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Acute toxicity of crude oil from NNPC and artisanal refineries in Niger Delta on selected aquatic biota

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Abstract

The spill of Crude oil from artisanal refineries and government owned pipelines has become recurrent situation in the Niger Delta, leading to devastating effects on the aquatic ecosystem. The toxicity of Crude oil from NNPC (Nigerian National Petroleum Corporation) refinery and selected artisanal refineries in Bolo, Twon-Brass and Ekpemu of the Niger Delta were investigated. The physicochemical properties of the products from the artisanal refineries short fall of the standards of Crude oil for refineries, as they contained impurities. The toxicity of the Crude oil was tested using three representatives of different trophic levels in the aquatic habitat; Fish (*Tilapia guineensis*), Crusteceans (*Paleamonetes africanus*), and Moluscs (*Tympanotomus fuscatus*). The LC_{50}, NOEC, LOEC, and TU_a were the indices used for toxicity assessment of the crude oil on the test organisms. The study revealed that all the Crude oil samples were toxic to the organisms. The degree of toxicity of crude oil showed the following trend; Ekpemu (LC_{50} – 0.02ppt)> Twon-Brass (LC_{50} – 0.06ppt)> Bolo (LC_{50} – 0.11ppt)> NNPC (LC_{50} – 4.63ppt), while the degree of sensitivity was; *Tilapia guineensis* > *Paleamonetes africanus* > *Tympanotonus fuscatus.* The findings further emphasize the need to control Crude oil spillage into the aquatic ecosystem.

Keywords: Toxicity; Acute toxicity; Aquatic habitat; Artisanal refinery; Niger delta

1. Introduction

Oil exploration and exploitation has been on-going for several decades in the Niger Delta region of Nigeria which is located in the southern part of the country (1). The region which serves as crude oil and natural gas hub of Nigeria comprises mainly of states trans-divided by the river Niger and its tributaries (Collins, 2018). The states are; Akwa Ibom, Rivers, Delta, Bayelsa and Edo states. However, due to recent discoveries in oil and gas explorations, there have been other states that have been agitating to be part of the Niger Delta. But due to geographical locations, tribal differences, cultures and others features, states like Ondo and Lagos in the West, Abia, Anambra and Imo states in the east which equally produces oil, although in lesser quantity have joined the league and all states that produces oil are now classified and called oil producing states (2). The impact of oil exploration does not only affect the Niger Delta but also neighboring states to oil producing states in Nigerian at large.

Crude oil exploration in the Niger Delta Region has been on the increase since 1958 when it was discovered in commercial quantity in Olobiri in today Bayelsa State (3). These replaced earnings from agriculture which was the main stay of the Nation's economy. The Niger Delta Region of Nigeria which is richly endowed with natural resources, oil and gas deposit and abundance of human and material resources including good agricultural lands, extensive forests, excellent fisheries, as well as with a well-developed industrial base are subjected to severe environmental degradation due to largely ecologically unfriendly exploration of oil and state policies that expropriate the indigenous peoples of the Niger Delta of their rights to these natural resources (4).

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The region which consists of diverse ecosystems of mangrove swamps, fresh water swamps, rain forest and is characterized by complete contamination of streams and river and forest - destruction of biodiversity to oil pollution in the area. According to (5), this has affected the livelihood of the indigenous people who depend on the ecosystem services for survival. This ecologically productive Niger Delta has suffered extensive soil degradations, forest clearing, toxic discharges, habitat degradations, dredging fillings and significant alteration by extensive road and pipeline construction from the petroleum industry of particular concern in the Niger Delta, and frequent and extensive oil spill that have occurred (6, 7, 8).

The ecological devastation in the Niger Delta region occasioned by crude oil exploration and production has degraded most agricultural lands in the area and has turned the hitherto productive areas into wastelands. Aquatic life has also been destroyed with the pollution of traditional fishing grounds, exacerbating hunger and poverty (9, 10). Oil decreases Oxygen in the water column and coat breathing apparatus of aquatic organisms. Specifically, it starves mangroves of Oxygen by coating the breathing roots of the mangroves and scotch the tender structures of aquatic macrophytes of tidal fresh water vegetation.

