Physicochemical Properties of Soil Contaminated With Refined Petroleum Oil In Eluama Community, Abia State, Nigeria

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ABSTRACT
The physicochemical properties of soil polluted with refined petroleum was carried out between January and May, 2012, in Eluama community polluted with refined petroleum was carried out between January and May, 2012, in Eluama community, Abia State, Nigeria. The aim of this study is to examine the long-term kinetics of refined petroleum oil contaminated soil and to assess the extent of remediation with respect to length of time with the spill (11 years of spill). The soil physicochemical properties were evaluated using different analytical methods. Soil collected from unpolluted farmland was used as control. The results revealed that organic carbon, organic matter, calcium and magnesium increased with increase in pollution while nitrogen, potassium, sodium and phosphorus decreased with increase in pollution. The pH became more basic as pollution decreases. In addition, concentration of heavy metals increased as soil increases with pollution. This result reveals that the polluted soil when compared with the control (soil from unpolluted farmland) is unsuitable for agricultural activities as full remediation has not taken place except remediation can be hastened.

INTRODUCTION
There is growing public concern as a wide variety of toxic chemicals are being introduced inadvertently or deliberately into the environment. Petroleum hydrocarbons are one common example of these chemicals, which enter the environment frequently and in large volumes through numerous routes. Petroleum hydrocarbons come into the environment through accidents, spills or leak, urban input, industrial releases and commercial or domestic uses (Ou et al., 2004; Wang and Stout, 2007). The site of oil pollution is not necessarily the site of wwe use, hence oil has been transported...
several kilometers to reach its various destination (Onyeagba and Isu, 2006). In Nigeria, the mode of transportation has been through pipelines, barges, oil tankers and road tankers. The losses are mainly as a result of lack of regular maintenance of the pipelines as most of the pipelines are obsolete. Other causes of petroleum pollution include oil-well blow-out, corrosion of oil pipelines, pipeline vandalism and human errors etc; all resulting in petroleum pollution (Sakari et al., 2008; http;/www.marineornithology.org).

Pollution of the natural environment like soil by petroleum is a universal problem because of their effect on soil ecosystem (Akoto et al., 2008). Petroleum oil pollution exerts adverse effects on plants indirectly by making toxic minerals in the soil available to plants (Adams and Ellis, 1960). Crude oil pollution also leads to deterioration of soil structure, loss of organic matter contents, loss of soil minerals nutrients such as potassium, sodium, sulphate, phosphate, and nitrate etc (Akubugwo et al., 2009). It also exposes soil to leaching and erosion (Palese et al., 2003). The environmental significance of the enhanced levels of these pollutants is judged in terms of the degree of toxicity, the extent of exploitation of the pollutants, their application, concentration and consequent mobilization into the soil. The presence of these pollutants obviously has resulted to loss of soil fertility, poor crop yield and harmful implications on humans and the entire ecosystem.

With the high degree of ecological degradation resulting from petroleum pollution, there is need for continuous monitoring and evaluation in order to cope up with new strategies and policies that will aid in protecting and preserving the environment. This work is aimed at assessing the suitability of the polluted soil in Eluama community for agricultural purposes by examining their physicochemical properties and the level of remediation since the spill in 2000.

MATERIALS AND METHODS

Study Area: Eluama is a community in Isuikwuato LGA of Abia State, Nigeria. It is located along the Nigeria National Petroleum Corporation (NNPC) high pressure oil pipelines used for the distribution of petroleum products from the refinery in Port Harcourt, River State, to other parts of the country. Being a rural community, the people survive on subsistence farming. However, due to vandalism of the pressure pipelines by members of the community in year 2000, some part of the area was gutted by fire from oil spill, thus damaging the vegetation and soil.

