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Assessment of: Benzene, Toluene Ethylbenzene, Xylene in Water and Sediments from Itu, Ibeno and Ibaka River Estuary of Akwa Ibom State, Nigeria

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Abstract: ***Some aromatics often enter the environment due to accidental oil spills, leakage and improper oil-related waste disposal. It therefore becomes imperative to assess pollution of water and sediments by Benzene Tuolene, Ethylbenzene and Xylene in coastal water bodies of Akwa Ibom State, Nigeria.Headspace solid phase micro extraction (HS-SPME) technique was used to trace BTEX in samples.Gas chromatographic analyses were realized with a Varian 450 GC instrument equipped with a Flame Ionization Detector (FID) and Programmed Temperature Vapourizer (PTV) detector. VF-1ms capillary column (30 m x 0.33 mm x 0.25 µm) was used to isolate and determine BTEX.The result shows that:for total BTEX concentration in the sampled rivers, Itu recorded the highest concentration (4.4546ppm), followed by Ibeno river (3.2388ppm) the least concentration of Total BTEX (2.9310ppm) was recorded in Ibaka river.In terms of total BTEX concentration in the sediments, Ibeno recorded the highest concentration (6.9437ppm), followed by Itu river with (5.3820ppm) while the least concentration of total BTEX (4.2986ppm) was recorded at Ibaka river.The Anova shows that the value of the highest concentration of Benzene(0.0490ppm) obtained from Ibeno was significantly (P<0.05) higher than the values obtained in Ibaka (0.0321ppm) and Itu surface water (0.0242ppm). The Anova equally shows that the value of Benzene concentration (0.0321ppm) obtained from Ibaka river was significantly (P<0.05) higher than the level of concentration of Benzene(0.0242ppm) obtained from Itu.***

Keywords: Benzene, Aromatics, Chromatographic, Sediments, Toluene, Xylene

1. Introduction

Surface run-off and erosion are the sources of diverse pollutants discharge into the rivers. Direct human discharges of wastes, industrialization and agricultural activities at different segments of the rivers no doubt accentuate pollution stress on the aquatic environments and endanger the lives of plants and fisheries resources (Pius and Happiness, 2012). These unhealthy activities have accentuated the levels of toxicants in water bodies. Among the toxicants, BTEX from petrochemical industries has been proven to impact the quality of water with deleterious effects on human health. When the physical and chemical conditions of the ecosystem are changed from their normal ranges, similar changes are expected to occur in individual organism, populations and the communities of the ecosystem (Adakole, 2000).

Surface water contamination caused by anthropogenic activities from point and non-point sources has become one of the main environmental issues and a challenge to the world population. Water contaminations have kept on creating upsetting ramifications for wellbeing and economic development in Nigeria (Esrey *et al.*, 1991).

BTEX (benzene; toluene; ethylbenzene; and *o*-, *m*-, and *p*-xylenes) are classified as priority pollutants regulated by many environmental organizations around the world. These monocyclic aromatics are highly water soluble and volatile compared to their aliphatic counterparts (Yang *et al* 2017). Small aromatics frequently enter air, soil, sediments, and groundwater due to accidental oil spills, leakage of gasoline and other petroleum fuels from underground storage tanks and pipelines, and improper oil-related waste disposal. Owing to their potential acute toxicity and health hazard to humans and aquatic life, BTEX are often required to be analyzed as one group whenever a hydrocarbon fuel is suspected to have been spilled (especially in relatively confined areas), Yang *et al* 2017.

Benzene, toluene, ethylbenzene, and xylenes are aromatic compounds of similar chemical structure, properties, and behavior in the environment. These compounds are important and widely used solvents and industrial chemicals. As constituents of crude oil they are present in refined petroleum products. In the context of gasoline and other fuels. BTEX compounds are used as indicators for evaluating the size, age, and toxicity of petroleum fuel spills and plumes (Popek 2018).

BTEX have other effects on human health. For example, exposure to toluene may cause neurological system symptoms and cardiovascular effects; it may also cause adverse effects in kidney and liver (Popek 2018). Ethylbenzene may cause developmental and neurological system effects. Exposure to xylenes may cause developmental, hepatic, neurological, and renal symptoms (Popek 2018). In view of the above submissions, it therefore becomes imperative to assess BTEX concentrations in the

water and sediments of sampled area and relate them with appropriate regulatory standards.

2. Materials and Methods

Study area

This study was carried out in three rivers of Akwa Ibom State, Nigeria: Ibeno, Ibaka and Itu rivers. Akwa Ibom State lies between latitudes 4º32' N and 5º33'N and longitudes 7º25' E and 8º25'E.

Itu is located on 5°10′0″N and 7°59′0″E in the South-South of Nigeria and is a Local Government Area of Akwa Ibom State. It is bounded in the North and North-East by Odukpani in Cross River State and Arochukwu in Abia State, in the West by Ibiono Ibom and Ikono Local Government Areas, in the South and South East by Uyo and Uruan Local Government Areas, respectively. The people in the support zone communities are mainly subsistence farmers and engaged primarily in farming, hunting, fishing and craft making (Jacob, *et al*., 2018).

Ibeno Local Government Area lies between latitude 4° 32' and 4° 39' North and longitude 7° 49' and 8° 21' East. It is bounded in the North by Eket and Esit Eket Local Government Areas, at the South by the Atlantic Ocean's Gulf of Guinea, at the West by Ikot Abasi Local Government and at the East by the Cameroun Republic (Esin *et al*., 2018). The entire Ibeno Local Government Area occupies an area of about 247.575km square and has Atlantic coastline of more than 129km, stretching from Okposo 1 at the Eastern Flank bordering Mbo Local Government Area and Bakassi-Penisula to Atabrikang Village on its Western Flank. The climate falls within tropical equatorial (Af) type, characterized by longer wet season and shorter dry season. Temperatures and relative humidity are high throughout the year with abundance annual rainfall (Abua and Ashua, 2015).

Ibaka, is situated in Mbo Local Government Area of Akwa lbom State, Nigeria, its geographical coordinates are 4° 39' 0" North, 8° 19' 0" East .

The people are predominantly fishermen, farmers, and traders.

