

# Effect of Petroleum Product Spillage on Agricultural Environment in the North Central Area of Nigeria

J J Musa<sup>1</sup>, P A Adeoye<sup>2</sup>, M Saidu<sup>3</sup> and S T Toloruntomi<sup>4</sup>

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A study was conducted to evaluate 14 heavy metals in dry sediment samples used to assess the contamination of farmland in Eluku/Ojutaye village after a protracted petroleum product spill. Six samples of water and soil were collected from different locations which were subjected to physical and chemical analysis using standard methods for the examination of the soil and water samples. Concentrations of these samples' elements were above compliance limit which may have long-term adverse effects on the soil and vegetation of the area. The pH and Electrical Conductivity (EC) were determined for both soil and water samples.

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**Keywords:** Crops, Environment, Petroleum products, Soil, Water

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## Introduction

Environmental concern is a global one which transcends all boundaries, including those of wealth, culture and language. Increasingly all nations are recognizing that it is not possible to treat or consider the environment on a national scale (Andrade *et al.*, 2004). In the past few years man's awareness of the environment has greatly increased, mostly as a result of observing the already caused environmental damage. Environment encompasses everything surrounding us. As such the environment is a huge pull of resources that helps us to satisfy our needs and fulfill our wants (Dang, 2006). None of the environmental resources is infinitely abundant. Therein, lays the trap into which we have fallen and which had led to our widespread pollution. If man is to survive longer than just a few generations, we must re-examine the man-earth relationship and attempt to understand, manage and control, as adequately as possible all our environmental resources. In re-evaluating the interrelation between man and the environment, one must not forget the dynamic nature of the environment. Pollution is the undesirable degradation of the environment, natural or man-made, while the waste, an undesirable substance, accumulated as a result of our inefficient utilization of the environmental resources (Chatterjee, 2005). In Nigeria,

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<sup>1</sup> Lecturer, Department of Agriculture and Bioresource Engineering, Federal University of Technology, P M B 65, Minna, Nigeria. E-mail: jogric2000@yahoo.com

<sup>2</sup> Lecturer, Department of Agriculture and Bioresource Engineering, Federal University of Technology, P M B 65, Minna, Nigeria. E-mail: pheterharday@yahoo.com

<sup>3</sup> Lecturer, Department of Civil Engineering, Federal University of Technology, P M B 65, Minna, Nigeria; and is the corresponding author. E-mail: mohsaidu@yahoo.co.uk

<sup>4</sup> Research Scholar, Department of Agriculture and Bioresource Engineering, Federal University of Technology, P M B 65, Minna, Nigeria. E-mail: thorpeedough@yahoo.com

there have been reported cases of petroleum and its product spillage on soil and water, which has led to water shortages and loss of agricultural land. Examples include the peculiar case of Ikot Ada Udo village in Ikot Abasi Local Government Area (LGA) of Akwa Ibom state, and Ikarama and Kalaba communities in Yenegoa LGA of Bayelsa state. Of particular interest is the case of people of Eluku/Ojutaye village in Ilorin east LGA of Kwara state, who are now counting their losses after the oil spill from the ruptured Nigerian National Petroleum Corporation (NNPC) tanks located within the community. Due to non-replacement of ageing tanks and pipeline, the oil gets into the soil and the river—a source of irrigation for the farms in the village—leading to the loss of vegetable farms. The people of Eluku/Ojutaye are mostly engaged in subsistence farming, mostly growing vegetables for a living, which has sustained several families as they use the agricultural products to meet their household needs by keeping some of the harvest for domestic consumption as well as for sale. The entire scenario changed when the NNPC located their depot in this area. The people can no longer enjoy the full benefit of their lands, as petroleum product spillage has ruined several farmlands. Petrol is a byproduct of petroleum, which is a mixture of many organic substances. It has properties that can cause fire, explosion, health and environmental hazards. The properties of petrol can vary widely depending on its extraction source. Petrol adsorbed into the soil is known to impart toxicity and has a strong effect on the flora and fauna within the contaminated area, its subsequent dispersion will depend on the movement of air causing evaporation. The extent and duration of the pollution will also depend on the quantity and duration of the petrol released.