Collection of Soil Samples: The sampling area was mapped out (100 meters). The mapped land was divided into five at 20 meters distance spacing. The seepage area was also labeled. An unpolluted farmland in the community served as control. Soil samples were collected at different distances at a depth of 0-15cm using an auger and kept in sterile plastic bags. The samples were then transported to Federal College of Land Resources and Technology, Owerri, Imo State for analysis in refrigerated coolers to arrest microbial growth.
Preparation of Samples for Analysis:
Soil samples were air-dried and sieved with a 2mm mesh according to Allen et al (1974). The temperature of each sample was taken at the site by immersing the bulb of the thermometer in the soil and the reading in °C taken after one minute.

Soil pH was determined by the method of Bates (1954) using the air-dried samples. To 20g of air-dried soil in 50ml beaker, 20ml distilled water was added, the contents stirred occasionally with a glass rod and then allowed to stand for 30 minutes. The electrodes of the pH meter were inserted into the suspension and the pH reading recorded. The remaining air-dried soil samples were used to investigate the physical and chemical properties.

Particle Size Analysis: Particle size density was analyzed using the Bouyoucoous Hydrometer method. 5g of sieved soil was weighed and transferred into a 250ml beaker. The mixture was stirred and allowed to stand overnight. It was then transferred into a dispersion cup and distilled water was added to the 100ml mark. Immediately, the hydrometer was placed into the slurry and the reading taken after 40 seconds. Blank was analyzed the same manner using 50ml 5% calgon solution.

Calculation:
\[
\% \text{ silt} = 100 - \% \text{ sand} - \% \text{ clay} \\
\% \text{ clay} = \frac{A - B}{\text{wt of soil} \times 100} \\
A = \text{Sample} + \text{temperature}; B = \text{Blank} + \text{temperature}
\]

Organic Carbon /Matter: Organic carbon was determined using the method of Walkey and Black (1934). 1.0g of sieved soil was weighed into a 500ml Erlenmeyer flask. 10ml of 0.1m potassium dichromate was added. The soil was dispersed by swirling and then 20ml of concentrated sulphuric acid immediately added to wet the sample. 200ml of water was added with 4-5 drops of Ferroin indicator. The resulting mixture was titrated using 0.5m potassium permanganate.

Calculation:

\[\text{Organic Carbon} \% = \frac{\text{meg of K2cr2O7} - \text{meg FedO4} \times 0.36}{\text{oven-dried soil (g)}}\]

Organic matter \% = Organic Carbon \% x 1.724.

Total Nitrogen: Percentage nitrogen was determined following the method of the Association of Official Agricultural Chemists (AOAC, 1980). This was done by titrating distilled digested sample and 0.02m NaOH.

Calculation:

\[\% \text{N} = \frac{A_{1} \times 0.08 \times 100}{\text{Wt of soil}}\]

A\(_{1}\) = titre value

Exchangeable Cations: Exchangeable cations (\(\text{Ca}^{2+}, \text{K}^{+}, \text{Na}^{+}, \text{Mg}^{2+}\)) were determined using the method of Jackson (1970). 2.5g of soil sample was transferred into a conical flask followed by the addition of 25ml of 1m ammonium acetate (\(\text{CH}_3\text{COONH}_4\)). The mixture was shaken for 45 minutes and the extract was filtered into glass beakers. Aliquots of the filtrate was used to determine the \(\text{Ca}^{2+}, \text{K}^{+}, \text{Na}^{+}\) using flame photometer. Versanate EDTA
titration method was employed in determining the amount of soluble magnesium and calcium.

**Exchangeable Acidity**: This was determined 2.5g of sample transferred into a conical flask, followed by addition of 25ml of 1N potassium chloride. The mixture was shaken for 20 minutes and filtered. 10ml of filtrate was titrated using 0.1N sodium hydroxide. The Effective Cation Exchange Capacity and Base Saturation were estimated by formular:

\[
\% \text{ BS} = \frac{\text{TEC} \times 100}{\text{ECEC}}
\]

BS = Base saturation; TEC = Total Exchange Base Cation; ECEC = Effective Cation Exchange Capacity.

