

Evaluation of the impact of crude oil spillage on soil and cassava plant (*Manihot esculenta*) in Uzere, Isoko south LGA of Delta State Nigeria.

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Abstract

An evaluation of the impact of crude oil spillage on soil, cassava tubers and leaves in Uzere (contaminated site) and Ekrejeta (control site) communities of Delta State were carried out. Three representative soil samples, cassava tubers and leaves were collected from three different points within each study site and determined in triplicates. Physicochemical parameters, heavy metal content, polycyclic aromatic hydrocarbons (PAHs) and total hydrocarbon contents (THC) of soil, heavy metal content and PAHs in cassava tubers and leaves were determined using standard analytical methods. Parameters determined include pH, conductivity, nitrate, sulphate, PAHs and THC as well as concentration of some heavy metals (Cd, Cr, Ni, Pb, Zn, Fe) in both soil and cassava samples. Concentrations of heavy metals were determined using Atomic absorption spectrophotometry. The average heavy metals detected in the soil include iron (Fe) 989.11mg/kg, cadmium (Cd) 1.50mg/kg, chromium (Cr) 8.26mg/kg, nickel (Ni) 3.92mg/kg, zinc (Zn) 10.04mg/kg, lead (Pb) 7.08mg/kg while average heavy metal detected in cassava tubers and leaf samples include lead (Pb) 3.13 and 3.22mg/kg, iron (Fe) 69.23 and 62.45mg/kg, cadmium (Cd) 0.00 and 0.22mg/kg, nickel (Ni) 2.73 and 6.38mg/kg, zinc (Zn) 14.04 and 32.72mg/kg respectively. The average pH of soil samples from the test site (Uzere) was 5.5, conductivity 58.67 μ s/cm. The average PAHs content of the soil was 0.17mg/kg. THC of 151.83mg/kg was detected in the soil. These findings suggest that the study site is heavily impacted by the crude oil spillage.

Keywords: Soil, cassava tubers, cassava leaves, physicochemical parameters, heavy metals

1. Introduction

Nigeria is one of the world's largest producers of crude oil with a proven reserve of 35 billion barrels (5.6x10⁹m³) with most of her exports going to the US; the 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). 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 spillage is known to be a major environmental problem in Nigeria, most especially in the Niger-Delta. It is reported that oil spillage has caused a constant threat to farmlands, crop plants and forest tree species (Ogri 2001; Agbogidi, 2003). It destroys soil fertility, causes alterations in soil physicochemical and microbiological properties, thereby having detrimental effects on the terrestrial and aquatic ecosystems.

Similarly, Spillage from oil exploration in the Niger Delta has led to massive environmental degradation. Environmental degradation causes problems such as contamination of water bodies, a threat to aquatic life, destruction of farmlands, crops and loss of lives (Badejo and Nwilo, 2010). According to ERA (2013), oil spills of traditional fishing grounds which has destroyed aquatic lives, exacerbating poverty and hunger in fishing communities and concomitant loss of land to pollution has resulted in forced migration of farmers to other communities in search of better livelihood, exerting additional pressure on resources in such area. The indirect effects of oil spills in soil include oxygen deprivation of plant roots as a result of exhaustion of the soil oxygen by oil-degrading microorganisms, which create anaerobic conditions that may lead to the formation of hydrogen sulphide (Agbogidi *et al.*, 2005). The direct effect on the ecosystem includes damage of fur and feathers of birds, making them prone to death by freezing. As a result of these effects on the ecosystem, the release of oil into the environment has caused serious environmental concern and attracts public attention (Roling *et al.*, 2002). It is in this regard that this research was carried out and is aimed at evaluation of the impact of oil spills on the

physicochemical properties as well as accessing the concentration of heavy metals and polycyclic aromatic hydrocarbon (PAHs) in soil, cassava leaves and tubers (*Manihot esculenta*) in Uzere community (test site) and Ekrejeta community (control site).

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 (Majirioghene 2014). This study has become very pertinent due to the environmental degradation occasioned by the oil spill in Uzere community.