Study Area (GPS Coordinates of Sampling points):

IBAKA

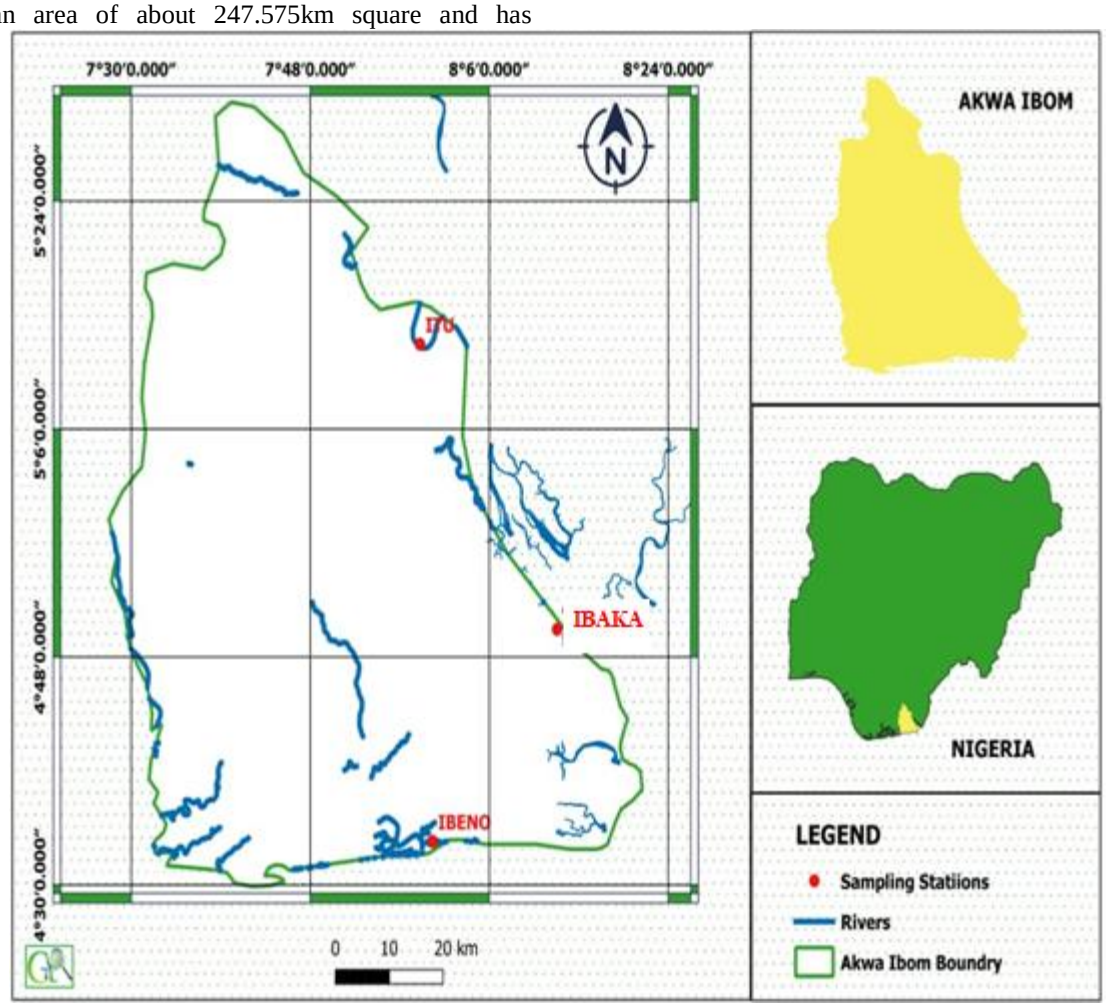
Lattitude (N)	Longitude(E)	Elevation
04^0 39. 127	008^0 18.935	-13m

IBENO

Lattitude (N)	Longitude(E)	Elevation
04^0 34. 039	007^0 58.373	-15m

ITU

Lattitude (N)	Longitude(E)	Elevation
05^0 12. 098	007^0 58.657	-5m



Sample Collection

A reconnaissance survey was carried out to have first-hand information and to establish the sampling points. Global Positioning System was used to establish Coordinates and elevation of sampling points. Samples for water analysis were collected with sterile glass bottles. The sediments were collected with a grab facilitated by fisher men in the locality.

Preparation of samples for BTEX analyses

Headspace solid phase micro extraction (HS-SPME) technique was used to trace BTEX in samples. 5.0 mL of sample was placed in a 10 mL headspace vial (5 replicate vials for each sample) to adsorb BTEX. The vials were placed in a heating block for 45 min at 50°C. Extraction of volatile compounds was done using a 100 µm Polydimethylsiloxane fibre in a solid phase micro extraction(SPME) manual holder (Ho-Sang Shin, 2012). Direct injection in HS mode was performed in 280°C in a Programmed Temperature Vapourizer (PTV) injector.

Apparatus and chromatography

Gas chromatographic analyses were realized with a Varian 450 GC instrument equipped with a Flame Ionization Detector (FID) and PTV detector. VF-1ms capillary column (30 m x 0.33 mm x 0.25 µm) was used to isolate and determine BTEX. A temperature for flame ionization detector (FID) was held at 280°C. Nitrogen was used as carrier and make-up gas for both analyses. Hydrogen and air were flame detector gases with 30 ml/min and 300 ml/min, respectively. Injections of BTEX were done in injector PTV directly by using Head-Space mode (280°C for 15 seconds) of Polydimethyl Siloxane fiber. Quantification of BTEX was based on external standards. Three calibration points were selected with 10, 25 and 50 µg/L for BTEX. The method used for determination of Volatile Organic Contaminants (VOCs) in water samples by capillary GS was optimized for the duration and temperature of extraction, and GC parameters. Determination of limit of detection (LOD) and limit of quantitation (LOQ) was used to undertake quality control of the method (Ho-Sang Shin, 2012).

3. Results

BTEX concentration at IBENO, IBAKA and ITU river water and sediments, AKWA IBOM state

BTEX concentration in surface water at Ibeno, Ibaka and Itu rivers, Akwa Ibom State

The graphical presentation of the level of concentration of BTEX in water bodies at Ibeno, Ibaka and Itu rivers in Akwa Ibom state is shown in figure 1 below.

