Original Research Paper

IJES *Iranian Journal of Earth Sciences*
*Vol. 15, No. 2, 2023, 77-93.*
DOI: 10.30495/ijes.2022.1943042.1663

# Contamination of arable topsoil by organic and inorganic pollutants around petroleum products handling facilities

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Received 1 February 2022; accepted 24 May 2022

## Abstract

The concentrations of heavy metals (inorganics) and poly aromatic hydrocarbons (organics) were determined in soils around fueling stations and automobile workshops. Mean concentrations of nickel, lead, cadmium and vanadium were 636, 1379, 12.0 and 18.0 µg/kg, respectively. Flourene, benzo (a) pyrene, benzo (b) fluoranthene and benzo (ghi) pyrelene recorded means of 2.01, 2.014, 1.14 and 1.12 µg/kg, respectively, but other poly aromatic hydrocarbons recorded means <1. Heavy metals levels were higher at sites of activities than the control site. Phenanthrene, naphthalene and benzo (k) fluoranthene were present at control site but absent in some locations of activity. These showed they were not only from petroleum products handling facilities. Mean levels of both inorganics and organics were below world standards for agricultural soil quality. Principal component analysis of heavy metals produced two principal components that explained 40.72% and 36.90% of the total variance. These reflect geological weathering, automobile exhaust and petroleum combustion sources. Analysis of poly aromatic hydrocarbons data produced four principal components, which explained 36.30%, 19.96%, 15.19% and 12.81% of total variance. The sources of these organics are internal combustion of gasoline, kerosene and rock weathering. Diagnostic ratios ranged from 0.3-0.94 showing that poly aromatic hydrocarbons are of pyrogenic and petroleum combustion origin. Single pollution index means ranged from 0.0002-0.02 and Numerov composite pollution index attained a mean of 0.028. Therefore, the soil is unpolluted and heavy metals levels are not toxic to human health. The study provides information on sources of soil pollutants and their environmental and health risks.

***Keywords:*** *Single pollution index; fueling stations; diagnostic ratios; pollution index; principal component analysis*

## 1. Introduction

The subject of heavy metals contamination is of global concern owing to their carcinogenic, toxic and non-biodegradable nature (Aigbe et al. 2021). Heavy metals have toxic effects even at low concentrations. USEPA (2004) and Agency for Toxic Substances and Disease Registry (ATSDR 1999) classified Al, Fe, Cr, Sb, As, Be, Cd, Cu, Pb, Hg, Ni Se, Ag and Zn as primary contaminant metals. This is due to their potential threat to human health and harmful nature. Ali et al. (2019) enumerated Cr, Cu, Ni, Zn, Cd, Pb, Hg and As among environmentally relevant and most hazardous heavy metals and metalloids. Soils around mechanic workshops show potential contamination of the environment with heavy metals (Ogunkolu al. 2019). Heavy metals such as Cd, V, Zn and Pb are inorganic pollutants common in crude oil and drilling fluids at oilfields (Mustafa et al. 2015). Chinedu and Chukwuemeka (2018) showed that heavy metals present in petroleum include Mn, Fe, Cu, Co and Cd. Heavy metals pollutants are not biodegradable and accumulate in soil, water, plants, and pose a risk to environmental and human health (Dokmeci 2020). Inorganic pollutants are persistent in the environment but organic pollutants are non-persistent (Maloszeniska-kordybach et al. 2008). Inorganic and organic constituents of soil may pose health risk to humans through the food chain.

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(Sweetman et al. 2005). Soil pollution with toxic heavy metals ions and organic substances has resulted to shortage of arable land in the current century (Aigbe et al. 2022). Urban soils where there is gardening are of possible enrichment in anthropogenic contaminants (Barrio Parra et al. 2019). Aigbe et al. (2020) devised a means of sorption of heavy metals using bionancomposite (BNCs) which is ecologically friendly. Carbon Nano tubes (CNTs) serve as excellent absorbents in the removal of heavy metals from the environment (Chen and Liu 2016; Oyancha et al. 2021; Ukhurebor et al. 2021a).

