ABSTRACT

Monitoring of polluted sites require their assessment for effective management and environmental protection. This study assessed the soil properties including heavy metals (Fe, Zn, Mn, Cu, Cr, Pb, Cd and Ni) and total petroleum hydrocarbon (TPH) of a three-decade-old automobile workshop in Benin City. Top soil samples collected from outside the workshop and a control were analyzed using standard laboratory methods and their mean values were compared with critical limits for interpreting soil fertility as well as pollution status. The results showed that the texture of the polluted soil was unchanged but the pH has been modified from strongly to slightly acidic. Relatively slightly higher concentrations of the measured fertility parameters of the polluted site were not substantial for the very low organic C, N and Mg as well as the low for Ca, Na and EC because their ratings were not different from those of the control unlike the high ratings for K and P compared to medium and low in the control, respectively. Concentration of EA of the polluted soil was rated low as the control while effective CEC (cmol/kg) was low for the polluted (6.42) site compared to very low (4.80) of the control. Higher concentrations (mg/kg) of heavy metals in polluted soil were < their DPR target values, except Cd (5.1) which exceeded its limit (0.8). Increased concentration (mg/kg) of TPH from 0.22 to 825 was < its target value of 1,000. Decontamination of Cd from site should be carried out to avoid ill health of workers.

Keywords: Automobile workshop, Cadmium, Heavy metals, Polluted soil, Total petroleum hydrocarbon (TPH)
INTRODUCTION

Many Automobile workshops are the largest small quantity, more than 100 but less than 1,000 kg/month, generators of hazardous waste (Duramin-Iya et al., 2023) which due to indiscriminate discharge can pose threat to our environment. Services rendered at such sites: cleaning, painting, and changing of fluids (oil, transmission, and brake types) are usually accompanied with the dismantling of car components and spillage of both fresh and spent oil which release contaminants. These waste which constitute petroleum products led to soil contamination with heavy metal and petroleum hydrocarbon (NRC, 2003) and one of the components of hydrocarbon is total petroleum hydrocarbons (TPH) – complex mixtures of saturated (primarily paraffins, 60–80%) and aromatic (2–40%) hydrocarbons (Li et al., 2018).

Changes in soil physicochemical properties when contaminated by petroleum and its products are based on soil type, initial condition, and the type and concentration of contaminant (Zahermand et al., 2020). Although relatively higher organic C and reduced concentrations of major elements such as P and K have been reported (Stepanova et al., 2022), higher levels of N and P, on the contrary, also have been recorded (Nyarko et al., 2018). Generally, while heavy metals such as Cu, Zn, Mn, Si, V, Mo, and Fe are found in gasoline and petroleum products sold in Nigeria (Nworgu and Osahon, 2011), high levels of Pb and Cd as well as TPH have been reported by Muze et al. (2020) at auto mobile workshops in Aba and Port Harcourt, also located in southern Nigeria.

Anthropogenic sources of these elements in soil may pose risks and hazards to the ecosystem and humans through direct ingestion or contact with the soil and/or the food chain (Lombi and Gerzabek, 1998). Most refined hydrocarbons are very volatile and readily inhaled while TPH are highly lipophilic and are readily absorbed through skin and intact mucosae, except they have high viscosity (Dalefield, 2017).

Over the years – for up to a decade now, mechanics have been storing and selling waste engine oil which is used as weed killer, wood preservation, wood treatment, constituent of gear oil, and mixture with bitumen for road construction (Zitte et al., 2016). A practice that has reduced the volumes that used to spill on their workshop premises which implies the possibility of natural attenuation occurring in such environment. Consequently, there is need to characterize and assess the degree of risk of such sites to humans.

Thus, the objective of this study is to assess the effects of petroleum-based products and other wastes generated at automobile workshops on soil physicochemical properties: texture, pH, organic C, N, P, K, Ca, Mg, K, Effective cation exchange capacity (ECEC), EC (electrical conductivity); heavy metals (Fe, Zn, Mn, Cu, Cr, Pb, Cd and Ni); and total petroleum hydrocarbon (TPH) of a long-established polluted site in Benin City.