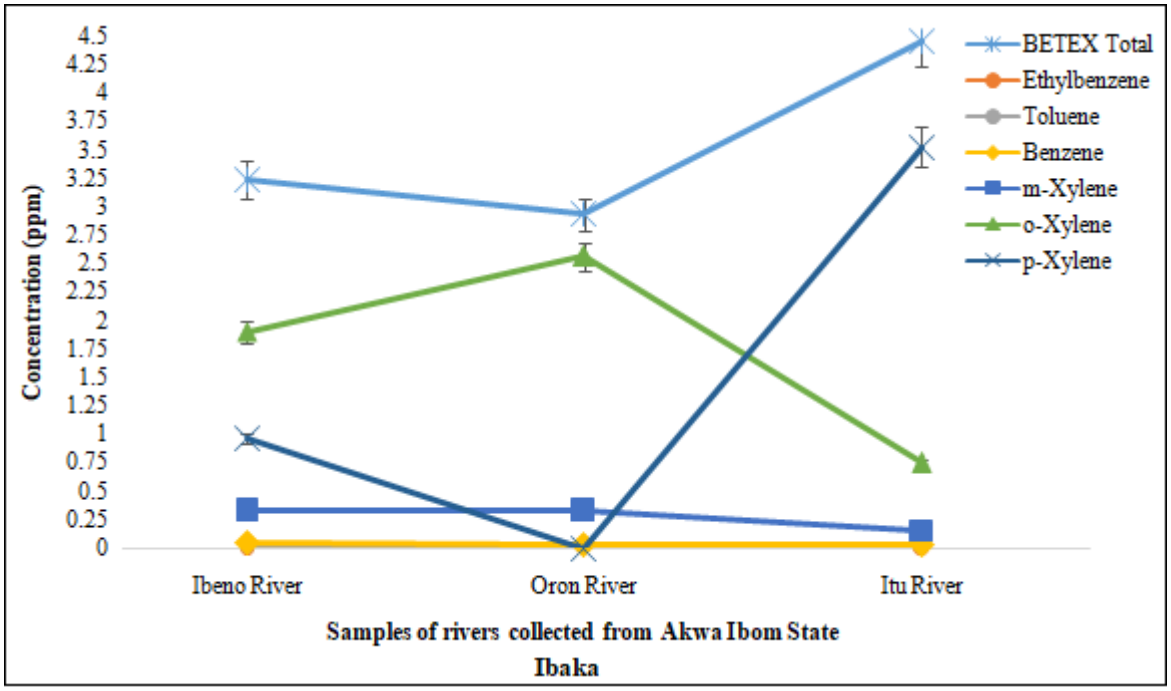


Figure 1: A line graph of the concentration of BTEX in in samples of rivers surface water collected from Akwa Ibom State

Figure 1 shows that Programmed Temperature Vapourizer Congruently, Ibaka river has the highest concentration of o-Xylene (2.5603ppm) in the sampled surface water bodies, followed by Ibeno river with (1.8994ppm) concentration of o-Xylene while the least concentration of o-Xylene (0.7459ppm) in the sampled surface water bodies was recorded in Itu river.

Nonetheless, Itu river has the highest concentration of p-Xylene (3.5218ppm) in the sampled surface water while the least concentration of p-Xylene (0.9591ppm) in the sampled surface water was recorded in Ibeno river. However, p-Xylene was not detected in Ibaka river.

In terms of total BTEX concentration in the sampled rivers, Figure 3 shows that Itu river has the highest concentration of BTEX (4.4546ppm) in the sampled surface water bodies, followed by Ibeno river with (3.2388ppm) concentration of total BTEX while the least concentration of Total BTEX (2.9310ppm) in the sampled surface water bodies was recorded from Ibaka river.

The Anova results of the extent of total BTEX concentration in water bodies at Ibeno, Ibaka and Itu river wateris presented in Table 1

Table 1: Anova result of BTEX concentration in water bodies at Ibeno, Ibaka and Itu rivers surface water, Akwa Ibom State

	Water Samples			
Parameter	Ibeno River (ppm)	Ibaka River (ppm)	Itu River (ppm)	$LSD_{(0.05)}$
BETEX Total	3.2388^{b}±0.050	2.9310^{c}±0.030	4.4546^{a}±0.020	0.0711
Ethylbenzene	0.0012^{a}±0.008	0.0027^{a}±0.005	0.0004^{b}±0.003	0.0011
Toluene	0.0042^{b}±0.004	0.0066^{a}±0.002	0.0042^{b}±0.005	0.0008
Benzene	0.0490^{a}±0.001	0.0321^{b}±0.004	0.0242^{c}±0.005	0.0075
m-Xylene	0.3258^{b}±0.004	0.3292^{a}±0.006	0.1582^{c}±0.003	0.0901
o-Xylene	1.8994^{b}±0.005	2.5603^{a}±0.001	0.7459^{c}±0.003	0.0075
p-Xylene	0.9591^{b}±0.070	ND	3.5218^{a}±0.050	0.0900

Values are mean ± standard deviation. The mean value in each row followed by different superscripts is statistically different at ($P < 0.05$). Mean separation was done using Least Square Difference (LSD) derived from QI Macros 2018 excel add in statistical package. ND = Not Detected.

The Anova result in Table 1 shows that the value of the highest concentration of Ethylbenzene (0.0027ppm) obtained from Ibaka river surface water was significantly ($P<0.05$) higher than the values obtained for Ibeno river surface water (0.0012ppm) and Itu river surface water (0.0004ppm). The Anova result in Table 4.3 also shows that the value of Ethylbenzene concentration (0.0012ppm) obtained from Ibeno river surface water was significantly ($P<0.05$) higher than the level of concentration of Ethylbenzene (0.0004ppm) obtained from Itu river surface water. This implies that there exists significant difference in the level of concentration of Ethylbenzene in the three samples rivers collected from Akwa Ibom state. Therefore, the order of concentration of Ethylbenzene in the three samples of rivers collected from Akwa Ibom state is as follows; Ibaka river surface water > Ibeno river surface water > Itu river surface water.

Similarly, the Anova result in Table 1 shows that the value of the highest concentration of Toluene (0.0066ppm) obtained from Ibaka river surface water was significantly ($P<0.05$) higher than the values obtained for Ibeno river (0.0042ppm) and Itu river (0.0042ppm). The Anova result in Table 1 also shows that the value of Toluene concentration (0.0042ppm) obtained from Ibeno river was not significantly ($P > 0.05$) different from the level of concentration of Toluene(0.0042ppm) obtained from Itu river surface water. This implies that there exist significant differences in the level of concentration of Toluene in the three samples of rivers collected from Akwa Ibom state.

Correspondingly, the Anova result in Table 1 shows that the value of the highest concentration of Benzene(0.0490ppm) obtained from Ibeno river surface water was significantly ($P<0.05$) higher than the values obtained for Ibaka river (0.0321ppm) and Itu river (0.0242ppm). The Anova result in Table 1 also shows that the value of Benzene concentration (0.0321ppm) obtained from Ibaka river was significantly ($P<0.05$) higher than the level of concentration of Benzene(0.0242ppm) obtained from Itu river surface water. This implies that there exist significant differences in the level of concentration of Benzene in the three samples rivers collected from Akwa Ibom state. Therefore, the order of concentration of Benzene in the three samples of rivers collected from Akwa Ibom state is as follows; Ibeno river surface water >Ibaka river surface water > Itu river surface water.

Concomitantly, Table 1 shows that the value of the highest concentration of m-Xylene (0.3292ppm) obtained from Ibaka river was significantly ($P<0.05$) higher than the values obtained for Ibeno river (0.3258ppm) and Itu river surface water (0.1582ppm). The result in Table 1 also shows that the value of m-Xylene concentration (0.3258ppm) obtained from Ibeno river was significantly ($P < 0.05$) higher than the level of concentration of m-Xylene (0.1582ppm) obtained from Itu river. This implies that there exist significant differences in the level of concentration of m-Xylene in the three samples of rivers collected from Akwa Ibom state. Thus, the order of concentration of m-Xylene in the three samples of rivers collected from Akwa Ibom state is as follows; Ibaka river> Ibeno river surface water > Itu river surface water.