2. Material and methods

2.1. Sample Collection

The Crude oil samples were collected with sterile containers from artisanal refineries in Bolo community of Rivers State, Twon-Brass community of Bayelsa state, Ekpemu community of Delta state and NNPC in Port Harcourt, all in the Niger Delta region of Nigeria.

Figure 1 Map of Niger Delta Region showing the sample states

Source: Adati, 2012

2.2. Sources of organisms used for toxicity tests

- The brackish water juvenile shrimps (*Palaemonetes africanus*) were collected from Nigerian Institute for Oceanography and Marine Research (NIOMR), Buguma, Rivers State, Nigeria.
- The brackish water fish (*Tilapia guineensis*) were collected from Africa Regional Aquaculture Center (ARAC), Port Harcourt, Nigeria.
- *Tympanotonus fuscatus* (periwinkles) were collected from Nigerian Institute for Oceanography and Marine Research (NIOMR), Buguma, Rivers State, Nigeria.

2.3. Physicochemical quality of petroleum crude oil samples

2.3.1. Asphaltenes, C7

The standard test method for determination of asphaltenes (heptane insoluble) in crude petroleum and petroleum productsas described in ASTM D6560.

A test portion of the sample was mixed with heptane and the mixture heated under reflux, and the precipitated asphaltenes, waxy substances, and inorganic material were collected on a filter paper. The waxy substances were removed by washing with hot heptane in an extractor. After removal of the waxy substances, the asphaltenes were separated from the inorganic material by dissolution in hot toluene, the extraction solvent was evaporated, and the asphaltenes weighed.

2.3.2. Hydrogen Sulphide, Dissolved

ASTM D7621 is the standard test method for determination of hydrogen sulfide in fuel oils by rapid liquid phase extraction:UOP-163Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons by Potentiometric Titration: The liquid hydrocarbon sample was weighed into 2-propanol containing a small amount of ammonium hydroxide. The solution is titrated potentiometrically with alcoholic silver nitrate using a glass reference and silver-silver sulfide indicating electrode system. Hydrogen sulfide and mercaptan sulfur concentrations were calculated as mass ppm. Free sulfur complicates the potentiometric curve and instructions were given for interpreting the curve when free sulfur is present.

2.3.3. Sulphur Content

ASTM D4294 is the standard test method for sulfur in petroleum and petroleum products by energy dispersive x-ray fluorescence spectrometry: The sample was placed in the beam emitted from an X-ray source. The resultant excited characteristic X radiation was measured, and the accumulated count was compared with counts from previously prepared calibration standards that bracket the sample concentration range of interest to obtain the sulfur concentration in mass %.

2.3.4. Water Content

ASTM D4377is the standard test method for water in crude oils by potentiometric Karl Fischer titration: After homogenizing the crude oil with a mixer, an aliquot of the crude, in a mixed solvent, was titrated to an electrometric end-point using Karl Fischer reagent.

2.3.5. Salt in Crude Oil

ASTM D3230 is the standard test method for salts in crude oil (Electrometric Method). The test method measures the conductivity of a solution of crude oil in a mixed alcohol solvent when subjected to an electrical stress. It measures conductivity due to the presence of inorganic chlorides, and other conductive material, in the crude oil. A homogenized test specimen was dissolved in a mixed alcohol solvent and placed in a test cell consisting of a beaker and a set of electrodes. A voltage was impressed on the electrodes, and the resulting current flow is measured. The chloride (salt) content was obtained by reference to a calibration curve of current versus chloride concentration of known mixtures. Calibration curves were based on standards prepared to approximate the type and concentration of chlorides in the crude oils being tested.

2.4. Characterization of hydrocarbon content of crude oil and its products

Total Petroleum Hydrocarbons (TPH), and Polyaromatic Hydrocarbons (PAH) were extracted and quantified using Gas chromatograph fited with flame ionization detector (GC-FID) Model 6890 (Agilent instruments USA) according to method adopted from United States Environmental Protection Agency (11).

2.5. Toxicity of effluents on test organisms

Palaemonetes africanus a marine water shrimp, *Tillapia guineensis*, marine water fish and *Tympanotonus fuscatus* (periwinkles) were the higher organisms employed for toxicity testing. This is in accordance to specifications by (12).

