

IMPACT OF CRUDE OIL SPILLAGE ON WATER AND AFRICAN CATFISH (*CLARIAS GARIEPINUS*) IN UZERE, ISOKO SOUTH LGA OF DELTA STATE NIGERIA

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ABSTRACT

Study on the impact of crude oil spillage on water and African catfish (*Clarias gariepinus*), in Uzere (test site) and Ekrejeta (control site) communities of Delta State, Nigeria was carried out. Five water samples and 5 fish samples were collected from different locations within the test sites. Physicochemical parameters, heavy metal content, polycyclic aromatic hydrocarbons (PAHs) and total hydrocarbon contents (THC) of water and heavy metal content and PAHs in fish, were determined using standard analytical methods. Parameters determined include chloride, pH, conductivity, dissolved oxygen (DO), total suspended solids (TSS), turbidity, biochemical oxygen demand (BOD), nitrate, sulphate, PAHs and THC as well as the concentration of some heavy metals (Cd, Cr, Ni, Pb, Zn, Fe). Concentrations of heavy metals were determined using Atomic absorption spectrophotometry. Mean pH obtained were 6.00 ± 0.03 and 7.77 ± 0.03 , Conductivity $73.00 \pm 1.16 \mu\text{s}/\text{cm}$ and $57.00 \pm 1.16 \mu\text{s}/\text{cm}$, DO $2.62 \pm 0.01 \text{mg}/\text{l}$ and $6.20 \pm 0.01 \text{mg}/\text{l}$, TSS $31.00 \pm 0.58 \text{mg}/\text{l}$ and $6.40 \pm 0.01 \text{mg}/\text{l}$, Turbidity $48.63 \pm 0.52 \text{NTU}$ and $3.42 \pm 0.08 \text{NTU}$, BOD $4.12 \pm 0.07 \text{mg}/\text{l}$ and $0.97 \pm 0.03 \text{mg}/\text{l}$, Chloride $3.13 \pm 0.09 \text{mg}/\text{l}$ and $1.87 \pm 0.09 \text{mg}/\text{l}$, Nitrate $7.53 \pm 0.15 \text{mg}/\text{l}$ and $1.00 \pm 0.00 \text{mg}/\text{l}$, Sulphate $8.37 \pm 0.09 \text{mg}/\text{l}$ and $1.00 \pm 0.00 \text{mg}/\text{l}$, THC $75.00 \pm 62.50 \text{mg}/\text{l}$ and $0.01 \pm 0.00 \text{mg}/\text{l}$ for water samples collected from Uzere and Ekrejeta respectively. Similarly, both water samples contained a detectable amount of metal elements however, the levels of iron $2.86 \pm 0.10 \text{mg}/\text{l}$ and cadmium $0.10 \pm 0.00 \text{mg}/\text{l}$ were higher in oil polluted water when compared to that from the controlled site. The concentration of PAHs for test and control samples for water are $41.60 \pm 0.43 \text{mg}/\text{l}$ and $0.00 \pm 0.00 \text{mg}/\text{l}$ respectively. Concentration of heavy metals were iron $52.56 \pm 0.02 \text{mg}/\text{kg}$ and $39.45 \pm 0.03 \text{mg}/\text{kg}$, zinc $23.63 \pm 0.01 \text{mg}/\text{kg}$ and $15.28 \pm 0.01 \text{mg}/\text{kg}$ for fishes collected from test and control site respectively. Findings suggest that the water from the study site is heavily impacted crude oil spillage.

Keywords: Crude oil spillage, *Clarias gariepinus*, physicochemical parameters, water, control site.

INTRODUCTION

Background of the Study

In recent years, tremendous concerns have been focussed on environmental degradation resulting from man's activities which adversely affects the ecosystem. One of such activity that has drawn so many concerns and interest is the spate of oil spillage resulting from over 55 years of oil exploration and exploitation in the Niger Delta region of Nigeria. Sequel to oil exploration in the region, uncountable oil spills in the Niger Delta region has caused serious damages to the environment due to the high retention time of oil in the soil (Chindah and Braide, 2000). This oil spill in soil prevents proper soil aeration, affects soil temperature, structure, nutrient availability, pH with attendant consequence of crop destruction.