Equally, Table 1 shows that the value of the highest concentration of o-Xylene (2.5603ppm) obtained from Ibaka river surface water was significantly ($P<0.05$) higher than the values obtained for Ibeno river (1.8994ppm) and Itu river (0.7459ppm). The result in Table 1 also shows that the value of o-Xylene concentration (1.8994ppm) obtained from Ibeno river was significantly ($P < 0.05$) higher than the level of concentration of o-Xylene (0.7459ppm) obtained from Itu river . This implies that there exist significant differences in the level of concentration of o-Xylene in the three samples of rivers collected from Akwa Ibom state. Thus, the order of concentration of o-Xylene in the three samples of rivers collected from Akwa Ibom state is as follows; Ibaka river surface water > Ibeno river surface water > Itu river surface water.

Furthermore, Table 1 shows that the value of the highest concentration of p-Xylene (3.5218ppm) obtained from Itu river surface water was significantly ($P<0.05$) higher than the values obtained for Ibeno river surface water (0.9591ppm). This implies that there exist significant differences in the level of concentration of p-Xylene in the samples of rivers collected from Akwa Ibom state. Thus, the order of concentration of p-Xylene in the three samples of rivers collected from Akwa Ibom state is as follows; Itu river > Ibeno river>Ibaka river .

In terms of total BTEX concentration in the sampled rivers, Table 1 shows that the value of the highest concentration of Total BTEX (4.4546ppm) obtained from Itu river surface water was significantly (P<0.05) higher than the values obtained for Ibeno river surface water (3.2388ppm) and Ibaka river (2.9310ppm). The result in Table 1 also shows that the value of total BTEX concentration (3.2388ppm) obtained from Ibeno river was significantly (P < 0.05) higher than the level of concentration of total BTEX (2.9310ppm) obtained from Ibaka river. This implies that there exist significant differences in the level of concentration of total BTEX in the three samples of rivers collected from Akwa Ibom state. Thus, the order of concentration of total BTEX in the three samples of rivers collected from Akwa Ibom state is as follows; Itu river surface water > Ibeno river surface water >Ibaka river.

Further analysis was carried out to determine the percentage concentration of BTEX in the surface water ofthe three samples of rivers collected from Akwa Ibom State. A pie chart of the percentage concentration of BTEX in the surface water of the three samples of rivers collected from Akwa Ibom State is presented in figure 2

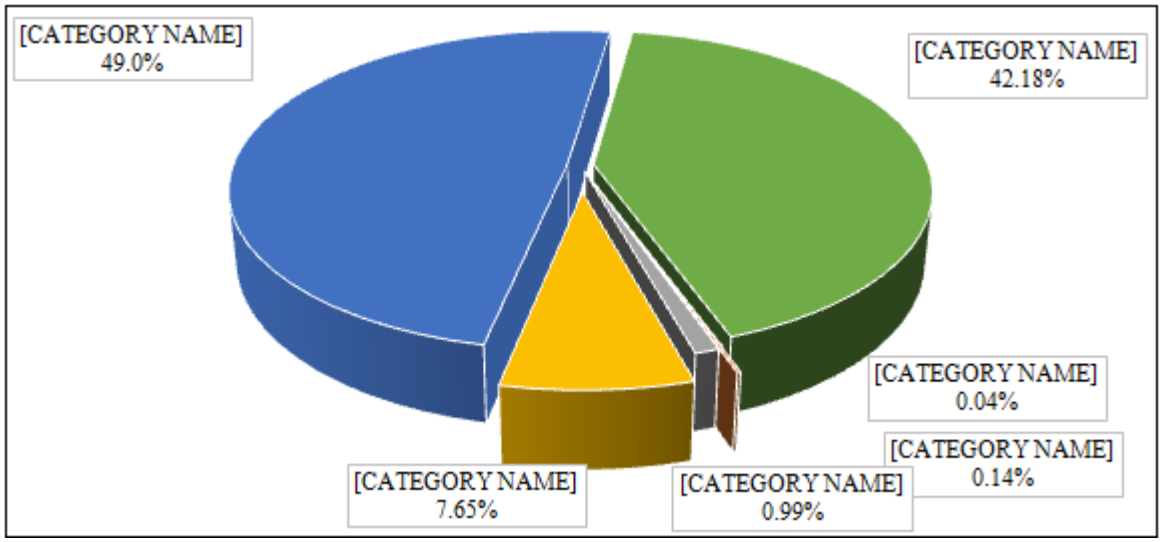


Figure 2: A pie chart of the percentage concentration of BTEX in the surface water of the samples of rivers collected from Akwa Ibom State

The pie chart shows that o-Xylene has the highest percentage concentration (49.0%) in the three rivers samples collected from Akwa Ibom for this study, followed by p-Xylene percentage concentration (42.18%), followed by m-Xylene percentage concentration (7.65%), followed by Benzene percentage concentration (0.99%), followed by Toluene percentage concentration (0.14%) and by Ethylbenzene percentage concentration (0.04%). This implies that o-Xylene is the most abundantly form of BTEX found in the surface water of the three samples of rivers collected from Akwa Ibom state whereas Ethylbenzene was the least form of BTEX found in surface water.

Correlation analysis was employed to measure the extent of the relationship between the concentration of BTEX in samples of rivers surface water collected from Akwa Ibom State and the result of the analysis is presented in Table 2 below

Table 2: Correlation analysis result of the relationship between the concentration of BTEX in samples of rivers surface water collected from Akwa Ibom State

CORREL	Ethylbenzene	Toluene	Benzene	m-Xylene	o-Xylene	p-Xylene	BTEX
Ethylbenzene	1.000	0.939	0.143	0.777	0.946	-0.909	-0.875
Toluene		1.000	-0.205	0.515	0.778	-0.710	-0.656
Benzene			1.000	0.733	0.455	-0.543	-0.604
m-Xylene				1.000	0.939	-0.969	-0.985
o-Xylene					1.000	-0.995	-0.985
p-Xylene						1.000	0.997*
BTEX							1.000

Source: Computed by the researcher from experimental result figures of the concentration of BTEX in the samples of river surface water collected from Akwa Ibom state.