MATERIALS AND METHODS

Study Area

An auto mobile workshop at Evbareke, latitude 6.36453ºN and longitude 5.60973ºE, established over 35 years ago situated 100 m high above sea level within the city was randomly selected for this study. Rainfall in Benin City is usually of high intensity ranging between 1,800 – 2,780 mm (Atedhor et al., 2010) with a mean monthly temperature of 28ºC which may reach 34oC between the months of February and March. The humidity usually records highest value of 80 - 90% around August and lowest of 40 –50% from November-March. The environment is well known for the daily influx of people who purchase spare parts for mechanics to fix in their workshops. However, these artisans in the process of maintaining the vehicles dump spent engine oil and spill other lubricants e.g. break-fluid and
hydraulic oil which contains petroleum hydrocarbons and heavy metals around their workshops. Abandoned vehicles along with condemned lead batteries and scrap metal parts are also common on such sites.

Collection of soil samples
Soil samples were collected in triplicates from the top soils at 0 -10 cm depth at each sampling point within the workshop. A total of seven soil samples were collected at random and bulked together to form a representative sample. Soil samples were similarly collected as the control from a grassland at a distance of about 200 m away from the workshop which were labelled in separate bags and taken to the lab for analysis.

Analysis of soil samples
The soil samples were air dried, crushed and passed through a 2mm sieve before they were analyzed for physicochemical parameters. The soil pH was determined in a 1:2 soil/water ratio with a pH meter. Electrical conductivity (EC) was measured using a conductivity meter at 1:2 soil/water ratio. Particle size was determined by the hydrometer method of Bouyoucus as modified by Day (1965). Organic carbon was determined by the chromic acid wet oxidation procedure (Methods of Soil Analysis, 1996). Total nitrogen content was determined by the MicroKjeldahl procedure (Bremner and Mulvaney, 1983) and available phosphorus was measured in soil extracts by the ascorbic acid method (Bray and Kurtz, 1945).

Exchangeable Ca and Mg were determined on atomic absorption spectrophotometer (AAS) using perchloric acid while Na and K were measured on a flame photometer (Udo and Ogunwale, 1986). Ammonium acetate extracts of soil samples were used to determine the exchangeable bases (EB) by adding the values of the exchangeable cations (Ca$^{2+}$, Mg$^{2+}$, Na$^+$ and K$^+$). Exchangeable acidity (EA) was assessed by KCl extraction method (McLean, 1965) and calculated as the sum of exchangeable H$^+$ and Al$^{3+}$ ions while the effective Cation exchange capacity (ECEC) was calculated by adding the values of the total EA and total EB.

Determination of heavy metals followed the procedure of weighing the powdered sieved soil sample of 1g into a 125 ml conical flask and 20 ml of conc. HNO$_3$, 5 ml of HClO$_3$, and 2 ml of H$_2$SO$_4$ were added before the mixture was digested on a hot plate. The flask was cooled slightly and the digest was diluted to about 50ml with distilled water and filtered. The filtrate was made up to 100 ml mark and the tested trace metals (Fe, Zn, Mn, Cu, Cr, and Pb) were determined with an atomic absorption spectrophotometer (AAS).

Determination of TPH was assessed based on a modified version of EPA method 418.1 which involves extraction with N-Hexane as described by USEPA (1983). Five (5) grammes air dried soil sample that passed through a 2 mm sieve was weighed into a 50 ml glass tube and 20 ml of n-hexane was added to the soil in the tube. The tube was covered tightly and shaken for 15 mins and allowed to stand for 10 mins. The solvent phase was then decanted into a spectrophotometer cuvette and the % transmittance of the solution read at 420 nm.

Data Analysis
Data obtained were analyzed with Microsoft Excel into mean values and interpretation of the standard routine soil tests was adapted from Landon (1991), Beernaert and Bitondo (1992) as well as Gong (2022) while the heavy metals and TPH were compared with DPR (Department of Petroleum Resources) critical limits in soils.
RESULTS AND DISCUSSION

Results of the physicochemical properties of the polluted and control soil are shown in Table 1a. Although the clay content of the control (170 g/kg) was more than the polluted soil (130 g/kg) but the texture of both was sandy loam.