Acute toxicity tests were carried out with aquatic organisms (*Palaemonetes africanus, Tillapia guineensis* and *Tympanotonus fuscatus)* by exposing the organisms to the toxicants at various concentrations, using the semi-static agitation test procedure, recommended by the Department of Petroleum Resources (DPR) for a period of 96 hours (13).

2.6. Acclimatization procedure

All test organisms were first acclimatized for ten days at room temperature (28-30℃). The organisms were placed in a holding tank, and aerated by the help of an aerator (14). The holding brackish water was changed on a daily bases to increase nutrient availability and removed unwanted pollutants. After the acclimatization period, ten test organisms of fairly equal size were randomly caught with the aid of hand net and carefully transferred into the test container. Only healthy and active organisms were selected.

2.7. Preliminary range finding test

The preliminary range finding test is performed to estimate the lowest concentration of the toxicant that will cause a zero effect on the test organisms, and the highest concentration that will cause 100% mortality. The results are then used to determine the range of the definitive toxicity test.

2.8. Definitive Toxicity test procedure

The procedure used for toxicity was adapted from (15). Toxicity tests were carried in out in a set of five aquarium glass container for 0.01ppt, 0.1ppt, 1.0ppt, 10ppt, and 100ppt and concentrations of each of the toxicants respectively. A control was set up in which it was 100% brackish water and no toxicant was added. Each set were labeled appropriately according to their concentrations. Ten (10) active test organisms were introduced into each container, and monitored for 96hrs.

The same experimental setup was prepared for *Palaemonetes africanus, Tillapia guineensis* and *Tympanotonus fuscatus.*

The containers were properly aerated with an aerator, and observations were made between 0 hour to 96 hours to ascertain the mortality of the test organisms. At the end of each exposure period, dead organisms were counted and removed.

The percentage mortality was derived by dividing the number of organisms that died at each exposure hour by the total test organism and multiplying by 100.

$$\%\text{Mortality} = \frac{\text{Number of dead organisms}}{\text{Total number of organisms}} \times 100$$

2.9. Determination of acute toxicity response

The acute response of the test organisms was determined using Probit analysis at 95% confidence limit to calculate the LC_{50} (lethal dose of the toxicant that will kill 50% of the test organism), NOEC (No Observed Effect Concentration is the highest tested concentration of an effluent or toxicant that causes no observable adverse effect on the test organisms), LOEC (Lowest Observed Effect Concentration is the lowest concentration of the test sample with an effect different from the control) and TU_a (Toxic Unit - Acute is 100 times the reciprocal of the effluent concentration that causes 50 percent of the organisms to die).

3. Results and discussion

3.1. Physicochemical Properties of the Crude Oil Samples

The physicochemical properties of the crude oil samples are summarily represented in Table 1.

The Ashphaltene content of the crude oil sample from the NNPC station where in conformity with the standards set by the department of petroleum resources (DPR). Ashphaltene has been implicated as a major problem in petroleum (16), as it forms dense flocculation's and deposits in the reservoir, leading to transportation and operational problems (17).

Sulphur content in Crude and petroleum products leads to production of Sulphur dioxide during catalytic cracking and may in turn lead to acid deposition (18). The petroleum and products from the NNPC station did not have trace of Sulphur in them, however the Crude oil sample from the artisanal refinery in Bolo and Ekpemu had Sulphur content <0.5%, hence they are termed sweet crude. Crude oil with Sulphur content greater that 0.5%, is referred to as sour Crude. Sulphur has been report to be a relative heavy element and its presence will therefore add to the specific gravity of the crude oil sample. Hence products with low Sulphur content are reported to have low specific gravity, while those with high Sulphur content will have higher specific gravity. (19). Sweet Crude oil samples have been reported to have

less corrosion and pollution abilities resulting in low cost of production and have been notable for producing well refined products. Most Crude oil sample in Nigeria falls into the light Crude category, and this makes Crude oil from Nigeria more preferable in the international oil markets. (3).