The result of the correlation analysis of the relationship between the concentration of BTEX on samples of river collected Akwa Ibom state shows that most of the BTEX species exhibited a strong correlation with each other. However, some of these relationships were significant ($P \leq 0.05$) while other were not significant ($P \geq 0.05$). According to the results reported in Tables 2, the correlation coefficients (R^2) between BTEX concentration levels at the surface water are quite high.This is a clear indication that all pollutants have the same origin, as expected. These results show that the correlation coefficients obtained are very close to 1, and significant at 5% level, indicating strong positive correlations. The correlation coefficient of (0.997) of the relationship between BTEX and p-Xylene is significant at

5% level indicating that a positive relationship exists between BTEX and p-Xylene. Thus, increase in p-Xylene leads to increase in total BTEX. Ethylbenzene-Toluene correlation coefficient (0.939), o-Xylene-Ethylbenzene correlation coefficient (0.946), o-Xylene-m-Xylene relationship (0.939) and p-Xylene-Ethylbenzene correlation coefficient (-0.909), p-Xylene-m-Xylene correlation coefficient (-0.969), p-Xylene-o-Xylene correlation coefficient (-0.995), Ethylbenzene-BTEX correlation coefficient (-0.875), m-Xylene-BTEX correlation coefficient (-0.985), o-Xylene-BTEX correlation coefficient (-0.985) and p-Xylene-BTEX correlation coefficient (0.997) indicates existence of a very strong relationship among these BTEX species. A high correlation exists in the relationships between m-Xylene-Ethylbenzene (0.777), m-Xylene-Benzene (0.733), o-Xylene-Toluene (0.778) p-Xylene-Toluene (-0.710), and Toluene-BTEX (-0.656), indicating existence of a strong positive or negative relationship among these BTEX species as applicable. A moderate correlation existed between m-Xylene-Toluene (0.515), Benzene-o-Xylene (0.455), p-Xylene-Benzene (-0.543) and Benzene-BTEX (-0.604), indicating existence of a moderate positive relationship among these BTEX species. Every other relationship among the BTEX species were found to be low. This is a clear indication that all BTEX contamination of surface water in the sampled rivers in Akwa Ibom state have the same origin, as expected. These correlations coefficients are similar to those reported by (Sisira *et al*., 2012). There the level of occurrences of each of the BTEX speciesin the surface water was not as a result of reactivity of the species but as a result of similitude in the sources from where these BTEX species enters the surface water.

BTEX concentration in water sediments at Ibeno, Ibaka and Itu rivers, Akwa Ibom State

For the concentration of BTEX at the sediments of the three samples of rivers collected from Akwa Ibom State, the graphical presentation of the level of concentration of BTEX at the sediments of the water bodies at Ibeno, Ibaka and Itu rivers in Akwa Ibom state is shown in figure 5 below.

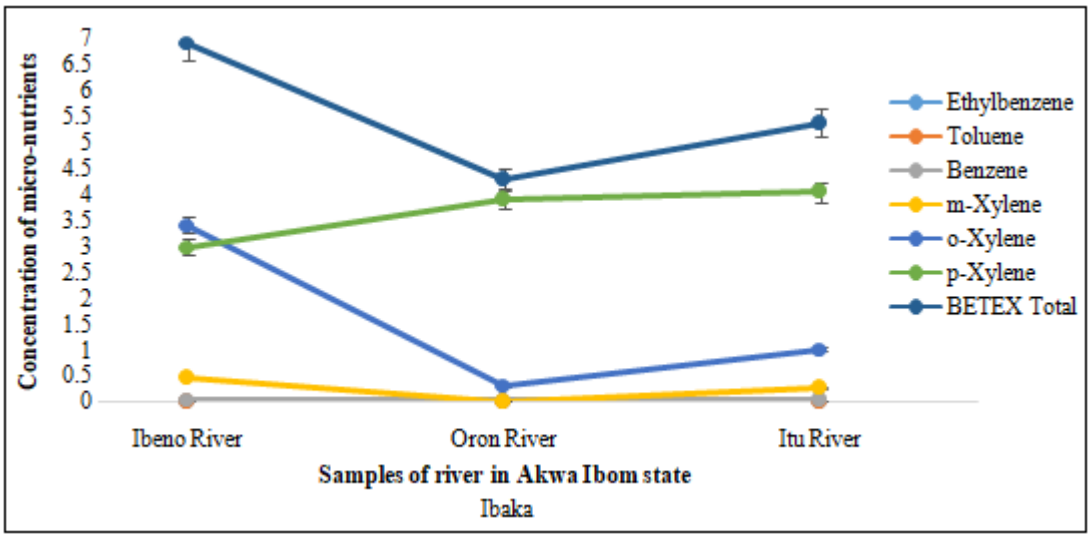


Figure 3: A line graph of the concentration of BTEX at the sediment of the samples of rivers collected from Akwa Ibom State

Figure 3 shows that Ibaka river has the highest concentration of Ethylbenzene (0.0037ppm) at the sediment of the sampled water bodies in Akwa Ibom state, followed by Ibeno river with (0.0027ppm) concentration of Ethylbenzene while the least concentration of Ethylbenzene (0.0011ppm) in the sediment of the three samples of rivers collected from Akwa Ibom state was recorded at Itu river.

Concomitantly, figure 3 shows that Ibeno river has the highest concentration of Toluene (0.0043ppm) at the sediment of the samples of rivers collected from Akwa Ibom state, followed by both Itu river with (0.0042ppm) concentration of Toluene and by Ibaka river with (0.0016ppm) concentration of Toluene.

More so, Figure 3 shows that Ibeno river has the highest concentration of Benzene (0.0537ppm) at the sediments of the samples of rivers collected from Akwa Ibom state, followed by Ibaka river with (0.0509ppm) concentration of Benzene while the least concentration of Benzene (0.0261ppm) was recorded from Itu river.

Equally, Ibeno river has the highest concentration of m-Xylene (0.4642ppm) at the sediment of the sampled water bodies in Akwa Ibom state, followed by Itu river with (0.2778ppm) concentration of m-Xylene while the least concentration of m-Xylene (0.0053ppm) was recorded from Ibaka river.

In addition, Ibaka river has the highest concentration of o-Xylene (3.4243ppm) in the sediments of the samples of water bodies collected from Akwa Ibom state, followed by Itu river with (1.0233ppm) concentration of o-Xylene while the least concentration of o-Xylene (0.3237ppm) in the sediments of the samples of water bodies collected from Akwa Ibom state was recorded from Ibaka river. Nonetheless, Itu river has the highest concentration of p-Xylene (4.0495ppm) in the sediments of the sampled water bodies in Akwa Ibom state, followed by Ibaka river with (3.9134ppm) concentration of p-Xylene while the least concentration of p-Xylene (2.9946ppm) in the sediments of the sampled water bodies in Akwa Ibom state was recorded at Ibeno river.

In terms of total BTEX concentration in the sediments of the three sampled rivers, Figure 5 shows that Ibeno river has the highest concentration of total BTEX (6.9437ppm) in the sediments of the sampled water bodies in Akwa Ibom state, followed by Itu river with (5.3820ppm) concentration of total BTEX while the least concentration of total BTEX (4.2986ppm) in the sediments of the sampled water bodies in Akwa Ibom state was recorded at Ibaka river.

An analysis of variance was undertaken to determine whether there are significant differences existing in BTEX concentration in the sediments of the samples of rivers collected from Akwa Ibom State and the results is presented in Tables 4.5.