Nigeria is one of the world's largest producers of crude oil with a proven reserve of 35 billion barrels ($5.6 \times 10^9 \text{ m}^3$) with most of her exports going to the US; US accounts for 40% of Nigeria's total oil exports making 10% of her overall oil imports emanating from Nigeria. These statistics placed Nigeria as the 5th largest source of US imported oil (Badejo and Nwilo, 2010). Crude oil was discovered in large quantities in the Niger Delta in 1956. The discovery of oil has positively transformed Nigeria's economy and has generated around \$340 billion in the last 40 years. The large deposit of crude oil in Nigeria located in the Niger Delta area has not only impacted positively on Nigeria's economy but on the other hand has resulted to uncountable spills that have obnoxious impact on farmlands, fishing rivers, lakes, creeks and ponds which are the main source of livelihood of people dwelling in the oil producing communities. Oil spills between 1970 and 2000 in the Niger Delta have amounted to over 7000 spills (John, 2010). Oil spillage is a common event in Nigeria (Baird, 2010). Fifty percent of oil spills occur due to pipeline and tanker accidents, other causes of oil spillage include sabotage, corrosion of pipelines and inadequate or non-functional production equipment.

Sabotage and oil theft have become an issue of concern in Niger Delta which also has contributed to further environmental degradation (Anderson, 2005). Oil spillage has a major effect on the ecosystem. According to a statement credited to Baird, (2010); many dwellers have lost basic human rights such as good health, access to food, clean water and ability to work. Other consequences of oil spills include the depletion of the fish population in an aquatic environment which have a chain effect on farmers which rely on fishes for protein sources and their effects also cascade down to their family members.

The Niger Delta which belongs to the South-South geo-political zone is officially defined by the Nigerian government to extend over 70,000 km² and makes up 7.5% of Nigeria land mass. The Niger Delta region is located on the Atlantic coast of Southern Nigeria where the River Niger divides into several tributaries. The region cuts across nine states of Nigeria (Abia, Akwa-ibom, Bayelsa, Cross-River, Delta, Edo, Imo, Ondo and Rivers States) and lies between latitude 4° 49' 60" north of the equator and longitude 6° east of the Greenwich meridian.

Uzere is located in Isoko South Local Government Area of Delta State of Nigeria. It is one of the largest oil producing communities in Nigeria. The exploration of oil started in Uzere in 1957. There are two oil fields in Uzere (Uzere west and Uzere east) with a total of 43 oil wells producing about 53,000 barrels per day. The scope of this research includes investigation of the physicochemical properties of water and fishes in Uzere (test site) and Ekrejeta (control site), bioaccumulation of certain environmental pollutants and the levels of hydrocarbon present in both study sites. This research is aimed at examining the environmental impact of crude oil spillage on water and some selected fishes (*Clarias gariepinus*) in Uzere, Isoko South LGA of Delta State.

MATERIALS AND METHODS

Collection of Samples

Five Fresh samples of water and five *Clarias gariepinus* (Figure 1) were collected from different locations of oil-polluted site in Uzere Community (Figure 2) and Ekrejeta Community of Isoko South and Ethiope East of Delta State, Nigeria respectively. Water samples were collected using glass amber bottles (for BOD) and 25cl plastic sampling bottles, kept at a temperature between 0°C and 4°C and taken straight to the laboratory. Five

pieces of *Clarias gariepinus* sample were collected from each site, carefully wrapped in foil plates and kept in an ice chest for transportation to the laboratory.