Table 1 Physicochemical properties of Crude oil from the sample stations

Parameter	NNPC	Bolo	Twon-Brass	Ekpemu	Standard
Ashphatenes	0.041± 0.40	1.35± 0.10	5.25± 0.30	11.00± 0.60	0.0032
Sulphur Content (wt %)	<0.01	0.03± 0.1	0.031± 0.4	0.09± 0.2	0
Water Content (vol %)	0.37± 0.8	5.0± 0.3	4.5± 0.4	2.9± 0.2	0
Salt Content (ppm)	2.18± 0.1	2.56± 0.5	2.9± 0.4	3.0± 0.1	0
Iron Content (mg/l)	4.68± 0.5	4.69± 0.1	4.90± 0.4	6.80± 0.2	
Potassium Content (mg/L)	0.07± 0.4	0.19± 0.1	0.195± 0.7	0.381± 0.4	
Sodium Content (mg/L)	0.79± 0.1	3.60± 0.3	3.95± 0.9	3.98± 0.2	

The crude oil from the artisanal refineries had high percentage of water contents in them. Water content in crude oil have been reported to be associated with corrosion problems, and thus are used as a major parameter to check the quality of crude oil (19). Corrosion of storage tanks for crude oil has been traced to the presence of water in the products (3).

Salt content of the crude oil samples ranged from 2.18ppm to 3.0ppm. Salt content is an important index for refining operations as high value of salt increases the potential of corrosion. The crude oil from Ekpemu recorded the highest value of salt content, indicating that the sample has the highest potential for corrosion (19).

Iron has been implicated in playing major activity in catalytic cracking during Crude oil refining. The Iron contents of the Crude oil samples however ranged from 4.68mg/L to 6.80mg/L. The Iron content of the Crude oil sample was relatively low, compared to reports of (20). The Iron content of the petroleum products were however less than 0.001mg/L.

Potassium content in the Crude oil sample ranged from 0.07mg/L to 0.38mg/L. Also the Sodium content of the Crude oil samples ranged from 0.79mg/L.

Table 2 Total Petroleum Hydrocarbon Characterization of Crude oil from the sample stations.

Group name	Compound name	NNPC	Bolo	Twon-Brass	Ekpemu
C_8	n-Octane	100.9268	98.7321	127.8910	903.6783
C_9	n-Nonane	26.9562	27.8819	30.7822	890.2791
C_{10}	n-Decane	61.2858	56.3892	59.8510	393.3588
C_{11}	n-Undecane	2542.5045	1992.2739	2927.5045	1735.9861
C_{12}	n-Dodecane	1172.9697	2781.9092	1677.1012	1932.3589
C_{13}	n-Tridecane	149.2218	300.1553	209.6780	867.9878
C_{14}	n- Tetradecane	333.4025	301.0872	396.9870	586.1267
C_{15}	n-Pentadecane	1968.3582	2191.3538	2871.2661	2691.7727
C_{16}	n-Hexadecane	1560.8323	1855.7622	2019.1777	2781.7382
PR	Pristene	349.6568	291.0982	50.1782	573.9920
C_{17}	n-Heptadecane	154.5292	250.2578	140.5672	793.9211
C_{18}	n-Octadecane	329.4529	177.1983	356.0911	583.9200
PH	Phytene	318.1570	353.1966	410.44478	593.8299
C_{19}	n-Nonadecane	149.3394	200.7622	281.2677	930.9322