Table 3: Anova result of BTEX concentration in the sediment of Ibeno, Ibaka and Itu rivers in Akwa Ibom State

	Water Samples			
	Ibeno River	Ibaka River	Itu River	
Parameter	(ppm)	(ppm)	(ppm)	$LSD_{(0.05)}$
BETEX Total	$6.9437^{a}\pm0.020$	$4.2986^{c}\pm0.050$	$5.3820^{b}\pm0.030$	0.0071
Ethylbenzene	$0.0027^{b}\pm0.001$	$0.0037^{a}\pm0.003$	$0.0011^{c}\pm0.004$	0.0006
Toluene	$0.0043^{a}\pm0.005$	$0.0016^{b}\pm0.004$	$0.0042^{a}\pm0.002$	0.0008
Benzene	$0.0537^{a}\pm0.002$	$0.0509^{b}\pm0.005$	$0.0261^{c}\pm0.003$	0.0007
m-Xylene	$0.4642^{a}\pm0.005$	$0.0053^{c}\pm0.005$	$0.2778^{b}\pm0.003$	0.0009
o-Xylene	$3.4243^{a}\pm0.010$	$0.3237^{c}\pm0.020$	$1.0233^{b}\pm0.050$	0.0006
p-Xylene	$2.9946^{c}\pm0.050$	$3.9134^{b}\pm0.030$	$4.0495^{a}\pm0.010$	0.0007

Values are mean ± standard deviation. The mean value in each row followed by different superscripts is statistically different at ($P < 0.05$). Mean separation was done using Least Square Difference (LSD) derived from QI Macros 2018 excel add in statistical package.

The Anova result in Table 3 shows that the value of the highest concentration of Ethylbenzene (0.0037ppm) obtained from the sediment of Ibaka river was significantly ($P<0.05$) higher than the values obtained from Ibeno river sediment (0.0027ppm) and Itu river sediment (0.0011ppm). The Anova result in Table 3 also shows that the value of Ethylbenzene concentration (0.0027ppm) obtained from Ibeno river sediment was significantly ($P<0.05$) higher than the level of concentration of Ethylbenzene (0.0011ppm) obtained from Itu river sediment. This implies that there exists significant difference in the level of concentration of Ethylbenzene in the three samples Rivers collected from Akwa Ibom state. Therefore, the order of concentration of Ethylbenzene in the sediments of the three samples of rivers collected from Akwa Ibom state is as follows; Ibaka river sediment> Ibeno river sediment> Itu river sediment

Similarly, the Anova result in Table 3 shows that the value of the highest concentration of Toluene (0.0043ppm) obtained from Ibeno river sediment was significantly ($P < 0.05$) higher than the values obtained from Ibaka river sediment (0.0016ppm) but was not significantly ($P > 0.05$) higher than the value of Toluene concentration (0.0042ppm) obtained from Itu river sediment. The Anova result in Table 3 also shows that the value of Toluene concentration (0.0042ppm) obtained from Itu river sediment was significantly ($P < 0.05$) different from the level of concentration of Toluene(0.0016ppm) obtained from Ibaka river sediment. This implies that there exist significant differences in the level of concentration of Toluene in the sediments of the three samples of rivers collected from Akwa Ibom state.

Correspondingly, the Anova result in Table 3 shows that the value of the highest concentration of Benzene(0.0537ppm) obtained from Ibeno river sediment was significantly ($P<0.05$) higher than the values obtained from Ibaka river sediment (0.0509ppm) and Itu river sediment (0.0261ppm). The Anova result in Table 3 also shows that the value of Benzene concentration (0.0509ppm) obtained from Ibaka river sediment was significantly ($P<0.05$) higher than the level of concentration of Benzene(0.0261ppm) in Itu river sediment This indicates that there is significant heterogeneity in the level of concentration of Benzene in the sediments of the three samples rivers collected from Akwa Ibom state. Therefore, the order of concentration of Benzene in the sediments of the three samples of rivers collected from Akwa Ibom state is as follows; Ibeno river sediment > Ibaka river sediment > Itu river sediment

Concomitantly, Table 3 shows that the value of the highest concentration of m-Xylene (0.4642ppm) obtained from Ibeno river sediment was significantly ($P<0.05$) higher than the values obtained for Ibaka river sediment (0.0053ppm) and Itu river sediment (0.2778ppm). The result in Table 3 also shows that the value of m-Xylene concentration (0.0053ppm) in Ibaka river sediment was significantly ($P < 0.05$) lower than the level of concentration of m-Xylene (0.2778ppm) in Itu river sediment This implies that the level of concentration of m-Xylene in river sediments differs among the three samples of rivers collected from Akwa Ibom state. Thus, the order of concentration of m-Xylene in the three samples of rivers collected from Akwa Ibom state is as follows; Ibeno river sediment> Itu river sediment>Ibaka river sediment

Congruently, Table 3 shows that the level of concentration of o-Xylene (3.4243ppm) in Ibeno river sediment was significantly ($P<0.05$) higher than the level of concentration of o-Xylene (0.3237ppm) in Ibaka river sediment and (1.0233ppm) in Itu river sediment. The result in Table 3 also shows that the level of concentration of o-Xylene (1.0233ppm) in Itu river sediment was significantly ($P < 0.05$) higher than the level of concentration of o-Xylene (0.3237ppm) in Itu river sediment. This implies that the level of concentration of o-Xylene differs significantly among the three samples of rivers collected from Akwa Ibom state. Thus, the order of concentration of o-Xylene in the three samples of rivers collected from Akwa Ibom state is as follows; Ibeno river sediment > Itu river sediment >Ibaka river sediment

Furthermore, Table 3 shows that the level of concentration of p-Xylene (4.0495ppm) in Itu river sediment was significantly ($P<0.05$) higher than its levels of concentration at Ibeno river sediment(2.9946ppm) and at Ibaka river sediment (3.9134ppm). Likewise, the level of concentration of p-Xylene (3.9134ppm) in the sediment of Ibaka river is significantly higher than the level of concentration of p-Xylene (2.9946ppm) in the sediment of Ibeno river. This implies that there exist significant differences in the level of concentration of p-Xylene in the sediments of the samples of rivers collected from Akwa Ibom state. Thus, the order of

concentration of p-Xylene in the three samples of rivers collected from Akwa Ibom state is as follows; Itu river sediment >Ibaka river sediment > Ibeno river sediment.

In terms of total BTEX concentration in the sampled rivers, Table 3 shows that the level of concentration of Total BTEX (6.9437ppm) in Ibeno river sediment was significantly ($P<0.05$) higher than the levele of total BTEX concentration (4.2986ppm) in Ibaka river sediment and (5.3820ppm) in Itu river sediment. The result in Table 3 also shows that the level of total BTEX concentration (4.2986ppm) in Ibeno river sediment was significantly ($P < 0.05$) lower than the level of concentration of total BTEX (5.3820ppm) in Itu river sediment This implies that there exist significant differences in the level of concentration of total BTEX in the sediments of the three samples of rivers collected from Akwa Ibom state. Thus, the order of concentration of total BTEX in the sediments of the three samples of rivers collected from Akwa Ibom state is as follows; Ibeno river sediment > Itu river sediment > Ibaka river sediment.

