State.

pH Determination: Sediment pH values were determined using the pH meter probe (Model: Jenway 3015) .For each sediment sample 5 gram (5.0g) of the river sediment sample in a sample cell was each added to 50ml of distilled water. The lump of the

Scientia Africana, Vol. 15 (No. 1), June 2016. Pp 151-157
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sediments (Ikpoba River sediment and Ethiope river sediment) were each stirred to form homogenous slums, and then the pH meter probe (Jenway 3015 model) was immersed into the sample, allowed to stabilize at room temperature and pH of the two samples were recorded. The electrical conductivity of the two samples was measured using the conductivity meter (Jenway 4010 Model).

Heavy Metal Analysis of the Sediments

The extraction of sediment samples was done by dissolving one gramme of the dried powdered sediment samples in a clean 100ml beaker. This was followed by the addition of 5ml of concentrated HNO_3 and 1ml of perchloric acid. The mixture was covered with watch glass and heated to near boiling for one hour. It was filtered hot and made up to mark with distilled water in a 100ml volumetric flask. The concentration of heavy metals (Fe, Mg, Zn, Cu, Cr, Cd, Ni, and V) in the extract was determined using atomic absorption spectroscopy (M-series AAS, Auto sampler (F595) Zeeman furnace GF95z,England) (Tessier *et al*.,1979)

Determination of Total Hydrocarbon

Five grammes sediment samples ware weighed into a 100ml plastic bottle. 25ml of n-hexane was added and mechanically shaken for 10 minutes and left to stand for two hours. It was then filtered, and the filtrate was read at 460nm (Parsons *et al*. 1984).

Organic Carbon Determination: The sediment samples (10g) were passed through a 2mm sieve and the fine sediment were ground to a fine consistency for carbon and Nitrogen determinations. From the grinded samples, 0.5g soil sample and 0.05g sludge was weighed into a 250ml conical flask and 10ml of $K_2Cr_20_7$ and H_2SO_4 was added. This was shaken for 1 minute and the mixture was allowed to cool on an asbestos sheet. To the cold solution, 60ml of distilled water was added to make the volume up to 150ml and allowed to cool. After the addition of 5ml phosphoric acid and 8-10 drops of 1% diphenylamine solution, the solution turned to violet in colour. Titration was then perfumed using the sample and 0.4N ferrous ammonium sulphate solution until the colour change to green. About 0.2g of glucose was weighed and titrated against the sample solution in triplicate. Blank titration was equally carried out by using 10ml of $K_2Cr_20_7$ solution (Gaudette *et al*. 1974).

Calculation

%C = Titre x 0.24

%C = Blank – Titre x 0.2

RESULTS AND DISCUSSION

The analysis revealed that the physical parameters identified in the river sediments of Rivers Ikpoba and Ethiope were in varied concentrations. For example the pH of Rivers Ikpoba and Ethiope were 4.97 and 6.59 respectively; the EC were 869 $\mu S/cm^{-1}$ and 320 $\mu S/cm$ for Ikpoba and Ethiope respectively.

The heavy metals and the organic matter concentration detected were also in varied concentrations. The Fe concentration of the Ethiope River sediments was higher (361.00 mg/kg) that the Ikpoba River sediments (246.90 mg/kg). Additionally, the heavy metals in the Ethiope River sediments were higher than its counterparts in the Ikpoba river sediments. However, Cr was not detectable in Ikpoba River sediments. The organic components detected were also in varied concentrations. The THC concentrations in Ethiope River was higher (42.10 mg/kg) than that detected in Ikpoba river (6.50 mg/kg).

The pH of both Rivers were acidic, but the Ikpoba River sediment was more acidic compared to the Ethiope river sediment. The low pH observed in both rivers may be attributed to the dissolved carbon dioxide arising from bacterial decomposition of organic matter/respiration of animals and plants in water. The pH is an "index" of the amount of hydrogen ion present in a substance and it is used to categorize the latter as acid, neutral or alkaline (basic) (Obahiagbon *et al*., 2008).

The electrical conductivity (EC) of both River sediments was high, which may be attributed to the dissolved solids in the waters. In other words, the electrical conductivity is a measure of the dissolved solids in water. A linear relationship thus exists between the E.C. and total dissolved solids (Ademoroti, 1996).

The elemental constituents detected in both Rivers are present everywhere in nature and they play significant roles in the health of the humans, depending on their concentrations. The iron concentrations in both rivers were higher than the recommended value of iron by WHO for drinking water. WHO (1984) recommended 0.3mg/l for drinking waters. Additionally, the elements detected in both rivers cannot be synthesized by living organisms, but they are required daily in human diet to meet the recommended dietary intakes (FEPA, 1991).The THC for Ethiope River sediment (42.10mg/kg) was higher than that of Ikpoba River (6.50mg/kg),an indication of pollution (possibly from oil spillage, pipe leakages) in Ethiope river.

The results are as presented in Tables 1 and Fig. 1 – 3 below.

Table 1: Physical parameters of Rivers Ikpoba and Ethoipe (sediments).