**Heavy Metals**: Heavy metals were determined using the method described by AOAC (2005). 1g of air-dried soil was weighed and transferred into a beaker with the addition of 10ml concentrated HNO₃. The mixture was heated and evaporated to dryness. The residue was dissolved in 25ml HCl and heated for approximately 15 minutes in open air. The sample was then transferred into a 100ml volumetric flask and diluted to volume with distilled water. The sample was filtered to remove suspended particulate matter before analysis. The prepared samples were analyzed for heavy metals using Atomic Spectrophotometer with the specific wavelengths for each metal set for precision.

**Calculation**: 

\[
C = \frac{\text{Co} \times V}{M}
\]

C=concentration of heavy metals in sample (mg/g); Co= the metal concentration read from calibration curve; V= the total volume of solution (ml); M=the weight of dried sample taken for analysis (g).

**Statistical Analysis**: The values obtained were expressed in Bar Charts for quick appreciation of the data.

**RESULTS**

The results of particle size density were shown in Table 1. The results revealed that percentage sand increased as pollution increased with the seepage area recording the highest (85%) and the control with the least (63%) while percentage silt and clay decreased as pollution increased. The seepage area recorded the least (4% silt and 11% clay) while the control recorded the highest (10% silt and 27% clay) (Table1)

The organic carbon, organic matter, and total exchangeable acids increased with increase in pollution. However, total nitrogen increased as pollution decreased (0.11 for the seepage area and 0.25 after a distance of 100m). The control recorded 0.68. The pH values showed increase in acidity as pollution increased (4.50 for seepage area and 5.45 after 100m distance away from seepage area). The control recorded a pH of 6.20 (Table 2).

Table 3 showed the exchangeable cations. Ca²⁺, Mg²⁺ and Cation exchange capacity (CEC) increased as pollution increased, however, Na⁺ and K⁺ increased with decease in pollution. The CEC decreased from polluted sites to control sites. The
seepage area has the highest value for the heavy metals (iron, copper, manganese and lead) while the control recorded the lowest (Table 4). The results were expressed in Bar charts for quick appreciation of the data (Figures 1, 2, 3, 4).

**Table 1: Particle Size Density (Percentage) of Soil Samples**

<table>
<thead>
<tr>
<th>Samples (Meters)</th>
<th>Sand (%)</th>
<th>Silt (%)</th>
<th>Clay (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seepage area</td>
<td>85.00</td>
<td>4.00</td>
<td>11.00</td>
</tr>
<tr>
<td>10M</td>
<td>85.00</td>
<td>4.00</td>
<td>11.00</td>
</tr>
<tr>
<td>30M</td>
<td>83.00</td>
<td>5.00</td>
<td>12.00</td>
</tr>
<tr>
<td>50M</td>
<td>72.00</td>
<td>5.00</td>
<td>23.00</td>
</tr>
<tr>
<td>70M</td>
<td>71.00</td>
<td>5.23</td>
<td>23.77</td>
</tr>
<tr>
<td>100M</td>
<td>67.00</td>
<td>6.00</td>
<td>27.00</td>
</tr>
<tr>
<td>Control</td>
<td>63.00</td>
<td>10.00</td>
<td>27.00</td>
</tr>
</tbody>
</table>