2. Materials and Methods

2.1 Collection of Samples,

Three representative surface soil samples, (Figure 1A), cassava tubers (Figure 1B) and leaves (Figure 1C) were collected from three different points within Uzere Community in Isoko South and Ekrejeta Community in Ethiope East of Delta State, Nigeria respectively. Surface soil samples (0-15cm) were collected with the aid of a stainless steel soil auger. The soil samples collected were immediately placed in cellophane bags, tightly tied and labelled using a masking tape and marker pen. The samples were preserved in plastic cooler and taken to laboratory for analyses for soil chemical parameters.



Figure 1: Top soil (A), cassava tubers (*Manihot esculenta*) (B) and cassava leaves (C) from the oil spill area in Uzere (June 2015)

2.2 Sample Preparation for Determination of Heavy metals

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

2.3 Atomic Absorption Spectroscopy (AAS) Analysis

For each of the metals, atomic absorption spectroscopy was calibrated using metal standards (Cr 357.90 nm, Cd 228.80 nm, Zn 213.90 nm, Pb 283.30 nm, Mn 279.50 nm). Samples were determined with the aid of Atomic Absorption Spectrophotometer Analyser 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.

2.4 Determination of PAHs

Fresh tubers and leaves were washed, dried and ground to a powder using mortar and pestle and then kept in an airtight container ready for extraction. The extraction method used was the Texas Natural Resource Conservation Commission, Texas (TNRCC 2001) method with dichloromethane as the extraction solvent.

2.5 Extraction Procedure

Two grammes of each of the sample was weighed into a clean extraction container. Ten millilitres of extraction solvent (dichloromethane) was added 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. Glass wool was packed to about 1 cm thick and 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. A 0.5cm of sodium sulphate was added to the top of the column. 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. Eight millilitres of the eluent were collected and were labelled aliphatics.

2.6 Gas Chromatographic Analysis

The concentrated aliphatic fractions were transferred into labelled vials with rubber crimp caps for gas chromatographic analysis. One microliter 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.

2.7 Determination of pH and Electrical Conductivity

Ten grammes of soil sample was weighed into a test tube and 10ml of distilled water was added. It was allowed to stand for 30 minutes and stirred occasionally with a glass rod. The Hanna digital pH meter (previously calibrated) was inserted into the partly settled suspension without stirring and the pH measured. Similarly, the Electrical conductivity of the soil samples was measured with Hannah conductivity meter. The probe of the meter was inserted in the water sample and a steady reading recorded as the conductivity of the sample in $\mu\text{S}/\text{cm}$

2.8 Determination of Soil Mechanical Properties

2.8.1 Procedure

Fifty-one gramme of air dry soil was weighed. 50cc of 5% sodium hexametaphosphate along with 100cc distilled water was added and stirred with a stirring rod in a cup. The sample was allowed to stand for 30minutes. The soil suspension was further stirred with the multi mix machine for 15minutes. The suspension was transferred from the cup into a glass cylinder. Hydrometer was used to take two readings with a 3hours interval. The first reading measures the percentage of silt and clay in the suspension while the second reading indicates the percentage of clay in the suspension (van Reeuwijk 2002).

2.9 Determination of organic in soil

2.9.1 Procedure

A sample of the soil was taken and ground to pass through 0.5mm sieve. The soil sample was weighed out in duplicate and transferred to 250ml Erlenmeyer flask. A 10m of $\text{K}_2\text{Cr}_2\text{O}_7$ was added into the flask and swirled gently to disperse the soil. 20ml concentrated H_2SO_4 was added directly into the suspension using an automatic pipette. The flask was then further swirled until soil and reagents were mixed. The flask was then allowed to stand on an asbestos for 30minutes. 100ml of distilled water was added and allowed to stand for 30minutes. Four drops of ferroin indicator were added and titrated with 0.5N ferrous sulphate solution (van Reeuwijk 2002).

2.10 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% ($p < 0.05$).