Parameter	Ikpoba river	Ethiope river
pH	4.97	6.59
EC (μS/cm)	869	320
Clay (%)	4.10	3.80
Silt (%)	1.70	1.00
Sand (%)	94.20	95.20
E.A (mg/kg)	0.40	0.20

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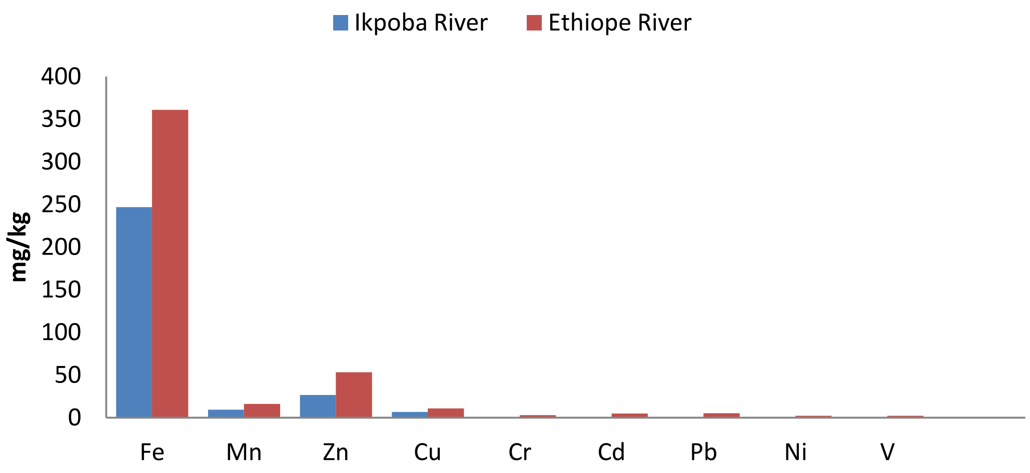

Figure1: Heavy Metal concentrations of Ikpoba and Ethiope

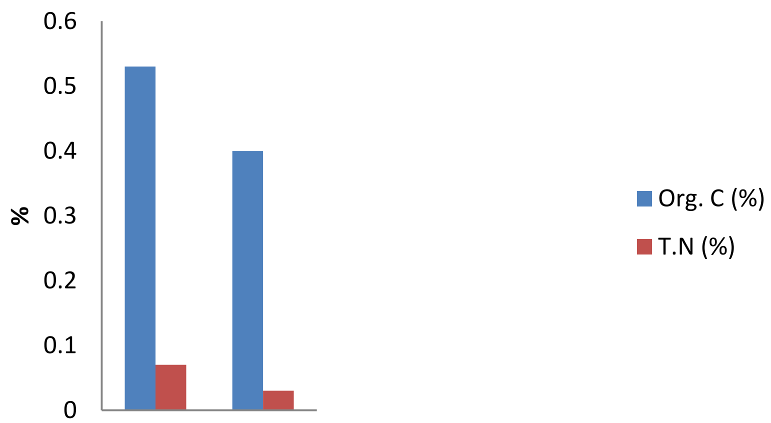

Figure 3: Organic C. and total N of Ikpoba and Ethiope river.

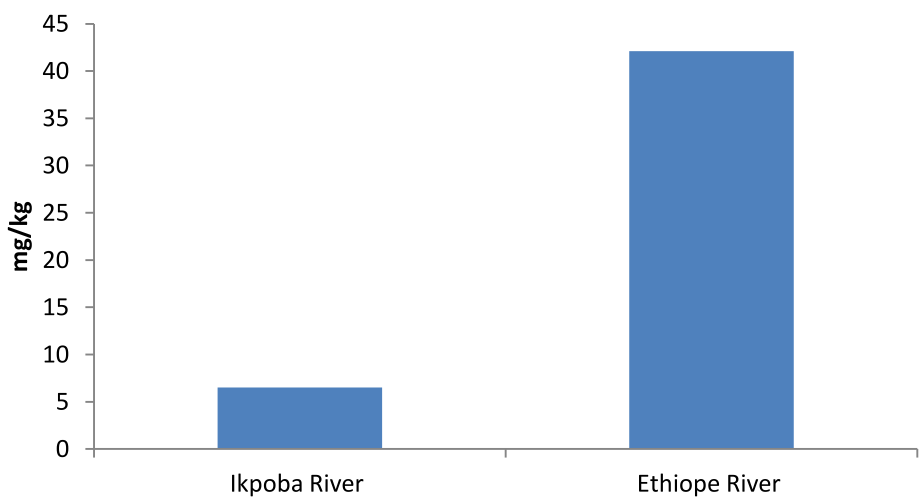

Figure 2: The THC Concentration of Rivers Ikpoba and Ethiope

The concentration of some of the heavy metals detected in both rivers were quite higher than the recommended values in drinking water. For example, the lead, iron, Cu and Zn concentrations. Research has indicated that there are more than twenty (20) heavy metals, but four are of particular concern to human health. These are lead, cadmium, mercury and inorganic arsenic. They are highly toxic and can cause damaging effects even at very low concentrations (Ilori and Obahiagbon, 2011).

These studies on the total hydrocarbons and organic contents in the sediments of rivers Ikpoba and in Edo State and Ethiope in Delta State have shown that: both micro and macro (heavy metals) elements were present in the two rivers, in varied concentrations. Besides, some heavy metals concentrations detected were higher than the permissible levels by WHO in drinking waters. Though the organic components of the two river sediments were low, the THC of the Ethiope river sediments was higher than the standard concentration recommended by WHO and other world bodies.

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