Figure 1 Cat fishes (*Clarias gariepinus*)



Figure 2 Crude oil polluted waters in Uzere (June 2015)

Determination of Heavy metals Sample Preparation

Fresh fish specimens were washed with water, drained and weighed in the electronic balance. The weighing was done to ascertain the original weight of the fish. The weighed fish samples were then spread on the racks of the hot air drying oven set at 70°C for 18hours. The fish was then removed from the oven and ground to powder with mortar and pestle. Two grammes of the fish samples were weighed into porcelain crucibles and placed in the muffle furnace which was then set at 550°C for ashing. After 18hours, the muffle furnace was switched off and allowed to cool to room temperature. The ash was then retrieved from the furnace. Concentrated nitric acid (HNO₃) 3ml was used to make a solution of the ash with the aid of a glass rod in a beaker. The solution was further diluted with 15ml of distilled water. The ash mixture was filtered into the 100ml volumetric flask and made up to the mark with extra distilled water. The ashed and filtered samples were then transferred into 120ml plastic bottles and sent for atomic absorption spectroscopic analysis

Atomic Absorption Spectroscopy (AAS) Analysis

For each of the metals, atomic absorption spectroscopy was calibrated using metal standards (Cr 357.90nm, Cd 228.80nm, Zn 213.9nm, Pb 283.30nm, Mn 279.50nm). Samples were determined with the aid of Atomic Absorption Spectrophotometer A Analyzer 200 (USA) according to AOAC (2000). The extracts were aspirated directly into the absorption spectroscopy machine. An acetylene air mixture was used as the flame. The working standard for each of the metals was aspirated into the flame in the order of 0.0 ppm, 0.8 ppm and 1.6 ppm. The samples were then aspirated into the flame and the values were obtained.

Determination of PAHs

The method of extraction: The extraction method used was the Texas Natural Resource Conversion Commission, Texas (TNRCC TX) method. The extraction solvent used was dichloromethane. Fresh samples were dried and ground to a powder using mortar and pestle and then kept in an airtight container ready for extraction.

Extraction Procedure

Two grammes of the sample was weighed into a clean extraction container. Ten millilitres of extraction solvent (dichloromethane) was added to the samples and mixed thoroughly and then allowed to settle. The mixture was carefully filtered into a clean solvent rinsed extraction bottle using filter paper fitted into a Buchner funnel. The extract was concentrated to 2ml and then transferred for separation.

Separation

A 1 cm of moderately packed glass wool was placed at the bottom of a 10mm ID x 250mm chromatographic column. A slurry of 2g activated silica in 10ml methylene chloride was prepared and placed into the chromatographic column. To the top of the column was added 0.5cm of sodium sulphate. The column was rinsed with additional 10ml of methylene chloride. The column was pre-eluted with 20ml of dichloromethane. This was allowed to flow through the column for about 2 minutes until the liquid in the column was just above the sulphate layer. Immediately, 1ml of the extracted sample was transferred into the column. The extraction bottle was rinsed with 1ml of dichloromethane and added to the column as well. The stop cock of the column was opened and the eluent was collected with a 10ml graduated cylinder. Just prior to exposure of the sodium sulphate layer to the air, dichloromethane was added to the column in 1-2ml increments. Accurately measured volumes of 8-10ml of the eluent were collected and were labelled aliphatics.

Gas Chromatographic Analysis

The concentrated aliphatic fractions were transferred into labelled vials with rubber crimp caps for gas chromatographic analysis. One microlitre of the concentrated sample was injected by means of a hypodermic syringe through a rubber septum into the column. Separation occurred as the vapour constituent partitioned between the gas and liquid phases. The sample was automatically detected as it emerged from the column at a constant flow rate by the FID whose response is dependent upon the composition of the vapour.

Physicochemical Analysis

Standard analytical procedures were used in the determination of selected physical, chemical and biological water quality parameters of the samples. Selected physicochemical analysis such as pH, temperature, turbidity, conductivity, total suspended solids (TSS), Nitrites, Nitrates, total hardness, Magnesium hardness, Chlorides, dissolved CO₂, etc. was carried out.

