Analysis Of Selected Trace Metals From Oil (Petroleum Products) In A Polluted Soil (A Case Study Of Offa Local Government Area)


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ABSTRACT: The concentrations of heavy metals (Fe, Cu, Cr, Pb and Ni) in soil samples of filling stations and those of a control area (about a kilometer away from the filling stations) were investigated by sequential extraction method using Atomic Absorption Spectrometer (AAS). Results obtained showed the mean concentrations (mg/kg) of Fe, Cu, Cr, Pb and Ni in soil of studied areas as 18.43, 0.01, 0.012, 0.02, and 0.01 respectively while in controlled area soil are Fe, Cu, Cr, Pb and Ni had concentrations (mg/kg) of 10.376, 0.007, 0.004, 0.005 and 0.0048 respectively. Levels of the heavy metals in soils of both studied areas were observed to be lower than European Union safe limits.

Keywords: Heavy metals, soil, Concentrations, Atomic Absorption Spectrometer.

1.0 INTRODUCTION

Oil is defined as a broad range of hydrocarbon-based substances, which are of two types: mineral oil such as different specific distillates of crude oil, and organic oil such as animal fats and vegetable oils. Natural gas, crude oil, tars and asphalts are types of petroleum hydrocarbons [1]. The word "petroleum" means "rock oil" or "oil from the earth" [2]. Petroleum widely used in our daily life plays a vital role in our modern economy. We are dependent on it in many ways as it provides great benefits to society. It is not only the main energy source for heating, transportation and manufacturing, but also acts as a raw material for plastics and synthetic rubber [3]. Petroleum hydrocarbons (PHCs) are used to describe mixtures of organic compounds found in or derived from geological substances such as oil, bitumen and coal [4]. They are composed of two categories: Gasoline range organics which refers to small chain alkanes (C6-C10), e.g. methane, ethane, propane, volatile aromatic compounds (e.g. BTEX) and common oxygenates (e.g. MTBE and ethanol) and Diesel range organics are the alkanes with longer chains (C10-C40) or non-halogenated semi-volatile organic compounds and hydrophobic chemicals such as PAHs (e.g. naphthalene, phenanthrene, anthracene, benzopyrene) [5][1]. The small chain alkanes, such as isopentanes, always have low boiling point between 60 and 170°C. Pollution is defined by Robert (1971) [6] as the contamination of the environment with any material or state of condition that create a stress on or unfavorable situation of an individual or organism, population, community or ecosystem beyond what is found in natural environment condition”. Nest (1982) [7] defined environmental pollution as “an undesirable change in the physical and biological characteristics of our air, land, water that may adversely affect human living conditions. Any situation which therefore disturbs in anyway the condition under which any person or thing lives or develop and hamper the development of life and character is environmental pollution [8]. Contamination of heavy metals in the environment has been shown to be of major concern because of their toxicity and threat to human life and the environment. Several studies have been carried out on trace elements contamination in soils from various anthropogenic sources such as industrial wastes[9].