Further analysis was carried out to determine the percentage concentration of BTEX in the sediments ofthe three samples of rivers collected from Akwa Ibom State. A pie chart of the percentage concentration of BTEX in the sediments of the three samples of rivers collected from Akwa Ibom State is presented in figure 4

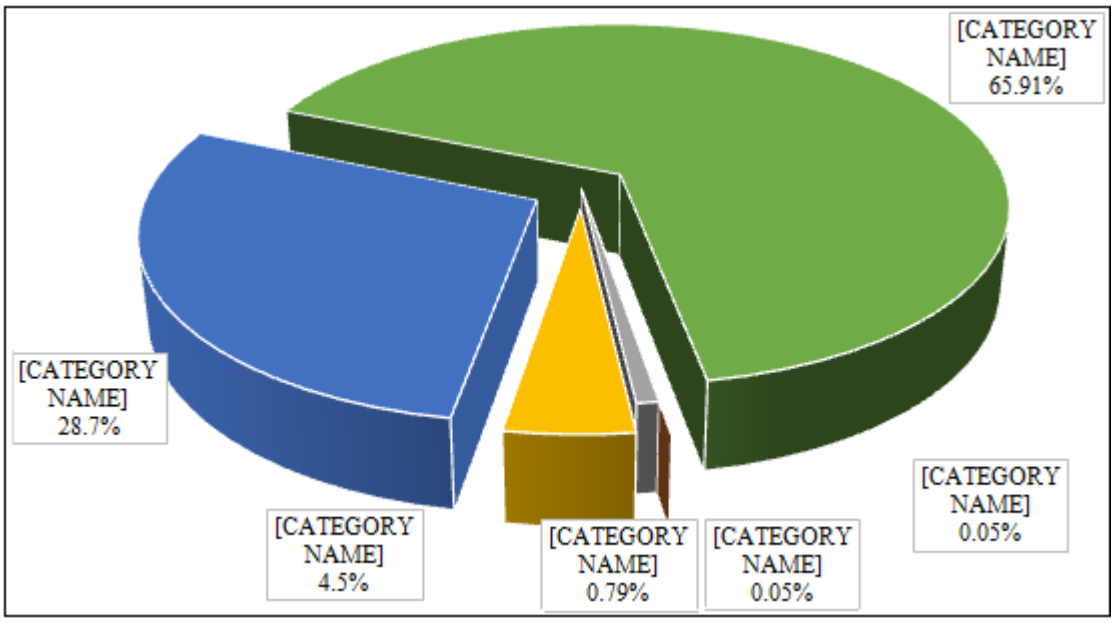


Figure 4: A pie chart of the percentage concentration of BTEX in the sediments of the samples of rivers collected from Akwa Ibom State

The pie chart shows that p-Xylene has the highest percentage concentration (65.91%) in the three rivers samples collected from Akwa Ibom for this study, followed by o-Xylene percentage concentration (28.7%), followed by m-Xylene percentage concentration (4.5%), followed by Benzene percentage concentration (0.79%), followed by Toluene percentage concentration (0.05%) and by Ethylbenzene percentage concentration (0.05%). This implies that p-Xylene is the most abundant form of BTEX found in the sediments of the three samples of rivers collected from Akwa Ibom state whereas Toluene and Ethylbenzene were the least form of BTEX found in the sediments of the three samples of rivers collected from Akwa Ibom state.

Correlation analysis was employed to measure the extent of the relationship between the concentration of BTEX in the sediments of the samples of rivers collected from Akwa Ibom State and the result of the analysis is presented in Table 4.6 below

Table 4: Correlation analysis result of the relationship between the concentration of BTEX in sediments of samples of rivers collected from Akwa Ibom State

CORREL	Ethylbenzene	Toluene	Benzene	m-Xylene	o-Xylene	p-Xylene
Ethylbenzene	1.000	-0.772	0.885	-0.479	-0.084	-0.249
Toluene		1.000	-0.388	0.928	0.698	-0.424
Benzene			1.000	-0.016	0.389	-0.670
m-Xylene				1.000	0.915	-0.731
o-Xylene					1.000	-0.944
p-Xylene						1.000

Source: Computed by the researcher from experimental result figures of the concentration of BTEX in the sediments of the samples of river collected from Akwa Ibom state.

The result of the correlation analysis of the relationship between the concentration of BTEX on samples of river water sediments collected Akwa Ibom state shows that most of the BTEX species exhibited a strong correlation with each

other, however these relationships were not significant, indicating that the level of occurrences of each of BTEX species in the water sediments of the samples of rivers collected from Akwa Ibom state was not as a result of the presence of other BTEX species or the reactivity between these BTEX species but as a result of the sources from where these BTEX species enters the water bodies in the study area. According to the results reported in Tables 4, the correlation coefficients (R^2) between BTEX concentration levels at the surface water are quite very high for Benzene-Ethylbenzene relationship (0.885), m-Xylene-Toluene relationship (0.928), o-Xylene-m-Xylene relationship (0.915) and p-Xylene-o-Xylene relationship (-0.944) indicating existence of a very strong positive or negative relationship among these BTEX species as applicable. A high correlation exists in the relationships between Toluene-Ethylbenzene (-0.772), o-Xylene-Toluene (0.698), p-Xylene-Benzene (-0.670) and p-Xylene-m-Xylene (-0.731) indicating existence of a strong positive or negative relationship among these BTEX species as applicable. A moderate correlation existed between m-Xylene-Ethylbenzene (0.479) indicating existence of a moderate positive relationship among these BTEX species. Every other relationship among the BTEX species were found to be low. Toluene, m-Xylene, o-Xylene and p-Xylene had a very strong relationship with the total BTEX. This is a clear indication that all BTEX contamination of water in the sampled rivers in Akwa Ibom state have the same origin, as expected.

Comparison of the values of the concentration of BTEX obtained at the surface water and Sediments of the samples of rivers collected from Akwa Ibom state with the recommended standards by USEPA(1996), WHO (1987), and NESREA (2011)

The mean concentration of BTEX in surface water and sediments at Ibeno river, Ibaka river and Itu river were compared with the acceptable tolerable values of these elements in water by US EPA, WHO and NESREA and the result is presented in Table 5.