The aim of this study is to establish the effect of petroleum and its products on soil and water of agricultural areas and the constituent of the soil and water affected by the spillage.

## **Materials and Methods**

### **Study Area**

Soil and water samples were collected from farms in Eluku/Ojutaye Oke-Oyi area Ilorin East Local Government Ilorin, Kwara state, at different locations. The village is situated very close to the NNPC, Ilorin depot in Kwara state which lies between latitude 7° 15' and 11° North and longitude 2° 30' and 6° 45' East. The soil map unit for the area is composed of about 60% Lithic Ustorthents, 35% rock outcrops and 5% soils of minor extent.

The Lithic Ustorthents are soils that occur dominantly on upper hill slopes and summits. They are very shallow and excessively drained. Typically, the surface layer is about 15 cm thick comprising dark, cobbly loamy sand, the sub-surface layer has very dark brown, very cobbly loamy sand that is underlain by unweathered quartz-schist at a depth of about 30 cm. Permeability of the Lithic Ustorthents is moderately rapid. The effective rooting depth is limited by unweathered bed rock at the depth of about 15-50 cm. The available water capacity is very low.

## Method of Water Analysis

After shaking the bottle containing the sample thoroughly, 50-100 mL of the sample was placed in a beaker and 5 mL concentrated nitric acid ( $\text{HNO}_3$ ) was added (Nathanail and Bardos, 2004). This was boiled slowly on a hot plate and allowed to evaporate to about 20 mL. Another 5 mL concentrated  $\text{HNO}_3$  was added. It was then covered with a watch glass and heated. Concentrated  $\text{HNO}_3$  and heat were continually supplied until the solution appeared light in color and clear, indicating the completion of digestion.

## Determination of Heavy Metals in the Water Sample

A mixed calibration standard containing every metal was prepared by pipetting aliquots of 1000 mg/L standard solution into a series of volumetric flasks (50-100 mL). Concentrated  $\text{HNO}_3$  measuring 1 mL was added to each flask and was diluted to the mark. The Atomic Absorption Spectrophotometer (AAS) was switched on and the appropriate hollow cathode lamp was selected, and the lamp current adjusted to the value recommended in the instrument manual. The monochromator and slit settings were set to the recommended value. The wavelength setting was fine-tuned and the beam was aligned.

The gain setting was then optimized, and the fume hood turned on, switching on the flame according to the recommended procedure. The sample was aspirated, standardized and blanked into the flame of AAS equipped with the appropriate hollow cathode lamp and operated at the wavelength recommended.

## Determination of Major Anions

The major anions present in the water sample were tested by titrating with standard 0.0141 M NaCl solution. Aliquots measuring 20 mL of the standard NaCl solution in 100 mL conical flask were pipetted into a conical flask and the pH adjusted between 7 and 10. Chromate indicator solution, measuring 1 mL, was added and titrated with  $\text{AgNO}_3$  to the first appearance of the red silver chromate. The result of the first titration was discarded and the titration repeated three times on separate aliquots of NaCl solution. A blank titration was carried out by adding 1 mL of chromate indicator solution to 20 mL of laboratory water and titrated with  $\text{AgNO}_3$ . The volume of the titrant required for the blank titration was subtracted from the volume of titrant required for the titration of NaCl solution and the molarity of the standard  $\text{AgNO}_3$  solution was calculated.

## Anion Analysis ( $\text{Cl}^-$ )

This was done by pipetting 100 mL of water sample into a 250 mL conical flask and the pH was adjusted between 7 and 10. A pH paper was used instead of a pH meter as the electrode may contaminate the sample. The indicator was added and titrated as above. A blank titration was also repeated using 100 mL of laboratory water and the volume of titrant used was corrected. The titration was repeated with three aliquots of each sample and the average taken. The concentration of the chloride in the sample was calculated from the concentration of standardized  $\text{AgNO}_3$  solution. Also the corrected volume of titrant used and the volume of the sample were calculated.

### **Anion Analysis ( $\text{SO}_4^{2-}$ )**

A sample of 100 mL was taken in a 250 mL conical flask and placed on a magnetic stirrer, 20 mL of the NaCl-HCl solution and 20 mL of glycerol-ethanol solution was added while stirring. Approximately 0.3 g of barium chloride ( $\text{BaCl}_2$ ) was added and then stirred for two minutes.