The pH of the samples was measured using probe and electronic pH meter (Jaiswal, 2003). Turbidity and total suspended solids were measured using turbidometer. Conductivity was measured with conductivity meter while nitrate and nitrite methods were used to measure nitrates and nitrites respectively (Monica, 2006). Dissolved CO₂ and total hardness were measured using titration method whereas chloride was measured using DPD colorimeter

Determination of Total Hydrocarbon Content (THC)

Into a 500ml separating funnel, 250ml of water sample was added. The water was acidified with H₂SO₄ by the addition of 5ml of the acid solution, then 25ml n-hexane was added into the funnel and shaken vigorously for 3 minutes. The organic layer was allowed to separate. The aqueous layer was withdrawn and the organic layer was transferred into a tarred distillation flask of 250ml capacity. The process was repeated for about 3 times with the aqueous layer and the organic layer added to the 250ml distillation flask. A condenser was fixed to the flask and was refluxed on a heating mantle. When about 10ml of the organic fraction remained, the condenser was disconnected and the solvent boiled off. The flask was then dried on a steam bath.

Statistical Analysis

Student's t-test was used for paired comparison. The results are expressed as a mean \pm standard error of the mean (S.E.M). The confidence level was set at 95% ($p < 0.05$).

Results

Physicochemical parameters of water

Results obtained for physicochemical analysis of water samples collected from Uzere and Ekrejeta showed a significant difference $p < 0.05$ between the test site (Uzere) and the control site (Ekrejeta). The mean pH were 6.00 ± 0.03 and 7.77 ± 0.03 , Conductivity $73.00 \pm 1.16 \mu\text{S/cm}$ and $57.00 \pm 1.16 \mu\text{S/cm}$, Dissolved oxygen (DO) $2.62 \pm 0.01 \text{mg/l}$ and $6.20 \pm 0.01 \text{mg/l}$, Total suspended solids (TSS) $31.00 \pm 0.58 \text{mg/l}$ and $6.40 \pm 0.01 \text{mg/l}$, Turbidity $48.63 \pm 0.52 \text{NTU}$ and $3.42 \pm 0.08 \text{NTU}$, Biological oxygen demand (BOD) $4.12 \pm 0.07 \text{mg/l}$ and $0.97 \pm 0.03 \text{mg/l}$, Chloride $3.13 \pm 0.09 \text{mg/l}$ and $1.87 \pm 0.09 \text{mg/l}$, Nitrate $7.53 \pm 0.15 \text{mg/l}$ and $1.00 \pm 0.00 \text{mg/l}$, Sulphate $8.37 \pm 0.09 \text{mg/l}$ and $1.00 \pm 0.00 \text{mg/l}$, Total hydrocarbon content (THC) were $75.00 \pm 62.50 \text{mg/l}$ and $0.01 \pm 0.00 \text{mg/l}$ for water samples collected from Uzere and Ekrejeta respectively. The study clearly elucidates that statistical analysis of physicochemical parameters of a water sample from Ekrejeta has results that were significantly different $p < 0.05$ from that of Uzere. The assessment of the quality of water from the test site (Uzere) was done by comparing all results of physicochemical analysis with FEPA 1991 permissible limits. The results of physicochemical analysis of water sample from test site were below FEPA standard.

Table 1 Physicochemical, heavy metals and PAHs analysis of water samples from test site (Uzere) and control site (Ekrejeta)

S/N	Parameters	Oil Polluted Water	Control Water	FEPA Limi Values
1.	pH	6.00 ± 0.03^a	7.77 ± 0.03^a	6.5-8.5
2.	Conductivity ($\mu\text{S/cm}$)	73.00 ± 1.16^a	57.00 ± 1.16^a	250
3.	Dissolved Oxygen (mg/l)	2.62 ± 0.01^a	6.20 ± 0.01^a	5.0
4.	Total Suspended Solids (mg/l)	31.00 ± 0.58^a	6.40 ± 0.01^a	30