2.0 LITERATURE REVIEW

Adverse effects of crude oil contamination of the natural environment include the poisoning of animals and plants, altering of ecosystems, and the potential risk to human health if the contaminated product is ingested. Again, owing to their chemical structure, many synthetic organic compounds could be extremely resistant to natural breakdown processes. Therefore, when released into the environment, they may persist for years and even decades [10]. Volatile organic compounds (VOCs) are vapours emitted by various petroleum products, cleaning supplies and adhesives many of which have short- and long-term adverse health effects. The volatilization from contaminated materials can release substantial amounts of hydrocarbons up to 30 ppm (Akutam, 2012) [11] and contribute significantly to environmental degradation. The aromatic compounds which can induce carcinogenic and mutagenic reactions are particularly problematic because they pose serious health challenges for the population [11]. Groundwater is one of the many media through which human beings, plants and animals come into contact with petroleum hydrocarbon pollution [12]. The major concern therefore is its contamination potential and the challenge posed to clean-up. The poor miscibility of crude oil accounts for the accumulation of free oil on the surface of ground water and this may migrate laterally over a wide distance to pollute other zones very far away from the point of pollution [13]. In environments that are completely aquatic, oil sometimes floats on water surfaces where it is dispersed to shorelines by wind and wave actions invariably affecting the mangrove floor [14]. Furthermore, due to the release of mineral oil hydrocarbons (MOH), phenol, and polycyclic aromatic hydrocarbons (PAHs) often rich inlare amounts of tar, drinking water supplies have been endangered and often polluted [13]. Crude oil spills have been reported to affect soil...
fertility but the scale of impact depends on the quantity and type of oil spilled. Spent engine oil also, when present in the soil, creates an unsatisfactory condition for organic life in the soil due to the poor aeration condition established therein, immobilization of soil nutrients, and the lowering of soil pH \[15\]. Petroleum hydrocarbons contamination has also been reported to affect plants by retarding seed germination and reducing shoot height, stem density, photosynthetic rate and over all biomass yield (in the short run), and resulting in complete mortality in the long run. \[16, 17, 18\]. On land, crude oil spills have caused great negative impact on food production. For example, an appreciable percentage of oil spills that occurred on the dry land between 1978and 1979 in Nigeria, affected farmlands in which crops such as rice, maize, yams, cassava, plantain and other staples were cultivated and since this infraction has persisted till date, anticipated yields from harvest have remained largely illusory and so is food security in the zone of contamination. This invariably has shot up commodity prices and has also reduced living standards \[19\]. Again, because many toxic synthetic organic compounds are persistent in nature, when ingested by organisms at higher levels of the food chain, they tend to be stored in the fatty tissues due to their hydrophobic properties resulting in bioaccumulation \[20\]. These researchers also reported that PAHs and BTEX components of petroleum hydrocarbons have also been observed to affect the liver, lungs, kidneys and nervous system leading to cancer as well as immunological, reproductive, feto-toxic and geno-toxic effects or Biomagnifications. This may arise as a result of the physiological effects of the toxins in higher organisms. Again, at the highest level of the food chain, i.e. humans, these toxic organic compounds can be passed from mother to child either in uterus via the placenta orpost-natally via breast milk if ingested \[21\]. Crude oil spilled into mangrove environments under the tidal influences that characterize the marine ecosystem provides for wider dispersal and distribution in the intertidal flats (zones) resulting in the deposition of crude oil and or other petroleum products on the aerial roots and sediments \[22\]. Thus, crude oil covers the deposition of air and or other petroleum products on the aerial roots and sediments \[22\]. Thus, crude oil covers the breathing roots and pores, thereby asphyxiating the sub-surface roots that depend on the pores for oxygen transfer and in turn impairs the normal salt exclusion process resulting in the accumulation of excess salt in the plant thereby contributing to an enhanced stress condition of the plant and ultimately, to death/loss of mangrove plants, habitat destruction and degradation \[22\].

### 3.0 MATERIALS AND METHODS

#### 3.1 Triplicate of soil sample were collected each at a depth of 0.20cm with a stainless steel spoon from three different points of petrol stations. The distance from one sampling point to other was 10 meters. Controlled soil samples (soil without petrol) was also sample in triplicate from three different points of controlled area of about 500m away from the petrol stations. A polythene bag was used for sample storage.

#### 3.2 Soil samples were air dried in the laboratory at room temperature and sieved with a 200 mm to remove stones and fragments, was later dried at 105°C in an oven and crushed into fine powder.

#### 3.3 2.0 g of the samples were weighed into four different beakers and 10 ml of HNO\(_3\) and 5 ml of HCl was added to each samples on a hot plate and were allowed to digest for 3 hours, the digested samples were diluted with 10 ml of distilled water and were filtered, the filtrates were made up to 25 ml with distilled water and were transferred into the appropriate sample bottles. The concentration of trace metals Cr, Cu, Zn, Fe, Pb, Ni, and Cd was then determined using Atomic Absorption Spectrometer (AAS).