C_{20}	n-Icosane	390.2588	300.9765	485.3150	739.3621
C_{21}	n-Heneicosane	400.2923	392.1986	488.9021	379.0288
C_{22}	n-Doicosane	336.3181	425.0923	752.0166	1190.8932
C_{23}	n-Tricosane	283.1975	200.6398	398.0255	429.7382
C_{24}	n-Tetracosane	2201.0442	2735.2756	3319.2588	2981.5930
C_{25}	n-Pentacosane	2157.4370	3290.3500	2981.1662	1638.6930
C_{26}	n-Hexacosane	129.1497	273.9827	388.8100	883.9381
C_{27}	n-Heptacosane	87.1582	288.0377	177.2671	589.3292
C_{28}	n-Octacosane	75.8413	52.8762	66.3751	683.0133
C_{29}	n-Nonacosane	54.5035	290.1673	922.6614	1638.0299
C_{30}	n-Triacontane	32.4239	95.0268	199.3271	722.0199
C_{31}	n-Hentriacontane	24.0199	72.5818	18.2033	605.9383
C_{32}	n-Dotriacontane	14.2717	18.3570	133.0178	67.5289
C_{33}	n-Tritriacontane	10.8712	18.0922	129.2881	33.8922
C_{34}	n-Tetratriacontane	6.4304	3.3021	10.8210	0.8833
C_{35}	n- Pentatriacontane	6.5681	3.6701	8.5025	0.3289
C_{36}	n- Hexatriacontane	1.3439	0.3992	1.7109	0.1982
C_{37}	n- Heptatriacotane	0.2588	1.8663	0.9758	0.0659
C_{38}	n- Octatriacotane	0.3115	1.9833	0.5109	0.1723
C_{39}	n- Nonatriacotane	0.2332	0.2620	1.2290	0.3772
C_{40}	n- Tetracontane	17.9937	17.3903	55.7911	10.6388
	Total	15447.5195	19360.586	22097.963	28855.545

3.2. Total Petroleum Hydrocarbon Characteristics of Crude Oil from the Sample Stations

Table 2 represents the total petroleum hydrocarbon of crude oil from an NNPC station and selected artisanal refineries. The result shows that the entire crude oil sample contained carbon atoms from $C_{8\ to}$ C_{40} including Pristene and Phytene.

The TPH of the crude oil samples ranged in the order of NNPC <Bolo <Twon-Brass <Ekpemu. Crude oil from NNPC had TPH of 15447. 5195ppm, crude oil from artisanal refinery in Bolo had TPH of 19360.586ppm, crude oil from Twon-Brass artisanal refinery had TPH of 22097.963ppm, and crude oil from Ekpemu artisanal refinery had TPH of 28855.545 ppm.

3.3. Acute Toxicity Response of the Test Organisms to Crude Oil from the Sample Stations

The impact of Crude oil from NNPC station and selected artisanal refineries in the Niger Delta Region of Nigeria on aquatic fauna were carried out by methods stipulated in (13). The toxicity test was carried out using the categories of organisms which include: Fish (*Tilapia guineensis*), Crustacean (*Paleamonetes africanus*), and Moluscs (*Tympanotonus fucatus*), (13). Toxicity however have been attributed to a complex of mixtures in the sample, and the interaction of this complex in a milieu accounts for the total toxicity on organisms (15).

3.4. Tilapia guineensis

Tilapia guineensis an aquatic fish belonging to the phylum Vertebrata when exposed to the toxicants (Crude oil) increased mortality as the concentrations of the toxicant increased, with increasing exposure time. The highest mortality was recorded, for the highest concentration at the 96hrs of the exposure time. This result corroborates with the findings of (12, 15). The toxicity of the petroleum and its products however can be attributed to the various chemical components of the samples that are well known to be toxic to organisms.

The analysis of the mortality of *Tilapia guineensis* was calculated using Probit analysis to determine the 96hrs LC_{50}, NOEC, LOEC, and TU_a which is the referred to as the acute toxicity response of the test organism to the toxicant. Crude oil sample from the artisanal refineries and NNPC station recorded LC_{50} ranging from 0.02ppt to 4.63ppt, NOEC ranged from 0.0004 to 0.43ppt, LOEC (0.0025 to 0.9780ppt), and TU_a (21.60 to 5000ppt). The order of toxicity of the Crude oil samples on *Tilapia guineensis* was in the order of Ekpemu > Twon-Brass > Bolo > NNPC.