5.	Turbidity (NTU)	48.63 ± 0.52 ^a	3.42 ± 0.08 ^a	30
6.	BOD (mg/l)	4.12 ± 0.07 ^a	0.97 ± 0.03 ^a	2.0
7.	Chloride (mg/l)	3.13 ± 0.09 ^a	1.87 ± 0.09 ^a	60
8.	Nitrate (mg/l)	7.53 ± 0.15 ^a	1.00 ± 0.00 ^a	20
9.	Sulphate (mg/l)	8.37 ± 0.09 ^a	1.00 ± 0.00 ^a	50
10.	THC (mg/l)	75.00 ± 62.50 ^a	0.01 ± 0.00 ^a	10.0
11.	PAH (mg/l)	41.60 ± 0.43 ^a	0.00 ± 0.00 ^a	0.00
12.	Total Iron (mg/l)	2.86 ± 0.098 ^a	1.21 ± 0.01 ^a	1.00
13.	Calcium (mg/l)	0.71 ± 0.01 ^a	0.10 ± 0.00 ^b	0.01
14.	Cadmium(mg/l)	0.10 ± 0.00 ^a	0.00 ± 0.00 ^b	0.05
15.	Chromium (mg/l)	0.00 ± 0.00 ^a	0.00 ± 0.00 ^b	0.03
16.	Magnesium (mg/l)	0.56 ± 0.00 ^a	0.08 ± 0.00 ^a	0.01
17.	Nickel (mg/l)	0.00 ± 0.00 ^a	0.00 ± 0.00 ^b	NS
18.	Zinc (mg/l)	0.01 ± 0.00 ^a	0.00 ± 0.00 ^a	1.00
19.	Lead (mg/l)	0.00 ± 0.00 ^a	0.00 ± 0.00 ^b	0.05

Results presented are Means ± SEM for n = 3. Values in the same row with the same superscript (a) are significantly different at p<0.05 level.

Heavy metal and PAH concentrations in water

The average heavy metal concentration in water samples collected from Uzere and Ekrejeta communities are shown in Table 1. A total of six heavy metals were analysed for namely iron (Fe), cadmium (Cd), chromium (Cr), nickel (Ni), zinc (Zn) and lead (Pb). Both water samples from Uzere and Ekrejeta contained a detectable amount of metal elements analysed in varying concentrations, however the levels of Fe 2.86± 0.10mg/l and cadmium 0.10 ± 0.00mg/l were higher in oil polluted water when compared to water collected from the controlled site. The maximum permissible limits defined by FEPA (1991) were used to assess the potential health risk of heavy metals in the polluted water. The total mean concentration of PAHs for oil-impacted samples and control samples for water are 41.60±0.43mg/l and 0.00±0.00mg/l respectively. The concentration of PAHs in oil polluted water was higher than the control and surpassed the maximum permissible limit given by FEPA (1991) which suggests contamination by organic pollutants/petroleum products in the test site.

Physicochemical parameters of water

Water pollution affects the productivity and biodiversity of the aquatic ecosystem (Worldwide fund, 2006). Pollution of a river/lake affects its physical and chemical qualities and then cascade down destroying the community, disrupting the complex food web and impairing the use of the river/lake (Mohan *et al.*, 2009). A physicochemical parameter study is very pertinent as it gives an exact picture about the quality of the water as values obtained are compared to standard values (Patil *et al.*, 2012). The quality of water in this study was determined by making a comparison of its physicochemical parameters analysed with that of FEPA permissible limit as stated by FEPA (1991). Comparison between the physicochemical parameters analysed in water samples collected from Uzere (test site) and Ekrejeta (control site) showed that the mean concentration of pH 6.00 ± 0.03 for the oil polluted water is lower

than the control water 7.77 ± 0.03 with that of the oil-impacted water falling below the range of 6.5-8.5 recommended by FEPA (1991) for drinking water. This implies that the oil polluted water is slightly acidic and this affects the solubility of heavy metals and other chemicals (USGS, 2013). This also suggests the presence of pollutants which include acidic gases which in solution decrease the pH of the surface water and result in decreased photosynthetic rate and assimilation of carbon dioxide and bicarbonates (Patil *et al.*, 2012).