Some of the solutions were immediately poured into an absorption cell and the absorbance at 420 nm was measured after exactly three minutes. A series of calibration standard was prepared by pipetting aliquots of standard sulphate solution corresponding between 0.5 and 5.0  $\text{MgSO}_4^{2-}$  (i.e., 5-50 mL) into a 100 mL volumetric flask and made up to the mark with water.

Analyzed in the same way as the samples, some blanks were prepared by adding all the reagents except  $\text{BaCl}_2$  to 100 mL of sample and the absorbance measured. Blanked readings obtained were subtracted from each sample reading and by using the same sample to compensate for sample color and turbidity.

A calibration graph of absorbance against  $\text{MgSO}_4^{2-}$  was prepared. The amount of sulphate in the samples was read using the corrected absorbance reading and the concentration in the sample was calculated.

### **pH Determination**

The combination of pH electrode and meter was calibrated using a two-point calibration with buffer solutions of pH 7 and 4. Then the pH electrode was immersed in the water sample and a measurement taken, after the solution had come to rest.

The working potassium chloride (KCl) standard solution was placed in a beaker, and the conductivity cell was suspended, holding it 1.5 cm above the bottom of the beaker, making sure it was not in contact with any part of the beaker walls. The conductivity reading was adjusted to 100  $\mu\text{mho/cm}$ . The cell was rinsed with pure water and the measurement carried out on the sample.

### **Analysis of the Soil Sample**

#### ***Soil Conductivity Determination***

20 g of soil sample was weighed and then placed in a beaker (Corey, 1986). 40 mL of laboratory water was added and stirred vigorously on a magnetic stirrer. It was then allowed to stand for 30 minutes and the conductivity determined for the water samples, making sure the electrode cell was in the supernatant above the settled particles.

#### ***Soil pH Determination***

Soil sample measuring 20 g was weighed and placed in a beaker. To it was added 40 mL laboratory water and stirred vigorously manually, and was then allowed to stand for 30 minutes and the pH determined for the water samples.

#### ***Determination of Soil Cd, Zn, Ni, Hg, Fe, As, Cu, Mn, and Cr***

Air-dried and sieved (<2 mm) soil sample sediment was ground. Out of this, only 1.0 g was weighted and placed inside a 100 mL tall-form beaker, 30 mL of 1:1  $\text{HNO}_3$

[(10 mL) conc.  $\text{HNO}_3$ ] was boiled gently on a hot plate till the volume was reduced approximately to 5 mL. While stirring, 10 mL, 1:1  $\text{HNO}_3$  was added and repeated. The extract was cooled and filtered through a Whatman no. 541 filter paper. The beaker was washed with the filter paper with successive small portions of 0.25M  $\text{HNO}_3$ . The filtrate and washings were transferred to a 50 mL volumetric flask and diluted to the mark with the water. A series of calibration standard over the required range was prepared by diluting aliquots of the working metal solution with 0.25M  $\text{HNO}_3$ . A calibrate graph of absorbance against metal concentration was constructed and the concentration in the solid sample was read as concentration in soil (mg/kg) =  $C \times V/M$ , where  $C$  is the concentration of metal in the extract (mg/L),  $V$  is the volume of extract (mL) and  $M$  is the weight of sample (g).

### Determination of Soil-Sodium Adsorption Ratio

Fans *et al.* (2002) stated that two criteria are currently recognized in the scientific literature as indices of salinity. These are Sodium Adsorption Ratio (SAR) with a reported threshold of 12 (mol/kg)<sup>0.5</sup>, and Exchangeable Sodium Percentage (ESP) with a reported threshold of 15%.

$$\text{SAR} = [\text{Na}^+] / \{([\text{Ca}^{2+}] + [\text{Mg}^{2+}]) / 2\}^{0.5}$$

where, sodium, calcium and magnesium are in milliequivalents/L and SAR = Sodium Adsorption Ratio (mol/kg)<sup>0.5</sup>

### Results

The results obtained from the analysis of the three water samples as presented in Table 1, which shows the various levels of some major heavy metals present within the water bodies of the Eluku/Ojutaye community in the north central area of Nigeria.