Table 3 Acute Toxicity Response of *Tilapia guineensis* to Crude oil at 96 hrs

Parameter	NNPC	Bolo	Twon-Brass	Ekpemu
LC_{50} (ppt)	4.63	0.11	0.06	0.02
NOEC (ppt)	0.43	0.0004	0.0013	0.0008
LOEC (ppt)	0.9780	0.0125	0.0049	0.0025
TU_a (ppt)	21.60	909.09	1666.66	5000

3.5. Pateamonetes africanus

Paleamonetes africanus, an aquatic crustacean belonging to the phylum Arthropoda when exposed to Crude oil from NNPC station and selected artisanal refineries in the Niger Delta region in Nigeria was observed to have an increase in the percentage mortality of the organism, with increasing concentration of the toxicant and at longer exposure time. The same trend have been reported by (15, 21, 22). The concentration of the Crude oil able to kill fifty percent (50%) of the *Paleamonetes africanus* within 96 hrs (96hrs LC_{50}), NOEC, LOEC, and TU_a was calculated using methods stipulated in (13). The LC_{50} of crude oil samples from NNPC and the artisanal refineries on *Paleamonetes africanus* ranged from 8.40ppt to 68.13ppt, NOEC (0.0011 to 7.602 ppt), LOEC (0.557 to 16.16ppt), and TU_a (1.47 to 11.90ppt) in the order Ekpemu > Twon-Brass > Bolo > NNPC.

Table 4 Acute Toxicity Response of *Paleamonetes africanus* to Crude oil at 96 hrs

Parameter	NNPC	Bolo	Twon-Brass	Ekpemu
LC_{50} (ppt)	68.13	15.75	8.66	8.40
NOEC (ppt)	7.602	0.9742	0.729	0.0011
LOEC (ppt)	16.16	2.536	1.701	0.557
TU_a (ppt)	1.47	6.35	11.55	11.90

3.6. Tympanotonus fuscatus

Tympanotonus fuscatus is an aquatic mud creeper belonging to the phylum Mollusca. The mortality of *Tympanotonus fuscatus* was greatly increased by the increase in concentration of the toxicant, with increasing exposure time. This same trend was reported by (23, 24). The index for calculation of mortality used was the 96hrs $LC_{50,}$ which is the concentration of the toxicant, able to kill 50% of the test organism within 96hrs exposure, NOEC, LOEC, and TU_a. The LC_{50} of Crude oil on *Tympanotonus fuscatus* ranged from 55.81ppt to 668.03ppt, NOEC (3.369 to 668.03ppt), LOEC (10.10 to 135.07ppt), and TU_a (0.15 to 1.79ppt), in the order of Twon-Brass > Ekpemu > Bolo > NNPC.

Table 5 Acute Toxicity Response of *Tympanotonus fuscatus* to Crude oil at 96 hrs

Parameter	NNPC	Bolo	Twon-Brass	Ekpemu
LC_{50} (ppt)	668.03	84.49	55.81	79.04
NOEC (ppt)	58.47	8.9376	6.4515	3.4369
LOEC (ppt)	135.07	19.35	13.34	10.10
TU_a (ppt)	0.15	1.18	1.79	1.27

4. Conclusion

The physicochemical analysis of the Crude oil from NNPC station and the artisanal refineries showed that the products from NNPC where in line with world acceptable standard for petroleum products as recommended by the Department of Petroleum Resources, while the Crude oil from the artisanal refineries had a lot of impurities in them. The entire test organisms were susceptible to the Crude oil samples from the various stations, although some organisms were more susceptible than others, and some products were more toxic than others. However, the crude oil from the NNPC station

was generally less toxic than the products from the artisanal refineries. The toxicity of Crude oil showed the following trend; Ekpemu > Twon-Brass > Bolo > NNPC. The sensitivity of the crude oil sources showed the following trend; *Tilapia guineensis > Paleamonetes africanus > Tympanotonus fuscatus.*

Compliance with ethical standards

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Disclosure of conflict of interest

The authors have declared that no conflict of interest exists.

References

[1] Obenade M, Amangabara GT. Perspective: The Environmental Implications of Oil Theft and Artisanal Refining in the Niger Delta Region. Asian Review of Environmental and Earth Sciences. 2014; 1(2):25-29.

[2] Collins E. Oil Exploration in the Niger Delta: Its' Gains and Loss. International Journal of Geography and Environmental Management. 2018; 4(3):24-31.

[3] Sunday I, Bebeteidoh OL. Experimental Investigation of API Gravity of Gasoline in Dispensing Stations and its effects on Gasoline Engines in Bayelsa State, Nigeria. *International Journal of Applied Science and Technology*. 2015; 5(4): 74-78.