Table 1b shows the soil chemical properties. The pH of polluted site was slightly acidic (6.3) while the control was strongly acid (5.3) based on the rating by Batjes (1995). All the measured nutrient parameters of the polluted soil were only slightly higher than control, besides the high concentration of P (63.52 mg/kg) of the polluted which was nearly 6 times more than the low (9.46) of the control as rated by Landon (1991). Concentrations (g/kg) of organic C recorded as 2.51 and 2.40, and N measured as 0.36 and 0.20 for both polluted and control, respectively were rated as very low nutrient status (Landon, 1991). Low concentrations (cmol/kg) were interpreted for the basic ions which include Ca for the polluted (4.73) soils which was same as the control (3.50) and, Mg was very low for both polluted (0.42) like the control (0.25), Na was low (0.1–0.3) as the control while K rating for the polluted (0.74) was high in contrast to the control (0.54) which was medium based on the ratings by Beernaert and Bitondo (1992). Thus, EA (cmol/kg) was lower in the polluted soil (0.25) compared to the control (0.30) although the rating was low (<2.1) as the control. Consequently, the ECEC (cmol/kg) revealed a very low concentration for the control (4.80) compared to a low rating for polluted soil (6.42) as implied by Landon (1991). Although EC concentrations (mS/m) of the polluted site (34.6) was over three times (9.26) more than the control but both were of low (<80) ratings (Gong, 2022).

Accumulation of the tested heavy metals in both sites followed this order: Fe > Zn > Mn > Cu > Cr > Pb > Cd and Ni, with a general increase of about one and a half times in the polluted soils (Table 2). However, concentrations of all the tested metals were lower than the target value set by DPR (2002), besides Cd in the polluted soil (5.1 mg/kg) which was higher than the target value (0.8 mg/kg) by over 6 times. However, higher level of the element in the control (3.7 mg/kg) than the target value suggested contaminated. The concentration of TPH was significantly increased from 0.22 mg/kg to 825 mg/kg; which was less than the target value of 1000 mg/kg established by DPR (2002).

A relatively very high concentration of available P in the polluted soil suggests contamination. Studies by Jiang et al. (2021) revealed that high levels of Zn and P are found in waste lubricating oil among other elements. These elements are mainly from zinc dialkyl dithiophosphates (ZDDPs) which are commonly used lubricant additives. In addition, an increase in the soil pH of the polluted soil may have favoured the availability of the nutrient. Similar observations in this present study particularly about the increase of P in polluted soil as well as organic C and N have been reported by Nyarko et al. (2018) and Sattar et al. (2019) during their assessments of the soil of automobile workshops in Ghana and distribution of major elements in the soil profile of petroleum contaminated soils in Pakistan, respectively. In addition, Agbogidi et al. (2007) have reported that crude oil cause significant (p<0.05) higher concentrations of organic C, P, Ca, Mg and pH in soils.

High levels of EA of the control with a resultant lower pH implies more effect on soil conditions and processes in comparison to the polluted soil. These include increased bioavailability of Fe, Al, or Mn up to toxic levels (Liu et al., 2014); and fixation of P by Al causing its deficiency in plants (Thomson et al., 1993).

Soil EC relates well with other soil characteristics, especially fertility which indicates the availability of nutrients in soil (Seifi et al., 2010). Higher EC value implies more negatively charged sites in soil; and thus, the more cations held in the soil. Relatively higher EC values of the polluted soil recorded in this study imply more nutrients content, mainly due to the relatively higher P concentration. Unlike in the control soil, the EC value (34.6 mS/m) of the polluted soil exceeded the limit (20 mS/m) mentioned by Zaman et al. (2018) below which causes reduced water penetration,
degraded soil structure and promoted soil crusting, irrespective of the Na content. However, both were below the optimal EC levels in soil which range from 80–180 mS/m.

Although, increase of heavy metals in soils has been linked to pedogenic processes of weathering of parent materials and anthropogenic sources (Kabata-Pendias and Pendias, 2001; Osuji and Onojake, 2004) but the capacity of soil to retain contaminants is mostly caused by soil pH, type and amount of organic matter, content of (hydro-) oxides of Fe, Al and Mn, type and proportion of clay particles, soil biodiversity and moisture (FAO and UNEP, 2021). One or more of these soil properties interact and exert additive, synergistic, or antagonistic effects causing the loss of a contaminant either through volatilization or erosion.