The concentration of Dissolved oxygen was high in the control water with a value of 6.20 ± 0.01 mg/l and lower in the oil-polluted water with a value of 2.62 ± 0.01 mg/l. The DO of the oil polluted water trailed below FEPA (1991) permissible limit of 5mg/l which suggests contamination of the water by the huge amount of organic load (petroleum products) which requires a high level of oxygen for chemical oxidation and breakdown. The level of DO is influenced by temperature, pH and BOD. The solubility of oxygen decreases as temperature increases (Wetzel, 2001).

Biological oxygen demand (BOD) is the amount of dissolved oxygen required by aerobic microorganisms to break down or oxidise organic materials present in water. A high BOD implies a low DO because the DO is depleted by the microorganisms as they require it to break down the organic pollutant. The mean BOD obtained in this study were 4.12 ± 0.07 mg/l and 0.97 ± 0.03 mg/l for oil-impacted water sample and control water sample respectively. There was a significant increase ($p < 0.05$) for BOD in water samples collected from oil impacted site compared to BOD in control site. The BOD for this study far surpassed the FEPA permissible limit of 2mg/l which suggests the presence of organic pollutants in the test site.

Conductivity is a measure of the ability of water to pass electric current and hence is directly proportional to the levels of cations and anions present in it (Ahmad *et al.*, 2010). The electrical conductivity of water in the oil-polluted area was higher 73.00 ± 1.16 µs/cm than the control area, 57.00 ± 1.16 µs/cm, however this is lower than FEPA (1991) permissible limit of 250µs/cm. It was observed that the oil polluted water sample with high levels of electrical conductivity also had the highest concentrations of chloride, nitrate, sulphate, calcium and magnesium ions. Dara (1993) reported that natural water contains a reasonable amount of dissolved salts and the concentration of these salts varies from one water body to another. Electrical conductivity has also been correlated to the concentration of total dissolved solids (TDS) or salts which typically include cations such as sodium, calcium, magnesium, potassium and anions such as chloride, sulphate and bicarbonates.

Total suspended solids (TSS) are solid materials which include organic and inorganic materials that are suspended in water. This includes silts, algae, planktons and bacteria (Murphy, 2007). TSS is a significant factor in observing water quality. High concentrations of TSS can lower water quality by making it less clear and absorbing light; the water then becomes warmer which reduces the ability of the water to hold oxygen necessary for aquatic life. Also because TSS absorbs light, the level of light penetration will dwindle down which has been shown to reduce the rate of photosynthesis in aquatic plants with an attendant decrease in dissolved oxygen production (Lawson, 2011). The TSS observed in this study shows that TSS for oil-impacted water of 31.00mg/l was higher than that of the control 6.39mg/l and slightly above the permissible limit of 30mg/l as stated in FEPA (1991). This confirms the presence of pollution in Uzere waters.

Turbidity is the optical determination of water clarity (EPA, 2012). The turbidity observed in this study shows that the mean turbidity for crude oil impacted water 48.6 NTU was higher

than that of the control 3.423 NTU while when compared to the permissible limit of 1NTU stipulated by FEPA, it surpassed it. This result confirms the presence of pollutants in the test site. Turbidity can also inhibit photosynthesis by blocking sunlight. Halted photosynthesis means a decrease in plant survival and reduction of DO output level (Chesapeake, 2012).

Exchangeable ion concentrations ranged from 0.56 ± 0.00 mg/l for Mg to 8.37 ± 0.09 mg/l for SO_4^{2-} . Exchangeable ions analysed include cations and anions. Generally higher values were observed for cations and anions in oil polluted water than the control water, although both results were found to fall within the maximum permissible limit stipulated by FEPA (1991). Therefore there is a significant difference between the concentration of cations and anions ($p < 0.05$) between both study sites. Crude oil pollution has been shown to increase the level of salts (carbonate, sulphate, chloride, ammonium and nitrate) and salinity level of aquatic ecosystem (Rhykered *et al.*, 1995). Therefore the result of this study confirms the presence of organic pollutants (petroleum products) in the test site.