### 4.0 RESULTS AND DISCUSSION

#### RESULTS

#### 4.1 Heavy Metals determination

The results of elemental analysis of soils at the three locations and controlled area is summarized in Table 1

#### Table 1: Concentrations of Heavy Metals in Study Area (Mg/g)

<table>
<thead>
<tr>
<th>Locations</th>
<th>(Fe) mg/g</th>
<th>(Cu) mg/g</th>
<th>(Cr) mg/g</th>
<th>(Pb) mg/g</th>
<th>(Ni) mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>25031.31</td>
<td>16</td>
<td>20</td>
<td>31.25</td>
<td>6.12</td>
</tr>
<tr>
<td>A2</td>
<td>15656.37</td>
<td>10.25</td>
<td>6.25</td>
<td>13</td>
<td>4.75</td>
</tr>
<tr>
<td>A3</td>
<td>14593.87</td>
<td>10.25</td>
<td>9.37</td>
<td>19.87</td>
<td>2.75</td>
</tr>
<tr>
<td>Control</td>
<td>10376.75</td>
<td>7.0</td>
<td>4.75</td>
<td>5.125</td>
<td>2.75</td>
</tr>
</tbody>
</table>

#### Table 2: Mean concentration of Heavy Metals in Study Areas & EU Standards (mg/kg)

<table>
<thead>
<tr>
<th>Locations</th>
<th>(Fe) mg/kg</th>
<th>(Cu) mg/kg</th>
<th>(Cr) mg/kg</th>
<th>(Pb) mg/kg</th>
<th>(Ni) mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>25.03</td>
<td>0.017</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>A2</td>
<td>15.65</td>
<td>0.01</td>
<td>0.006</td>
<td>0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>A3</td>
<td>14.59</td>
<td>0.010</td>
<td>0.009</td>
<td>0.01</td>
<td>0.003</td>
</tr>
<tr>
<td>Control</td>
<td>10.37</td>
<td>0.007</td>
<td>0.004</td>
<td>0.05</td>
<td>0.003</td>
</tr>
<tr>
<td>EU Standard</td>
<td>1500</td>
<td>20-30</td>
<td>100</td>
<td>90-300</td>
<td>50.0</td>
</tr>
</tbody>
</table>

#### Table 3: Mean Concentrations of heavy metals in control area mg/g.

<table>
<thead>
<tr>
<th>(Fe) mg/g</th>
<th>(Cu) mg/g</th>
<th>(Cr) mg/g</th>
<th>(Pb) mg/g</th>
<th>(Ni) mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>18427.19</td>
<td>12.17</td>
<td>12.00</td>
<td>21.38</td>
<td>4.54</td>
</tr>
</tbody>
</table>

#### Table 4: Mean Concentrations of heavy metals in control area mg/kg.

<table>
<thead>
<tr>
<th>(Fe) mg/kg</th>
<th>(Cu) mg/kg</th>
<th>(Cr) mg/kg</th>
<th>(Pb) mg/kg</th>
<th>(Ni) mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.43</td>
<td>0.01</td>
<td>0.012</td>
<td>0.02</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 1 shows the concentrations of heavy metals (iron, copper, chromium, lead and nickel) in mg/g in the soil samples of various petrol filling stations and the controlled area, while table 2 shows the concentration in mg/kg and table 3 & 4 shows the mean concentrations of heavy metals in the soil samples. The metal content in the soil varied significantly from one sampling location to another and was also compared with the controlled area results. Iron (Fe)
content ranged from 14.59-25.03 mg/kg. Copper (Cu) ranged 0.01-0.02 mg/kg. Chromium (Cr) ranged from 0.009-0.02 mg/kg. Lead (Pb) ranged from 0.01-0.03 mg/kg while Nickel (Ni) ranged from 0.00-0.04 mg/kg. In this research the levels of concentration in increasing order Fe > Pb > Cu > Cr > Ni. The concentrations were lower than European Commission (EU limits) of 15000 mg/kg, 100 mg/kg, 100 mg/kg, 90-300 mg/kg and 50 mg/kg respectively. While the concentration in the control area are Fe 10.37mg/g, Cu 0.007 mg/g, Cr 0.004 mg/kg, Pb 0.005 mg/kg and Ni 0.003 mg/kg which are also lower than EU limits of 15000mg/kg, 100mg/kg, 100mg/kg, 90-300mg/kg and 50kg/g respectively.