Soil pH seemed to have had more influence on the contaminants in soil than clay content in this present study by regulating the surface charge of soil constituents and contaminant solubility. In acidic soils, the edges of clay, Fe, Mn, and Al (hydro-) oxides and amino (-NH2) groups in organic matter are protonated which causes many positive charges to attract anions on the binding sites.

Heavy metals in soil around automobile workshops are derived from various sources (NVSWCD, 2013). Lead is from the leaded gasoline, bearing and tire wear, lubricating oil and grease; Ni from diesel fuel, gasoline, lubricating oil, and brake emissions while Zn is from tires, motor oil, grease, brake emissions and corrosion of galvanized parts. There is Cd from tire wear, fuel burning, and batteries; Cr comes from air conditioning coolants, engine parts, brake emissions; Cu is released from bearing wear, brake emissions; Fe is from auto body rust and engine parts and Mn is used for improving stiffness, wear resistance, and hardness of some of the vehicle body part.

While the concentration and physicochemical properties of contaminants determine their fate and transport in soils, their chemical nature (e.g. hydrophobicity and volatility) affects their interaction with the soil matrix; however, size and spatial distribution will limit movement through soil pores (FAO and UNEP, 2021). Soil components (clays, (hydro-)oxides of Fe, Mn, and Al, and organic matter) possess charged positive and negative surfaces either permanent or variable (due to pH and salt in soil solution) which create binding sites for cations and anions to bind - determining their exchange capacities (Osman, 2013; Sumner and Miller, 1996).

Relatively low DPR target value for Cd (0.8 mg/kg) means that is very toxic to humans. Among the non-essential metals, the element is most known in the fields of soil science and plant nutrition because of its potential toxicity to human, and relative mobility in the soil-plant system (McLauglin and Singh, 1999). Cadmium is contacted through air, water, soil and food by man can accumulate both in plants and animals with a long half-life of about 25–30 years (Genchi et al., 2020). Exposure for a long time causes different types of cancer of the lung, breast, prostate, pancreas, and kidney as well as causes toxicity of some organs and systems. Toxicity for a long time can cause humans severe pain, bone fractures and osteomalacia (Lee et al., 2005).

Similar to the observation in this present study, Meindinyo and Agbalabga (2012) reported that hydrocarbon pollution increases soil acidity and heavy metals in soil. In addition to deterioration of soil physical, chemical, and biochemical properties; deficiency of O₂ and H₂O₂; limitation of N and P-based nutrients as well as plant growth in soils (Anm, 2018; Mohammadi et al., 2020). However, contrary to this present study, the concentrations of both N and P in the polluted soil were higher than in the control.

The lower concentrations of the metals and TPH in the polluted site over the years compared to the target value may be due to the transportation of the contaminants from such premises. During rainfall, these contaminants may dissolve surface soil water and get washed away, or transported with shallow subsurface water while adsorbed to mineral soil particles and dissolved organic matter (Ciffroy, 2018).
Pollution caused by TPH can affect soil quality for a short or long time (Edori and Kpee, 2019) including the living creatures within the area. After introduction of this compound to soil, the volatile ones evaporate while the heavier ones seep through soil and get to the groundwater (Laskova et al., 2007). The remaining ones become attached to soil particles for a long period while the others become degraded by microorganisms.

### Table 1a: Physical properties of polluted and control soils

<table>
<thead>
<tr>
<th>Site</th>
<th>Sand (g/kg)</th>
<th>Silt (g/kg)</th>
<th>Clay (g/kg)</th>
<th>Texture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polluted</td>
<td>780</td>
<td>90</td>
<td>130</td>
<td>Sandy loam</td>
</tr>
<tr>
<td>Control</td>
<td>680</td>
<td>150</td>
<td>170</td>
<td>Sandy loam</td>
</tr>
</tbody>
</table>