3. Results and Discussion

The Results of Physicochemical, heavy metals and PAHs analysis in soil are summarised and presented in table 1.

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

S/N	Parameters	Oil Polluted Soil	Control Soil	FEPA Limit Values
1.	pH	5.53 ± 0.15 ^a	7.20 ± 0.12 ^a	NS
2.	Conductivity (µS/cm)	58.67 ± 0.89 ^a	66.00 ± 1.16 ^a	NS
3.	Sulphate (mg/kg)	23.00 ± 1.16 ^a	4.27 ± 0.15 ^a	NS
4.	Nitrate (mg/l)	1.73 ± 0.17 ^a	8.50 ± 0.12 ^a	NS
5.	THC (mg/kg)	151.83 ± 0.12 ^a	0.01 ± 0.00 ^a	50
6.	Total Organic Carbon (%)	0.74 ± 0.02 ^a	0.33 ± 0.01 ^a	NS
7.	Total Organic Matter (%)	1.35 ± 0.00 ^a	0.55 ± 0.00 ^a	NS
8.	Sand (%)	83.65 ± 0.02 ^a	79.24 ± 0.02 ^a	NS
9.	Silt (%)	6.84 ± 0.03 ^a	6.24 ± 0.00 ^a	NS
10.	Clay (%)	9.51 ± 0.01 ^a	14.45 ± 0.02 ^a	NS
11.	Particle Size Distribution	0.00 ± 0.00 ^a	0.00 ± 0.00 ^b	NS
12.	PAH (mg/kg)	0.17 ± 0.07 ^a	0.01 ± 0.00 ^a	1.0
13.	Total Iron (mg/kg)	989.10 ± 0.02 ^a	308.65 ± 0.46 ^a	100
14.	Calcium (mg/kg)	39.47 ± 0.02 ^a	166.59 ± 0.01 ^a	NS
15.	Cadmium (mg/kg)	1.50 ± 0.02 ^a	0.00 ± 0.00 ^a	0.8
16.	Chromium (mg/kg)	8.26 ± 0.02 ^a	1.55 ± 0.00 ^a	100
17.	Magnesium (mg/kg)	45.54 ± 0.02 ^a	135.12 ± 0.02 ^a	NS
18.	Nickel (mg/kg)	3.92 ± 0.02 ^a	1.343 ± 0.02 ^a	35
19.	Zinc (mg/kg)	10.04 ± 0.02 ^a	6.65 ± 0.04 ^a	140
20.	Lead (mg/kg)	7.08 ± 0.04 ^a	2.75 ± 0.03 ^a	85

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. NS - Not Stated

3.1 Physicochemical parameters of soil

The mean concentrations of physicochemical analysis for soil samples collected from Uzere and Ekrejeta showed that there was a significant difference (p < 0.05) between soil samples collected from both sites (Table 1). The mean pH were 5.53 ± 0.15 and 7.20 ± 0.12, conductivity 58.67 ± 0.89 µS/cm and 66.00 ± 1.16 µS/cm, sulphate 23.00 ± 1.16 mg/kg and 4.27 ± 0.15 mg/kg, nitrate 1.73 ± 0.17 mg/kg and 8.5 ± 0.12 mg/kg, total hydrocarbon content 151.83 ± 0.12 mg/kg and 0.01 ± 0.00 mg/kg, total organic carbon 0.74 ± 0.02% and 0.33 ± 0.01%, total organic matter were 1.35 ± 0.00 and 0.55 ± 0.00% for soil samples collected for Uzere (test site) and Ekrejeta (control site) respectively.