Table 5: Comparison of the BTEX obtained at the surface water and sediments of the samples of rivers collected from Akwa Ibom state with the recommended standards by USEPA(1996), WHO(1987), and NESREA(2011)

	IBENO	Ibaka	ITU	USEPA	WHO	NESREA
Parameter	ppm	ppm	ppm	ppm	ppm	Ppm
Surface water concentration						
Ethylbenzene	0.0012	0.0027	0.0004	0.70	0.30	0.07
Toluene	0.0042	0.0066	0.0042	1.00	0.70	0.07
Benzene	0.049	0.0321	0.0242	0.05	0.01	0.07
m-Xylene	0.3258	0.3292	0.1582	3.33	0.50	0.07
o-Xylene	1.8994	2.5603	0.7459	3.33	0.50	0.07
p-Xylene	0.9591	ND	3.5218	3.33	0.50	0.07
BTEX (Total)	3.2388	2.931	4.4546	10.0	2.51	0.42
Water Sediment concentration						
Ethylbenzene	0.0027	0.0037	0.0011	0.70	0.30	0.07
Toluene	0.0043	0.0016	0.0042	1.00	0.70	0.07
Benzene	0.0537	0.0509	0.0261	0.05	0.01	0.07
m-Xylene	0.4642	0.0053	0.2778	3.33	0.50	0.07
o-Xylene	3.4243	0.3237	1.0233	3.33	0.50	0.07
p-Xylene	2.9946	3.9134	4.0495	3.33	0.50	0.07
BTEX (Total)	6.9437	4.2986	5.382	10.0	2.51	0.42

Note: Values of the parameters are as obtained from the laboratory experiment. ND = Not Detected.

The mean concentration of Ethylbenzene and Toluene, in both the surface water and sediments of the samples of rivers collected from Akwa Ibom state when compared with the acceptable tolerable value of this elements in water was found to falls within the acceptable limit by USEPA, WHO and NESREA. The mean concentration of Benzene in the surface water at Ibeno, Ibaka and Itu rivers were within the acceptable limit by USEPA and NESREA but exceeded the tolerance level by WHO standards. Contrastingly, the mean concentration of Benzene in the water sediments of Ibeno and Ibaka rivers exceeded the acceptable limit by USEPA and WHO but falls within the tolerance limit by NESREA. The mean concentration of Benzene in Itu river sediment exceeded the acceptable limit by WHO but falls within the tolerance limit by USEPA and NESREA.

The mean concentration of m-Xylene in the surface water and sediments of Ibeno, Ibaka and Itu rivers were within the permissible limit by USEPA and WHO but exceeded that of NESREA. Similarly, the mean concentration of o-Xylene in the surface water of Ibeno, Ibaka and Itu rivers were within the permissible limit by USEPA but exceeded the permissible limit by WHO and NESREA. However, the mean concentration of o-Xylene in the water sediment of Ibeno river exceeded the permissible limit by USEPA, WHO and NESREA, the mean concentration of o-Xylene in the water sediment of Ibaka river exceeded the permissible limit by NESREA but falls within the permissible limits by USEPA, WHO. The mean concentration of o-Xylene in the water sediment of Itu river exceeded the permissible limit by WHO and NESREA but falls within the permissible limit by USEPA.

The mean concentration of p-Xylene in the surface water of Ibeno river exceeded the permissible limit by WHO and NESREA but falls within the permissible limit by USEPA. However, the mean concentration of p-Xylene in the surface water of Ibaka river exceeded the permissible limits by USEPA, WHO and NESREA. For the water sediment, the mean concentration of p-Xylene in Ibeno river exceeded the permissible limit by WHO and NESREA but falls within the permissible limit by USEPA. However, the mean concentration of p-Xylene in Ibaka and Itu rivers sediment exceeded the permissible limits by USEPA, WHO and NESREA.

The mean concentration of BTEX in the surface water and sediments of Ibeno, Ibaka and Itu rivers exceeded the permissible limit by WHO and NESREA but falls within the permissible limit by USEPA

4. Discussion

BTEX Concentration

The finding of the study shows that Xylene concentration is the highest of all the forms of BTEX concentration in the sampled rivers in the study area. Among the Xylene concentration, o-Xylene, p-Xylene, and m-Xylene raked the highest in abundance in the studied rivers. These findings display that p-Xylene was the most abundant of the six

species of BTEX, regardless of time of day. The levels of other species of BTEX (Benzene, Toluene and Ethylbenzene) in the study area are actually low but may pose health risk to the community dwellers, visitors and the nearby dwellers because poisoning by BTEX can occur by ingestion of food, air or absorption through the skin. The main source of these chemicals in these rivers is associated with the industrial pollution. Several companies are nearly suited to these rivers and the discharge of their industrial effluents causes the accumulation of BTEX in these rivers. Cigarette smoke is also a major source of BTEX and some smokers dumping their left-over cigarette sticks inside the river when they go to wash their bodies, or rainfall washing some painting materials and adhesives that contains these chemicals into the river also helps to increase the accumulation of BTEX in these water bodies. However, industrial facilities discharge into these rivers constitute the largest source of BTEX in these water bodies. Each year, industrial facilities discharge into the environment large amount of chemicals leading to respiratory, neurological, developmental, reproductive disorders and cancer, yet communities close to such facilities, especially in poor nations seldom know the extent to which these discharges are affecting their health. Judging from the USEPA established permissible levels for chemical contaminants in drinking water known as maximum contamination levels (MCLS), as well as that of the World Health Organization (WHO) and the NESREA, the result of our study shows that some BTEX forms were high and well over the permissible limit for these chemicals in this water. This makes it obvious that the water from Ibeno River, Ibaka River and Itu River may not be safe for drinking and bathing possibly as a result of accumulation of these toxic compounds in the body due to long term exposure via inhalation, absorption and ingestion. The finding of this study on BTEX is in consonance with the reports of several other researchers as Correa *et al*., (2012); Kountouriotis *et al*., (2014); Marć *et al*., (2016); Sairat *et al*., (2015); Xiong *et al*., (2016) and Jiang *et al*., (2017). Acute and chronic exposure to benzene may cause drowsiness, dizziness, confusion, leukemia (International Agency for Research on Cancer (IARC). (1987)), plastic anemia resulting from suppression of bone narrow tissue Snyder, and Koests (1975). Deliberate breathing high levels of toluene can cause permanent damages to the nervous system, heart problems, coma and in some cases death (ATSDR, 2000)..Toxicity of ethylbenzene is low in humans although symptoms such as irritation of eyes and the respiratory tract have been reported at high levels of exposure in air. Xylenes when absorbed at high concentration levels by humans causes similar problems like toluene, benzene and ethylbenzene (IPCS, 1993; and IPCS, 1997).

5. Conclusion

Xylene concentration was the highest of all the forms of BTEX concentration in the sampled rivers in the study area. The levels of other species of BTEX (Benzene, Toluene and Ethylbenzene) in the study area were actually low but may still pose health risk to human life based on frequency of exposure. Considering the environmental and public health implications of BTEX pollution, it becomes imperative to enforce a more comprehensive monitoring of the Volatile Organic Contaminants in surface waters and sediments.

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