### Table 1b: Soil chemical properties of polluted and control sites

<table>
<thead>
<tr>
<th>Site</th>
<th>pH</th>
<th>C (g/kg)</th>
<th>N (g/kg)</th>
<th>P (mg/kg)</th>
<th>Ca (cmol/kg)</th>
<th>Mg (cmol/kg)</th>
<th>Na (cmol/kg)</th>
<th>K (cmol/kg)</th>
<th>EA (g/kg)</th>
<th>ECEC (mS/m)</th>
<th>EC (mS/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>6.3</td>
<td>2.51</td>
<td>0.36</td>
<td>63.52</td>
<td>4.73</td>
<td>0.42</td>
<td>0.28</td>
<td>0.74</td>
<td>0.25</td>
<td>6.42</td>
<td>34.6</td>
</tr>
<tr>
<td>C</td>
<td>5.3</td>
<td>2.40</td>
<td>0.20</td>
<td>9.46</td>
<td>3.50</td>
<td>0.25</td>
<td>0.21</td>
<td>0.54</td>
<td>0.30</td>
<td>4.80</td>
<td>9.26</td>
</tr>
</tbody>
</table>

Critical limits of interpreting level of soil fertility:

- VL: <5.8, <0.5, <2.0, <0.5, <0.1, <0.1, <5.0, <2.0, <0.5, <0.1, <5.0, <2.0
- L: 5.8-12.0, 0.50-1.25, 15.0-50.0, 2.0-5.0, 0.5-1.5, 0.1-0.3, 0.1-0.3, <2.1, 5.0-15.0, <80.0
- M: 12.0-25.0, 1.26-2.25, 15.0-50.0, 2.0-5.0, 1.5-3.0, 0.3-0.7, 0.3-0.6, 2.1-4.0, 15.0-25.0, 80.0-180.0
- H: 25.0-35.0, 2.26-3.0, >50.0, 10.0-20.0, 3.0-8.0, 0.7-2.0, 0.6-1.2, >4.0, 25.0-40.0, 180.0-250.0

### Table 2: Heavy metal levels and TPH in sampled soils and DPR critical limits in soil

<table>
<thead>
<tr>
<th>Metal</th>
<th>Fe (mg/kg)</th>
<th>Mn (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Zn (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Cd (mg/kg)</th>
<th>Cr (mg/kg)</th>
<th>Ni (mg/kg)</th>
<th>TPH (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>37.40</td>
<td>17.90</td>
<td>10.70</td>
<td>25.40</td>
<td>5.10</td>
<td>3.70</td>
<td>8.60</td>
<td>1.80</td>
<td>0.22</td>
</tr>
<tr>
<td>Polluted</td>
<td>52.50</td>
<td>27.80</td>
<td>15.40</td>
<td>40.00</td>
<td>8.00</td>
<td>5.10</td>
<td>11.40</td>
<td>3.60</td>
<td>825.00</td>
</tr>
<tr>
<td>DPR TV</td>
<td>5000</td>
<td>476</td>
<td>36</td>
<td>140</td>
<td>85</td>
<td>0.8</td>
<td>100</td>
<td>35</td>
<td>1000</td>
</tr>
</tbody>
</table>

DPR TV = Department of Petroleum Resources Target Value; TPH=Total petroleum hydrocarbon

**CONCLUSION**

This study revealed that the texture of the polluted site has not changed unlike the pH which has increased from strongly acidic to slightly acidic. Concentrations of all measured fertility parameters increased slightly in the polluted soil but not to a substantial extent for the very low ratings for organic C, N and Mg as well as the low for Ca and Na which were not different from those of the control. The high ratings for both K and P in the polluted site compared to medium and low of their respective concentrations in the control site implied considerable increment. Although the
low concentration of EC of the polluted soil was in the same range as the control but the value exceeded the limit (20 mS/m) which is insufficient for optimum growth of plants. Relatively lower level of EA recorded for the polluted soil was rated low as the control while concentration (cmol/kg) of effective cation exchange capacity (ECEC) was interpreted as low for the polluted (6.42) site compared to very low (4.80) for the control. Although, the site was contaminated with all the tested heavy metals and TPH but only the concentration (mg/kg) of Cd (5.1) exceeded the target value (0.8) set by DPR. Wastes generated at aged automobile workshops could considerably alter soil chemical properties which necessitate the use of protective gears until the decontamination of Cd is carried out, possibly with the employment of phytoremediation.

CONFLICTS OF INTEREST: The authors declare that they have no conflict of interest.

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