The metals present in lower concentration are Barium, Cobalt, Lead, Cadmium and Manganese. The presence of the above-mentioned metals did not bring any significant difference between the two sources of samples, nor did the sources differ with respect to barium content, but they did differ slightly with respect to boron, nickel, copper, and arsenic.

Mercury was not present in any of the three water samples while silver was present only in the second sample. The other metal present in greater concentration was boron (0.82-1.89 mg/L). It is observed that sample 3 had the lowest concentration since the point of collection of this very sample was about 120 meters away from the point source, which is an indication of diffusion of the metal soluble in the water. While the highly toxic copper had a range between 0.06-1.75 mg/L with sample 3 having a lower concentration closely followed by sample 2, sample 1 had the highest concentration which is also referred to as our point source of the oil spill. Arsenic had a range between 0.03 and 0.85 mg/L, manganese had a range of 0.12 and 0.314 mg/L, while nickel, cobalt and lead had ranges between 0.03 and 0.17 mg/L; 0.03 and 0.10 mg/L; and 0.04 and 0.09 mg/L, respectively.

As the residue of most of the chemical constituents carried by the water bodies leaves their effect within the soil, the effect of these chemicals cannot be over emphasized. From the analysis of the soil sample, it was observed that the Total Heavy Metal (THM) at

S. No.	Parameter	Samples		
		1	2	3
1.	pH	9.100	8.700	6.40
2.	ECR/Km	177.000	139.000	229.000
3.	Cl <sup>-</sup> (mg/L)	474.800	272.600	201.000
4.	SO <sub>4</sub> <sup>2-</sup> (mg/L)	451.000	523.000	247.000
5.	Lead (mg/L)	0.090	0.082	0.040
6.	Manganese (mg/L)	0.314	0.300	0.120
7.	Nickel (mg/L)	0.140	0.170	0.030
8.	Cadmium (mg/L)	0.010	0.020	0.005
9.	Cobalt (mg/L)	0.090	0.100	0.030
10.	Copper (mg/L)	1.740	1.620	0.060
11.	Boron (mg/L)	1.890	1.750	0.820
12.	Arsenic (mg/L)	0.850	0.610	0.030
13.	Mercury (mg/L)	NA	NA	NA
14.	Silver	NA	0.030	NA
15.	Barium (mg/L)	0.060	0.060	0.020

site 1 had a total content of 40.08 mg/L. The affected soil at site 2 had a THM of 36.64 mg/L which shows a significant reduction from site 1, while the heavy metals were virtually absent in site 3 which had THM of 3.33 mg/L. The water samples were less affected, as the water from site 1 had THM content of 5.18 mg/L and that from site 2, 4.74 mg/L in THM content. It was also not much in the control water, which had a THM content of 1.15 mg/L.

In the area of soil affected by the spill, oil had impregnated the roots of the plants constituting the predominant vegetation, gluing soil particles to the root. These areas exhibited a compact crust of very low porosity as discovered from the shallow rooting system of the vegetables present in the area.

Color of the soil range from black at site one, where it was responsible for the high resistance to penetration of the affected soil, through a shade of gray at site two where the crust was thinner and offered lesser resistance to penetration, as discovered from the length of the rooting system which ranges between 0 and 30 cm depending on the type of crop grown.

However, resistance to penetration was moderate in the control soil (site 3), as vegetables in these areas had longer rooting system, than the vegetables in site 1 and 2 on the Eluku/Ojutaye farms. The crust is composed of aggregates of fine material agglutinated by the oil,

S. No.	Test	Sites		
		1	2	3
1.	Clay (%)	14.900	15.900	22.400
2.	Sand (%)	78.500	80.000	68.500
3.	Silt (%)	7.000	4.900	9.120
4.	pH	8.500	9.200	8.100
5.	Cadmium (mg/g)	0.012	0.014	0.003
6.	Zinc (mg/g)	27.400	29.500	2.100
7.	Nickel (mg/g)	0.015	0.032	0.003
8.	Mercury (mg/g)	6.120	4.320	1.040
9.	Arsenic (mg/g)	0.300	0.290	0.020
10.	Copper (mg/g)	0.117	0.122	0.005
11.	Iron (mg/g)	6.120	4.320	1.040
12.	Manganese (mg/g)	0.360	0.344	0.160
13.	SAR	0.234	0.197	0.052
14.	EC ( $\Omega^{-1}\text{km}^{-1}$ )	577.000	539.000	134.000
15.	Chromium (mg/g)	0.006	0.021	NA

which in coating the final particles will have facilitated their entry and permanence in the larger pores and channels, gluing larger particles together and thus reducing porosity and permeability and increasing resistance to penetration, whereas under normal circumstances the particles of sandy soil reorganize during every cycle of wetting and drying and do not cohere, resulting in very low resistance to penetration (Andrade *et al.*, 2002).