Generally, excessive intake of toxic metals by animals and plants causes cancers in humans and physiological and morphological alterations and chlorosis in plants (Guatam et al. 2015). Human exposure to Pb in high dose causes abortion, cardiovascular issues, erectile dysfunction, itai itai, convulsion and renal failure (Jennings et al. 1996; Gautam et al. 2015; Tay et al. 2019). Cd is toxic even in a small dose and causes food poison, elevated blood pressure and kidney damage (ATSDR 1999; Rajappa et al. 2010). Excess Ni intake causes cell damage, loss of body weight, liver and heart damage and malfunctioning of the central nervous system (Kaaber et al. 1978; Ouryang et al. 2005; Guatam et al. 2015). Priority heavy metals and poly aromatic hydrocarbons (PAHs) are carcinogenic to human health and cancer is the leading cause of deaths around the world. Non-biodegradable nature of heavy metals make

them stay longer in soil and humans depend on plants that thrive on soil (Sarma et al. 2016). As, Cd, Cr, Pb and Hg ranked as priority heavy metals, because of their toxicity, they are of public health concern (Tchounwou et al. 2012). These elements induce multiple organ damage even at minimal concentrations of exposure. USEPA (2004) and International Agency on Research for Cancer (IARC) classified these priority heavy metals as human carcinogens.

There are studies on heavy metals and PAHs contamination on the environment due to petroleum products (Adesina and Adebayo 2014; Sarma et al. 2016; Ekanem et al. 2019; Sakshi et al. 2019Ukhurebor et al. 2021b). Ecological risks on soil around a gas plant showed strong and moderate correlations between Pb and Zn and also Cu and Ni (Radomirovic et al. 2020). The study showed that the main ecological risk from metal contamination was unconnected with paint industry production process itself, but from other activities. Heavy metals pollution studies around petrol stations in Nigeria indicated high degree of contamination by Pb, Cd, and Zn (Adu et al. 2012; Dau and Odor 2012).

The different types of petroleum products are gasoline, diesel oil, aviation fuel and heating oil (WHO 2005). Some petroleum products possess small constituents of PAHs. PAHs are natural constituents of fossil fuel formed due to incomplete combustion of gasoline, coal, wood and diesel oil (Mehrdad et al. 2015; Abdel-Shafy and Mansourr 2016). PAHs originate primarily from anthropogenic activities related to petroleum refineries as well as motor vehicle exhaust (Abdel-Shafy and Mansour 2015). PAHs and heavy metals coexist in petroleum and its products (Sarma et al. 2016). Soil acts as a sink for PAHs because of their high affinity for soil organic matter (Sweetman et al. 2005). Soil contamination by petroleum products negatively affects plant productivity and puts human and animals health at risk because of its toxicity to living organisms. European Environmental Agency (EEA) in 2006 reported that about 34% of contaminated sites in Europe were due to mineral oil. PAHs and volatile aromatic hydrocarbons (benzene, toluene, ethyl benzene and xylene) increase the risks of soil contamination (EEA). Soil contaminated with petroleum products is not suitable for crop growth for several months or years (Mehradad et al. 2015). Petroleum products constitute a nuisance to the environment due to their persistent nature and tendency to spread into soils (Mehradad et al. 2015). USEPA (2002b) classified hazardous primary PAHs pollutants into carcinogenic and non-carcinogenic types. The probable carcinogenic PAHs include chrysene (Chrys), benzo (a) fluoranthene (BaA), benzo (a) pyrene (BaP), Benzob, benzo (k) fluoranthene (Benzok)), dibenzo (ah) anthracene (Diben)) and indeno (123cd) pyrene (IndoP) (USEPA 2002b). PAHs are included in the list of priority organic substances by USEPA (2004). Hence, they are among substances subjected to frequent monitoring (Rabajczyk and Swiercz 2018). The International Organization for research on cancer (IORC) identified BaP as the main human carcinogen. Therefore, it is the most often tested PAH in environmental studies (USEPA 2004).