3.2 Heavy metals and PAHs concentration in soil

Statistical analysis of six heavy metals namely, iron, cadmium, chromium, nickel, zinc and lead (Table 1) indicates a significant difference (p < 0.05) between the crude oil polluted soil (Uzere) and the control soil (Ekrejeta). The concentrations of iron (989.11 ± 0.02 mg/kg), cadmium (1.50 ± 0.02 mg/kg), nickel (3.92 ± 0.02 mg/kg), zinc (10.04 ± 0.02 mg/kg) and lead (7.08 ± 0.04 mg/kg) were higher in oil polluted soil when compared to that of the control respectively. All levels of heavy metals fall within the maximum permissible limits of FEPA (1991) except iron and chromium which were higher in the oil-polluted soil. The total mean concentration of PAHs for oil impacted soil and control samples are 0.17 ± 0.07 mg/kg and 0.01 ± 0.00 mg/kg

respectively. The levels of PAHs analysed in soil samples were not significant ($p > 0.05$) and are within the maximum permissible limits as stipulated by FEPA (1991).

3.3 Physicochemical Parameters of Soil

The capacity of a specific kind of soil to function within natural or managed ecosystem boundaries to sustain plant and animal productivity, maintaining and enhancing water and air quality and supporting of human health cannot be over-emphasized (Karlen *et al.*, 1997). Assessing how well a soil performs in all its function is a major concern especially when considering the effects of crude oil pollution on soil fertility, soil structure, soil aeration and soil productivity. The average concentration of physicochemical parameters analysed in soil samples collected from test site (Uzere) and Control site (Ekrejeta) clearly exposed some alterations in soil quality of the oil-impacted area (Uzere). THC simply shows the petroleum hydrocarbons that are present in the sample. The mean concentration of THC 151.83mg/kg for the oil polluted soil was significantly higher ($p < 0.05$) than that of the control soil sample (0.01mg/kg) and also surpassed the maximum permissible limit of 50.0mg/kg stipulated by FEPA. This suggests the presence of hydrocarbon in the environment. Measured THC values for oil polluted soil samples suggest the relative potential of human exposure and potential human health effects. Compounds in THC have been shown to affect the function of the liver, kidney, blood, lungs, immune system and spleen (ATSDR, 1999).

The mean pH of the oil polluted soil (5.5) was significantly lower ($p < 0.05$) than that of the control (7.2). The oil pollution may have had some direct impact in reducing the pH of the soil; it might also be due to the production of organic acids by microorganism during degradation of organic pollutants (Olukunle, 2013; Okoye and Okunrobo, 2014).

The mean concentration of total organic carbon TOC and total organic matter TOM (0.74% and 1.35%) were observed to be significantly higher ($p < 0.05$) for the oil polluted soil than that of the control soil (0.33% and 0.55%). Similar reported on crude oil contaminated sites showed that oil increases the carbon content of soil thereby increasing the nitrogen content as well as the carbon/nitrogen ratios (Adinna *et al.* 2003; Olukunle, 2013) Findings from this study suggests some level of petroleum contamination in Uzere.

Comparison between Uzere and Ekrejeta for soil exchangeable cations and anions showed a significant difference ($p < 0.05$) between both sites. The average concentration of nitrate in the oil-polluted soil (1.73mg/kg) was lower than that of the control soil (8.50mg/kg); this is in agreement with the report of Adinna *et al.* (2003) who reported that oil increases the carbon content of the soil thereby increasing the nitrogen content. The level of calcium 39.47mg/kg, and magnesium 45.54mg/kg for polluted soil in Uzere were significantly lower ($p < 0.05$) lower than that of the control site calcium 166.59mg/kg, magnesium 135.12mg/kg while sulphate (23.00mg/kg) was significantly higher ($p < 0.05$) for the oil polluted soil. The total concentration of cations and anions directly affected the conductivity which was observed to be significantly lower ($p < 0.05$) for oil polluted soil in Uzere (58.67 μ S/cm) than that of the control site soil (66.00 μ S/cm).

3.4 Heavy metals and PAHs in soil

Results from this study also indicate detectable levels of heavy metals analysed in oil polluted soil of Uzere (test site). However some heavy metals predominated in the test soil when compared to the control and surpassed the maximum permissible limits given by FEPA (1991). Heavy metals that predominated include iron (Fe), cadmium (Cd) and chromium (Cr). The presence of heavy metals in the oil-impacted soil of Uzere suggests the presence of pollutants in the soil which emanated from the oil spillage. On the other hand, levels of PAHs (0.17mg/kg) in the oil-polluted soil of Uzere were lower when compared to FEPA (1991) limit of 1mg/kg while that of the control was not significant. The presence of heavy metals and PAHs in the soil also confirms the occurrence of oil spillage in Uzere.