Comparison between Total hydrocarbon content (THC) in water from Uzere and Ekrejeta clearly indicates significant difference ($p < 0.05$) between THC for both study sites. The high mean value 75.00 ± 62.50 mg/l of THC for oil polluted water compared to 0.01 ± 0.00 mg/l for control water is traceable to pollution from oil and gas. The THC levels in oil polluted water surpassed the maximum permissible limit of 10mg/l given by FEPA (1991). This confirms the occurrence of oil pollution in the study site.

Heavy metals are trace metals of which some of them are required for proper body maintenance mechanism. However their presence in excess amount results in their bioaccumulation and toxicity because of their non-biodegradable nature (Demirezen and Ahmet, 2006). Results obtained from this study showed that there were detectable amounts of heavy metals in the oil-polluted water of Uzere while levels of heavy metals in the control water were insignificant. However amidst detectable levels of heavy metals, Fe and cadmium surpassed the maximum permissible limit of 1.0mg/l and 0.05mg/l given by FEPA (1991). This is in agreement with the statement of Kauss and Hutchinson, (1975) that water soluble fraction (WSF) of crude oil contains metallic ions among other soluble contaminants. Edema, (2006) also reported that heavy metals detected in WSF of crude oil include Pb, Cu, Zn, Cd, Ni, Cr and V. Cadmium and lead have been reported the most toxic heavy metals in the aquatic ecosystem (Van den Broek *et al.*, 2002). Cadmium pneumitis has been shown to results from inhaling cadmium dust and fumes; this disease is characterised by death of the lung tissue linings because of excessive accumulation of fluids. An excessive amount of iron can seriously affect fauna and flora in aquatic bodies while too much cadmium can cause dis-functioning of the kidney (Abidemi, 2011). The presence of heavy metals in water of the test site (Uzere) invariably confirms levels of pollution by crude oil.

Polycyclic Aromatic Carbons PAHs sources in the environment can be classified as either petrogenic (if the source is derived from petroleum) or pyrogenic (if the source is derived from incomplete combustion of organic matter and fossil fuels (Baumard *et al.*, 1998). Bioavailability of PAHs depends largely on its molecular mass hence the solubility of PAHs decrease as their molecular mass increase (Johnsen *et al.*, 2005). The mean concentration of PAHs analysed in water samples from Uzere and Ekrejeta were 41.60mg/l and 0.00mg/l respectively. This indicates a significant difference in levels of PAHs in both sites. The levels of PAHs in water from Uzere were higher than that of the control and as well surpassed the maximum permissible limit stipulated by FEPA (1991). Bostrom *et al.* (2002) reported the carcinogenic effects of PAHs in animal studies with findings that PAHs have been linked to skin, lungs, bladder and stomach cancers. This suggests the health risk of people living within

Uzere (test site) are subjected to and also confirms the presence of petroleum pollutants in Uzere waters.

Table 2 Heavy metal and PAH analysis of cat fish (*Clarias gariepinus*) from test site (Uzere) and control site (Ekrejeta)

S/N	Parameters (mg/kg)	Oil Polluted Catfish	Control Catfish
1.	PAH	0.10 ± 0.00 ^a	0.00 ± 0.00 ^a
2.	Lead	0.01 ± 0.00 ^a	0.00 ± 0.00 ^b
3.	Total Iron	52.56 ± 0.02 ^a	39.45 ± 0.03 ^a
4.	Calcium	627.7 ± 0.02 ^a	408.3 ± 0.02 ^a
5.	Cadmium	0.05 ± 0.00 ^a	0.00 ± 0.00 ^b
6.	Chromium	0.00 ± 0.00 ^a	0.00 ± 0.00 ^b
7.	Magnesium	232.9 ± 0.0 ^a	116.6 ± 0.02 ^a
8.	Nickel	0.00 0.00 ^a	0.00± 0.00 ^b
9.	Zinc	23.63 ± 0.01 ^a	15.28 ± 0.01 ^a

Results presented are Means ± SEM for n = 3. Values in the same row with the same superscript (a) are significantly different at p < 0.05 level.