Contamination of soil with PAHs is a challenge of utmost concern (Submarayan et al. 1991). Contamination of arable soil by PAHs translate to their accumulation in crops, which has potential adverse effects on human health (Gao and Zhu 2004). Analysis and health risk assessment of PAHs in soil is for characterizing their fate and transport in the environment. These would help to design strategic plans for prevention or remediation of soil contamination (Agarwal et al. 2009; Baiger et al. 2010; Hu et al. 2014; Bina et al. 2020). Petrogenic sources of PAHs include crude oil and refined crude oil products such as gasoline, heating oil, asphalt and coal. In contrast, pyrogenic PAHs originate from fires, internal combustion engines and furnaces (Mauro and Roush 2008).

Some researchers assessed PAHs in soil around automobile workshops and industrial zones (Abdulimhen 2016; Aigberua et al. 2016; Daniel et al. 2020; Ilic et al. 2021). These studies determined PAHs sources using diagnostic ratios. Jiao et al. (2017) analyzed agricultural soils around coal a production plant and established PAHs levels more than 1 mg/kg prescribed by soil quality guidelines. Sun et al. (2014) analyzed PAHs and heavy metals levels in surface soil in industrial sites in Central China and recorded high levels at smelting sites. Hu et al. (2014) studied PAHs contents in soil in China and established that PAHs in fluvo-aquic soils were greater than paddy soils. Fluoranthene and pyrene (Pyr) were dominant PAHs in soil, which accounted for 19.7 and 13.3% for total mass of PAHs, respectively. Hu et al. (2014) demonstrated that levels of PAHs in soil increase with anthropogenic activities. The authors posited that increased activities such as fueling stations and mechanic workshops might have resulted to significant levels of PAHs in soil.

Samimi et al. (2009), Alharbi et al. (2018), Rabajczyk and Swiercz (2018), and Yazdi and Sharifi Teshnizi (2021) studied soil contamination by PAHs near fueling stations in Kielce, Tehran Iran and Saudi Arabia. The studies reported high PAHs levels. Soil contamination by leaking underground fuel storage tanks using total hydrocarbon content (THC), electrical conductivity (EC) and acidity (pH) by Alharbi et al. (2018) showed that pH had no observable impact. A study of carcinogenic PAHs and heavy metals in Romania revealed an individual risk of $1.07\times10^{-5}$ for children and $6.89\times10^{-6}$ for adults (Cocarta et al. 2017). Mustafa et al. (2015) established heavy metals trends of Pb>Ni>V>Zn>Cd in soil near petroleum products sites. The study showed that principal component analysis (PCA) is an effective tool in deciphering sources of pollutants in the environment. In Nigeria, different studies analyzed PAHs in soil around fueling stations and automobile workshops (Idugboe et al. 2014; Abhulimhen 2016; Aigberua et al. 2016;

Nwankwoala and Emenu 2018). The studies showed various ranges of soil contamination, some higher than the control sites, WHO and Nigerian Environmental Standards Regulations Enforcement Agency (NESREA) limits for agricultural soils. Diagnostic ratios of PAHs in an oil spill contaminated site in Port Harcourt, Nigeria showed a predominance of pyrogenic activities (Aigberua et al. 2016).

This study is to investigate environmental contamination associated with heavy metals and PAHs in soil around petroleum products handling facilities and assess their health risks. Petrol stations usually, consist of buildings with automobile service points, carwash, petrol pumps, and chambered underground fuel tanks. There are fueling stations and auto mechanic workshops in the area, which are sources of soil contamination with PAHs and heavy metals (Sarma et al. 2016; Ekanem et al. 2019). Heavy metals have their various health implications when taken by humans above safe concentrations. There is need for assessing the impact of soil contamination with PAHs and heavy metals (Adesina and Adebayo 2014; Abdulrashid et al. 2017; Ogunkolu et al. 2019; Dehghan and Yazdi 2023). The absorption of these heavy metals by plants and their accumulation in the food chain is a serious risk to human health. Assessing PAHs and heavy metals concentrations in soils around petroleum products handling sites is a positive step towards environmental remediation in future research. Residents of the study area cultivate farmlands and gardens in soils close to petrol stations and auto mechanic workshops, which are susceptible to soil contamination by PAHs and heavy metals pollutants. These methods of analyzing environmental samples using AAS and GC-MS are rapid, inexpensive with simple sample preparation, more affordable and accessible than other techniques. The test for validity of analytical results is simple. Some studies successfully applied heavy metals and PAHs analysis in soil around fueling stations and automobile workshops using AAS and GC-MS, respectively. This is documented in Dauda and Odoh (2012); Abdulimhen (2016); Adebola and Oyeleke (2017); Badowska and Bandzierz (2019); Nwaokwala and Ememu (2018); Ekanem et al. (2019).