The Results of heavy metals and PAHs analysis in cassava tubers and leaves (*Manihot esculenta*) are summarized and presented in tables 2 and 3 below.

Table 2: Heavy metals and PAHs analysis of cassava tubers (*Manihot esculenta*) from test site (Uzere) and control site (Ekrejeta)

S/N	Parameters (mg/kg)	Oil Polluted Cassava Tubers	Control Cassava tubers
1.	PAH	0.00 ± 0.00 ^a	0.00 ± 0.00 ^b
2.	Lead	3.13 ± 0.01 ^a	0.00 ± 0.00 ^a
3.	Total Iron	69.23 ± 0.01 ^a	22.63 ± 0.01 ^a
4.	Calcium	89.93 ± 0.02 ^a	224.74 ± 0.01 ^a
5.	Cadmium	0.00 ± 0.00 ^a	0.00 ± 0.00 ^b
6.	Chromium	0.00 ± 0.00 ^a	0.00 ± 0.00 ^b
7.	Magnesium	110.53 ± 0.0 ^a	261.92 ± 0.02 ^a
8.	Nickel	2.73 ± 0.02 ^a	0.67 ± 0.0 ^a
9.	Zinc	14.04 ± 0.02 ^a	7.86 ± 0.02 ^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.

Table 3: Heavy metals and PAHs analysis of cassava leaves (*Manihot esculenta*) from test site (Uzere) and control site (Ekrejeta)

S/N	Parameters (mg/kg)	Oil Polluted Cassava Leaves	Control Cassava Leaves
1.	PAH	0.00 ± 0.00 ^a	0.00 ± 0.00 ^b
2.	Lead	3.22 ± 0.00 ^a	0.00 ± 0.00 ^a
3.	Total Iron	62.45 ± 0.28 ^a	21.20 ± 0.13 ^a
4.	Calcium	452.08 ± 0.02 ^a	614.73 ± 0.06 ^a
5.	Cadmium	0.22 ± 0.02 ^a	0.00 ± 0.00 ^a
6.	Chromium	0.00 ± 0.00 ^a	0.00 ± 0.00 ^b
7.	Magnesium	188.06 ± 0.47 ^a	306.94 ± 0.11 ^a
8.	Nickel	6.38 ± 0.02 ^a	2.323 ± 0.02 ^a
9.	Zinc	32.72 ± 0.01 ^a	20.16 ± 0.01 ^a

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

3.5 Heavy metals and PAHs concentrations in cassava plants.

The result of average heavy metal concentrations in cassava tubers and leaves (Tables 2 and 3 respectively) for samples obtained from oil impacted site was significantly higher ($p < 0.05$) when compared with the control site. However, concentrations of heavy metals measured from both study sites were below the maximum permissible level of FEPA (1991). The total mean concentration of PAHs for oil-impacted site and control site samples for cassava tubers and leaves were not significant and are below the maximum permissible limits as stipulated by FEPA (1991). Values obtained for iron, nickel and zinc in cassava tubers and leaves from Uzere were significantly higher ($p < 0.05$) than that obtained from Ekrejeta. All levels of heavy metals and PAHs in cassava tubers and leaves were below the maximum permissible limit of FEPA (1991).

4. Conclusion

Pollution resulting from crude oil spillage is detrimental to the environment affecting the health and well-being of living organisms in general. It can therefore be concluded from the findings of this research that there are evidence of soil contamination in the test site (Uzere) with the presence of heavy metal pollutants. Environmental pollution resulting from oil spillage is capable of degrading the environment; altering the natural quality of soil with an attendant cascade of its impact down the food chain. The study reveals that the physicochemical parameters of the soil of the test area have been affected due to the incidence of oil spillage. By virtue of the findings of this study, 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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