[4] Watts M. Blood oil; the Anatomy of a Petro Insurgence in the Niger Delta. Niger Delta Economics of violence working Paper. No. 22.2008.

[5] Adati AK. Oil exploration and spillage in the Niger Delta of Nigeria. Civil and Environmental Research. 2012; 2(3): 28-33.

[6] AnukamLC. Case Study iv – Nigeria. In Water pollution control: A guide to the use of water quality management principle, Helmer, R. and Hespanhol (Eds). Taylor and Francis, Washington DC: WHO, UNEP. 2000.

[7] Owugah L. Oil Trans-nationals, State and Development in the Oil Producing Communities of the Niger Delta. Third World Network Africa. 2006.

[8] Egwu S. Oil Spill Control and Management. Petroleum Technology Development Journal Quarterly. 2012; 19(3): 457-478.

[9] Gbadegesin A. The Impact of Oil Exploration and Production Activities on the Environment, a Workshop Organized by Federick Elbert Foundation, Port Harcourt. 2000.

[10] Duru E. Oil Multinationals and the Niger Delta Crisis: Issues and Perspectives. Abuja: Thumbs-Prints International Company. 2010.

[11] United States Environmental Protection Agency. *Whole Effluent Toxicity Clean Water Act Analytical Methods*. US Environmental Protection Agency, Office of Environmental Information, Washinton DC. 2008.

[12] Odokuma LO Akponah E. Response of *Nitrosomonas, Nitrobacter* and *Escherichia coli* to drilling fluids.*Journal of Cell and Animal Biology. 2008;* 2(2): 043 – 054.

[13] DPR.*Environmental Guidelines and Standards for the Petroleum Industry in Nigeria* (EGASPIN), Revised Edition 2018.

[14] APHA. Standard Methods for the examination of Water and Wastewater. American Public Health Association. 19th Ed. 1988.

[15] Luke ME, Odokuma LO. Acute Toxicity of House Boat Effluents on *Paleamonetes africanus* and *Tilapia guineensis.IOSR Journal of Environmental Science, Toxicity and Food Technology. 2017;*11: 69-78.

[16] Nwadinigwe C. Studies on Precipitation performance of n-heptane and n-pentane in-heptane on C_7 and C_5/C_7asphaltenes and maltenes from 35^oC atmospheric residuum of three Nigeria Light Crudes. *Journal of Petroleum Exploration and Production Technology.* 2015; 5: 403.

[17] Struchkou IA. Laboratory Investigation of Astphatene Induced Formation Damage. *Journal of Petroleum Exploration and Production Technology.* 2019; 9: 1443.

[18] Speight JG, Arjoon KK. *Bioremediation of Petroleum and Petroleum Products*, Scrivener publishing LLC. 2012.

[19] Udeme JD, Etim IU. Physicochemical Studies of Nigeria Crude Oil Blends. *Petroleum and Coal.*2012; 54(3): 243-251.

[20] Mohammad PO, Ikeh BG, Usman BG, Shehu D, Sulawa K, Mikailu DA. Determination of Vanadium, Nickel, Copper and Iron as Complexes of Bis-Acetylpivalyl Methane (Ethylene Diamine) in Nigerian Onshore and Offshore Crude Oils using HPLC. *Journal of Natural Science Research*. 2013; 3(8): 104-111.

[21] Nrior RR, Odokuma LO. Comparative Toxicity of Drilling Fluids to Marine Water Shrimp (Mysidoposis bahia) and Brackish Water Shrimp (Palaemonetes africanus). IOSR Journal of Environmental Science, Toxicity and Food Technology. 2015; 9:73-79.

[22] Amaeze NH, Adetoro FA,Adegboro OA. Toxicity evaluation of effluent from the de-oiling works of a decommissioned Nigerian crude oil pipeline using *Palaemonetes africanus. African Journal of Aquatic Science. 2015;* 40(1): 57–61.

[23] Edori OS, George DMC,Edori ES. Diesel exposure of *Tympanotonus fuscatus* and its effects on enzyme activity. *Global Journal of Environmental Sciences*. 2013; 12: 21-28.