DISCUSSION
Ni concentration from three location range between 0.002-0.02 mg/kg and that of control area is 0.003 mg/kg which are lower than the recommended EU standard. The range of Ni concentration in all the soil samples in this research is also lower than what obtained in some other studies carried in the united state (2.44 mg/kg) (Shacklette and Boerngen 1984) [82], China (7.73 mg/kg) (Dudka, 1992), [83] Poland (2.0mg/kg) (Bradford et al., 1996) [84] Ethiopia (47.3 mg/kg) (Melaku et al., 2005[85]) and India (343 mg/kg[86]). Natural concentration of Nickel in soil is less than 100 mg/kg it can be exceptionally high in some cases especially the soil formed from ultra-basic rocks. Diseases related to high level of heavy metal in system include lung tissue damage respiratory illness, liver and kidney failure and others. [87] Pb concentration from the three locations ranged from 0.01-0.03 mg/kg and that of the control area is 0.005 mg/kg which are lower than the limit of 90-300 mg/kg recommended by EU standard. The range of Pb concentration in all the soil samples in this research is also lower than what obtained in some studies carried out in Lagos Metropolis was 69.20 mg/kg. The result of lead concentration in soil of old industrial cities like Uppsala (in northern European) have the mean Pb level in playground soil to be 26 mg/g (Ljung et al., 2006), [88] while cities such as Hong Kong which have their mean Pb level in playground soil to be 77.3 mg/kg (Sai et al., 2012)[89]. In Lagos Metropolis was 69.20 mg/kg. The result of lead concentration in soil of old industrial cities like Uppsala (in northern European) have the mean Pb level in playground soil to be 26 mg/g (Ljung et al., 2006), [88] while cities such as Hong Kong which have their mean Pb level in playground soil to be 77.3 mg/kg (Sai et al., 2012)[89]. The lead concentration in this research were lower than the range of 30-50 mg/kg reported by Nrigu (1992)[90] as typical concentration of lead in urban soils of African cities which gives cause for concern. However, the source of Pb in the urban could be more due to oil spillage during storage or rusted of the storage tanks or leakages. It was revealed by Atunya and Osegbe (2006)[92] that higher lead concentration in soil has toxic effect on microorganism inhabiting the soil which consequently alters the flora and fauna of the location. Lead has been found to be the major cause of hypertensions, impairment of central nervous system and other respiratory troublesome adult. [93] The upper limit of Cr in this research is (0.02 mg/kg) and that of the control area is 0.007 mg/kg which is less than the limit of 100 mg/kg recommend by EU standard. Trace amount of meta such as trivalent chromium entering the body through various routes is capable of inducing genetic and epigenetic alteration in different cancer related gene somatic and stem cells, thus involving in cancer stem cell formation and increasing the incidence of cancer.

The concentration of Fe for this research ranges from 14.39-25.03 mg/kg and that of control area 10.37 mg/kg which is lower than what was obtained in Lagos Metropolis. The concentration was found to be 1528.3 mg/kg Fe has to be found to occur at high concentration in Nigeria soil (Adefemi et al., 2007)[94] Olakanmi and Adeoye (2012) [95], as obtained in his study. The high concentration of these metals in soil samples may also be due to oils spillage or leakage of the storage tank in the filling station or the natural lithogenic or pedogenic processes (Woodhouse, 1983)[96], as well as anthropogenic factors which result in environmental pollution [96]. The concentration of Cu in this research ranged from 0.01-0.02 mg/kg and that of the control area is 0.007 which has lower than the EU standard limit 20-30 mg/kg this can be attributed to spilt of oil (petrol, diesel) during the storage or leakage from the storage tank. Cu is essential element, but may be toxic to both humans and the animals when its concentration exceeded the safe limit. Cu is used in numerous applications because of its physical properties. The toxicity for human is not very high (Poggio et al., 2009) [97] Cu normally accumulated in the surface horizons a phenomenon explained by bioaccumulation of metals and recent observed values of the Cu content did exceed the normal threshold value prescribed in soil 20-30 mg/kg [98].

5.0 CONCLUSION
Speciation analyses give relevant information on the toxicity and biological activity of elements because the effects of these elements in soils do not depend on their concentrations alone, but also on their oxidation states and/or chemical forms. The results obtained from the sequential analysis of soils collected filling stations Offa indicated that the concentrations of Fe, Cu, Cr and Pb and Ni were lower than permissible levels. Generally, the levels of heavy metals in soils in the study area were observed to be lower than those of previous studies in industrial and residential areas and also lower than allowable limits by relevant standard organizations, this may be due partly to the controlled and cautious activity of the filling stations.

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