**Figure 1: Bar Chart Representing Particle Size Density of soil Samples**

**Table 2: Exchangeable Acidity of Soil Samples**

<table>
<thead>
<tr>
<th>Samples (Meters)</th>
<th>Organic Carbon</th>
<th>Organic Matter</th>
<th>Total Nitrogen</th>
<th>pH</th>
<th>Total Exchangeable Acidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seepage area</td>
<td>2.2</td>
<td>3.7</td>
<td>0.11</td>
<td>4.5</td>
<td>2.00</td>
</tr>
<tr>
<td>10M</td>
<td>1.8</td>
<td>3.2</td>
<td>0.13</td>
<td>4.8</td>
<td>1.40</td>
</tr>
<tr>
<td>30M</td>
<td>1.6</td>
<td>2.8</td>
<td>0.14</td>
<td>5.0</td>
<td>1.30</td>
</tr>
<tr>
<td>50M</td>
<td>1.5</td>
<td>2.6</td>
<td>0.15</td>
<td>5.2</td>
<td>1.20</td>
</tr>
<tr>
<td>70M</td>
<td>1.2</td>
<td>2.2</td>
<td>0.17</td>
<td>5.3</td>
<td>1.00</td>
</tr>
<tr>
<td>100M</td>
<td>1.0</td>
<td>1.8</td>
<td>0.25</td>
<td>5.4</td>
<td>0.80</td>
</tr>
<tr>
<td>Control</td>
<td>0.8</td>
<td>1.3</td>
<td>0.68</td>
<td>6.2</td>
<td>0.64</td>
</tr>
</tbody>
</table>

**Figure 2: Bar Chart Representing Summary of Exchangeable Acids in the Different Soil Samples**

**Table 3: Exchangeable Cations of the Different Soil Samples**
<table>
<thead>
<tr>
<th>Samples (Meters)</th>
<th>Ca^{2+} (mg/g)</th>
<th>Mg^{2+} (mg/g)</th>
<th>K^+ (mg/g)</th>
<th>Na^+ (mg/g)</th>
<th>EC (mg/g)</th>
<th>BS (%)</th>
<th>P (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seepage area</td>
<td>3.3</td>
<td>1.6</td>
<td>0.0</td>
<td>0.0</td>
<td>7.0</td>
<td>71.5</td>
<td>7.0</td>
</tr>
<tr>
<td>10M</td>
<td>2.3</td>
<td>1.2</td>
<td>0.0</td>
<td>0.0</td>
<td>5.0</td>
<td>72.2</td>
<td>8.0</td>
</tr>
<tr>
<td>30M</td>
<td>1.8</td>
<td>1.0</td>
<td>0.0</td>
<td>0.1</td>
<td>4.2</td>
<td>69.4</td>
<td>9.0</td>
</tr>
<tr>
<td>50M</td>
<td>1.8</td>
<td>1.8</td>
<td>0.0</td>
<td>0.1</td>
<td>4.9</td>
<td>75.9</td>
<td>9.4</td>
</tr>
<tr>
<td>70M</td>
<td>1.6</td>
<td>0.8</td>
<td>0.0</td>
<td>0.1</td>
<td>3.5</td>
<td>72.1</td>
<td>9.5</td>
</tr>
<tr>
<td>100M</td>
<td>1.1</td>
<td>0.6</td>
<td>0.0</td>
<td>0.1</td>
<td>2.7</td>
<td>79.9</td>
<td>9.8</td>
</tr>
<tr>
<td>Control</td>
<td>1.8</td>
<td>0.8</td>
<td>0.1</td>
<td>0.2</td>
<td>3.7</td>
<td>82.7</td>
<td>14.04</td>
</tr>
</tbody>
</table>

Ca= calcium; Mg= Magnesium; K= Potassium; Na= Sodium; ECEC= Cation Exchange Capacity; BS= Base Saturation; P= Phosphorus.