Polluted soil differed from other unpolluted soils in permeability, porosity and resistance to penetration. Polluted soils had significantly higher values than control soil with respect to total Cu, Cr, Fe and Pb. Table 2 shows the various quality parameters for the various soil sites considered which shows the pH ranges between 8.1 and 9.2.

For crops generally to survey in any soil the pH range is between 6.5 and 8.5 which implies that only sites 1 and 3 satisfy this condition while site 2 had an extremely high value. Franklin (2001), stated that low pH values causes the accumulation of aluminium and manganese ions which are toxic to plant roots, reduces some useful soil organisms such as bacteria and earthworms and also causes the disintegration of clay minerals which are leached from the soil.

The Electrical Conductivity (EC) for the water sample ranged between 139 and 229 while that of the soil ranged between 134 and 577. When these results were compared with the standard values of the UN as presented by Carballeria *et al.* (2000), the values obtained

from the study area were discovered to be too high which is an indication that there are high concentration of heavy metals within the soil and water samples which do not support the growth of crops.

The  $\text{Cl}^-$  ion which is a major ion in the surface water varies between 201 and 474.8 mg/L in the water samples while  $\text{SO}_4^{2-}$  which is also a major ion occurring in natural water was found to be between 247 and 523 mg/L in water, the level of both  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in water samples were very high which exceeds the maximum amount admissible for water for irrigational purposes, thus having a harmful effect on plant (Vladimir and Miroslav 2001). The level of chloride in water supplies is limited to 250 mg/L, at higher concentration as in the case of the samples from the two sites, chlorides impacts a salty taste which make the water unpalatable for irrigational purposes. High chloride concentration is harmful to plants, some damages may occur at levels as low as 70-250 mg/L. This also contributes synergistically to the salt toxicity in plants which in turn inhibits plant growth and electron flow through the photo system. However, the synergistic effect of sodium and chlorides shows that neither of these ions alone is responsible for salt stress induced damage. This also applies in the case of  $\text{SO}_4^{2-}$ . The SAR of the soil sample varies between 0.052 and 0.234 mol/kg.

In the case of EC, values above 0.45 mmhok/L causes severe damage to plants. The value of SAR which ranges between (0.052-0.234) in the soil is very high. The application of this soil for agricultural purposes may increase soil salinity, as the alkali and the alkaline earth metal which are criteria in measuring SAR in soil contributes greatly to the salt stress, inducing damage to plants. Salinity becomes a problem when enough salt accumulates in the root zone to negatively affect plant growth. Excess salts in the root zone hinder plant roots from withdrawing water from surrounding soil. Thus, this lowers the amount of water available to plant regardless of the amount of water actually in the root zone (Mackay, 1988).

For irrigational purposes, the level of Cu in the water samples (0.06-1.74) is high, as the irrigation water quality criteria for heavy metal (for Cu) is 0.2 mg/L (Andrade *et al.*, 2002). Cu being very toxic, affects majorly the growth of the plants. The presence of the heavy metals in excess of the standard greatly affected the growth of the plants, by inducing temporary effects like narcosis and tainting of tissues, which usually subsides over time (Andrade *et al.*, 2004).

## Conclusion

As expected, the degree to which the study area has been affected, as reflected by the THM contents of the polluted soils, differed widely. However, the polluted soils exhibited all microscopic effect of pollution such as compact crust with significantly lower porosity and greater resistance to penetration than those of unpolluted soils at the same sites.

Pollution also significantly lowered intrinsic permeability, raised hydrophobicity, and increased greatly the concentrations of Cr, Cu, Fe, Pb and Ni. ■



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