Heavy metals and PAHs concentration in Fishes

In *Clarias gariepinus*, the mean concentration of heavy metals analysed as shown in Table 2 were iron 52.56±0.02mg/kg and 39.447±0.03mg/kg, lead, chromium and nickel were 0.00±0.00mg/kg and 0.00±0.00mg/kg cadmium 0.05±0.00mg/kg and 0.00±0.00mg/kg, zinc was 23.63±0.01mg/kg and 15.28±0.01mg/kg for samples of fishes collected from test site (Uzere) and control site (Ekrejeta) respectively. For all heavy metals analysed, iron measured higher in catfish while lead and chromium measured lowest. The mean concentration of all heavy metals analysed in both test and control fish samples trailed below the FEPA (1991) maximum permissible limits which are in agreement with the report of (Jonathan *et al.*, 2013). The total mean concentration of PAHs in fishes from oil impacted water and control are 0.1±0.00mg/kg and 0.00±0.00mg/kg respectively. The levels of PAHs in fishes analysed were insignificant and fell below the maximum permissible limits as stipulated by FEPA (1991).

Heavy metals and PAHs in fishes

Fish is a rich protein food which is widely consumed in many parts of the world. Fish contains minerals and elements such as calcium, phosphorus, iron, copper and some proportions of B-vitamins which are known to support good health (Tucker, 2007). Due to living and feeding in aquatic habitat, fishes are likely vulnerable to pollution because they cannot evade the detrimental impact of pollutants (Zaki *et al.*, 2014). Results from this study show that there were detectable levels of heavy metals in fishes from oil polluted water (Uzere). Iron measured highest while chromium measured lowest in fishes. Generally the

levels of heavy metals in the fish of oil impacted water (Uzere) were higher than that of fishes in control water (Ekrejeta) but trailed behind the maximum permissible limit stipulated by FEPA (1991). The presence of heavy metals in the fish of oil polluted water suggests the tendency of bioaccumulation over time and toxicity (Demirezen and Ahmet, 2006). Fishes are considered the most significant biomarkers in the aquatic ecosystem for the estimation of heavy metal pollution (Eisler, 1993). These results suggest that individuals consuming fish from the oil impacted water of Uzere may be at serious health risk resulting from bioaccumulation of these heavy metals. Furthermore, results showed that levels of PAHs in fish of oil polluted water ($0.10 \pm 0.00 \text{ mg/kg}$) were higher than the control ($0.00 \pm 0.00 \text{ mg/kg}$) which is insignificant and surpassed the maximum permissible limit given by FEPA. The presence of PAHs in fish obtained from Uzere waters suggests the carcinogenic health risk tendencies predisposed to consumers of such fishes and also confirms the presence of organic pollutants in the environment.

CONCLUSION

Environmental pollution resulting from oil spillage is capable of degrading the environment; altering the natural quality of soil and water with an attendant cascade of its impact down the food chain. It can therefore be concluded from the findings of this research that there are evidence of pollution on the test site (Uzere) with the presence of high levels of hydrocarbon and heavy metal pollutants. The study reveals that the physicochemical parameters of water of the test area have been affected due to the incidence of oil spillage. By virtue of this study, the water quality of Uzere lakes and ponds is detrimental to aquatic life as the mean levels of parameters such as turbidity, dissolved oxygen DO and biochemical oxygen demand BOD surpassed the maximum permissible limit of FEPA for surface water. The elevated content of BOD often reduces the amount of DO which is lethal to aquatic life. The levels of PAHs and heavy metals in water and fishes from test site confirms the presence of crude oil pollutants in that environment as well as the health risk to cancers and other complications looming around the local dwellers of Uzere. The study showed that water quality and aquatic life of Uzere is impaired following the incidence of crude oil spillage. However, modalities should be put in place to assuage the current condition and proactively forestall future crude oil spillage from crude pipelines and oil well heads in Uzere community.

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