**Figure 3:** Bar Chart Representing Summary of Exchangeable Cations in the Different Soil Samples

**Table 4:** Heavy Metals/ Micronutrients in Different Soil Samples

<table>
<thead>
<tr>
<th>Samples (Meters)</th>
<th>IRON (mg/g)</th>
<th>COPPER (mg/g)</th>
<th>MANGANESE (mg/g)</th>
<th>LEAD (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seepage (Meters)</td>
<td>51.20</td>
<td>4.62</td>
<td>16.24</td>
<td>5.60</td>
</tr>
<tr>
<td>10</td>
<td>38.23</td>
<td>3.92</td>
<td>12.88</td>
<td>4.90</td>
</tr>
<tr>
<td>30</td>
<td>35.22</td>
<td>3.64</td>
<td>9.10</td>
<td>4.62</td>
</tr>
<tr>
<td>50</td>
<td>31.77</td>
<td>3.08</td>
<td>8.82</td>
<td>4.34</td>
</tr>
<tr>
<td>70</td>
<td>23.72</td>
<td>2.04</td>
<td>8.40</td>
<td>4.06</td>
</tr>
<tr>
<td>100</td>
<td>22.00</td>
<td>1.26</td>
<td>8.26</td>
<td>3.50</td>
</tr>
<tr>
<td>Control</td>
<td>23.60</td>
<td>2.24</td>
<td>7.84</td>
<td>2.38</td>
</tr>
</tbody>
</table>
DISCUSSION

This work on the physicochemical studies of soil contaminated with refined petroleum in Eluama community, was designed to investigate the current suitability of the soil for land utilization, after over a decade of oil spill. The results shown in Table 1, revealed that percentage of sand increased as pollution increased, while the percentage of silt and clay decreased with increased pollution. The pH of the polluted soil was more acidic with the seepage area having a pH of 4.50 which increased as pollution decreased. The control sample from unpolluted farmland has a pH of 6.20 (Table 2). The increase in acidity of the soil samples associated with petroleum hydrocarbon pollution was also reported by other authors (Akubugwo et al., 2009; Nwaogu and Onyeze, 2010). The acidity of the polluted area can cause a shift in normal metabolism of living things within an ecosystem (Nwaogu and Onyeze, 2010).

The total nitrogen level decreased with increased pollution. This finding disagrees with the findings Akubugwo et al (2009) on the same polluted area, where total nitrogen level was more elevated in the impacted soil, compared with the control. The increase in total nitrogen level in the control sample compared with the polluted area could be as a result of the activities of nitrogen-fixing bacteria and other microbes associated with decomposition of organic matters, which might be inactivated in the polluted area. However, there were increases in organic carbon and organic matter when compared with the control. Osuji and Onojake (2006) attributed this to the metabolic processes following oil spillage that facilitates agronomical addition of organic carbon from petroleum hydrocarbon by reducing the carbon mineralizing capacity of the microflora.

The concentrations of Exchangeable cations (Ca$^{2+}$, Mg$^{2+}$, K$^{+}$, Na$^{+}$) show that Ca$^{2+}$ and Mg$^{2+}$ increased as distances approach seepage area while K$^{+}$ and Na$^{+}$ decreased with increase in pollution (Table 3). Akubugwo et al (2009) and Onyeike et al (2000) also reported such increase in Ca$^{2+}$ and Mg$^{2+}$ from refined petroleum and crude oil polluted soils.

Concentration of heavy metals from the polluted soil samples and the control were shown in Table 4. Values representing the maximum allowable limits (MAL) of heavy metals in soils vary from place to place. The value largely depends on the local or regional background and the threshold values (Nwachukwu et al., 2010). Results from this study revealed increased concentration of iron, copper, manganese and lead, compared with the control. The increase of these heavy metals in the polluted soil samples may be attributed to hydrocarbon pollution.

![Figure 4: Bar Chart Representing Summary of Heavy Metals/Micronutrients in the Different Soil Samples](image)
(Kakulu et al., 1985). Akubugwo et al (2009) on the same area agrees with this report. However, there are appreciable decreases of these heavy metals from this survey compared with the report of Akubuokwu et al (2009). Iron decreased from 52.2mg/g to 51.20, copper from 17.28 to 4.62, manganese from 17.58 to 16.24 and lead from 15.03 to 5.60 on the heavy polluted/seepage area. These figures with respect to the comparisms show that natural rehabilitation is in process. However, full remediation has not taken place and as such a longer period of time is needed for subsequent studies to check the extent of natural rehabilitation necessary for agricultural activities.

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affected by crude oil spillage. 