Onueke is a semi urban location with auto mechanic workshops and fueling stations to meet the needs of transporters and other vehicle owners. This study is important because it is first of its kind on heavy metals and PAHs contamination of soils around petroleum products handling facilities in the area. Related works done elsewhere considered heavy metals and PAHs contamination in soil around auto mechanic workshops and petrol stations separately. The studies did not estimate the distance of sample collection from the points of activity to understand how the distance influence the degree of soil contamination. In addition, the method of data interpretation in most studies did not incorporate diagnostic ratios and multivariate statistical techniques for a more comprehensive study. This research applied an integrated approach including environmental and human health risks analyses to bridge the gaps left by previous studies. Therefore, this study is more thorough in terms of data acquisition and interpretation with more credible results. This will serve as a guide to farmers cultivating on soils within the areas of petroleum product handling activities. The ultimate goal of this study is to evaluate the contamination of arable topsoil by toxic heavy metals and PAHs around petrol fueling stations and mechanic workshops. The aim is achievable through the following specific objectives: (i) Ascertain the concentrations of Cd, V, Ni and Pb in soil and analyze their risks using soil pollution indices. (ii) Estimate PAHs levels in soil used for cultivation petroleum products handling sites. (iii) Decipher the sources of heavy metals and PAHs in soil using Pearson correlation analysis, PCA and diagnostic ratios. (iv) Correlate heavy metals and PAHs contamination in soils around mechanic workshops and fuelling stations with world standard values. (v) Provide soil pollution information to regulate the use of contaminated soil for cropping and other possible human uses.

## 2. Materials and methods

### 2.1. Study Area Description

The study area is in Ezza, Ebonyi state southeastern Nigeria. It is located between latitudes N06° 10’ 23.0” to N06° 07’ 27.0” and longitude E08° 02’ 20.6” to E08° 01’ 33.3” (Fig 1). Ezza is the commercial center where the people sell their agricultural produce. The inhabitants are mostly farmers. They cultivate agricultural crops such as yam, cassava, rice, cocoyam, and many other crops. The area falls within the tropical rainforest belt of South East Nigeria. There are two distinct seasons in Abakaliki within the zone. The rainy season starts in April, end in October while the dry season commence in November, and terminate in March. The minimum and maximum temperatures of the study area are $27^0$C and $31^0$C respectively. The relative humidity of the area is between 60 to 89 percent. The area has an annual rainfall range of 1500-2000mm and the soil belongs to order utisol classified as type Haplastult (Ofomata 1975; FDALR 1985; Njoku and Ngene 2015).The seasonal climatic conditions are due to the North-South fluctuation of a discontinuity zone between the dry continental (Saharan) air and the humid maritime (Atlantic) air.

The drainage pattern is dendritic as a function of lithology. The drainage flows eastward to join the Cross River channel. The slope is gentle. Runoff is high during the rainy season. Surface water bodies are ephemeral and floods occur during the rainy season. The vegetation is luxuriant as common in the tropical rainforest. It is dense and interspersed with grasses and trees of different sizes. The area is characterized by undulating range of shale outcrop; the shale is either grayish or reddish brown depending on its content and degree of weathering. The area has its highest contour at 400ft and lowest contour at 100ft above the sea level.

### 2.2 Geology of the study area

Though geology of the local area lacks proper and full documentation, previous studies (Farrington 1952; Simpson 1954; Reyment 1965; Murat 1972;; Kogbe 1979 and Olade 1979) examined the geology of the area within Onueke but mainly on a regional scale. The rocks of the area within Onueke are classified into shale, sandstone, limestone, mudstone and ironstone. The shale is mainly rusty brown coloured; dominant in Amagu, Idembia, Amaezekwe, Achara and Umueze Akwa areas. Beneath the rusty brown colored shale are dark grey colored shale deposits showing great level of fissility, high degree of lamination, well jointed and with minor occurrence of iron fillings.

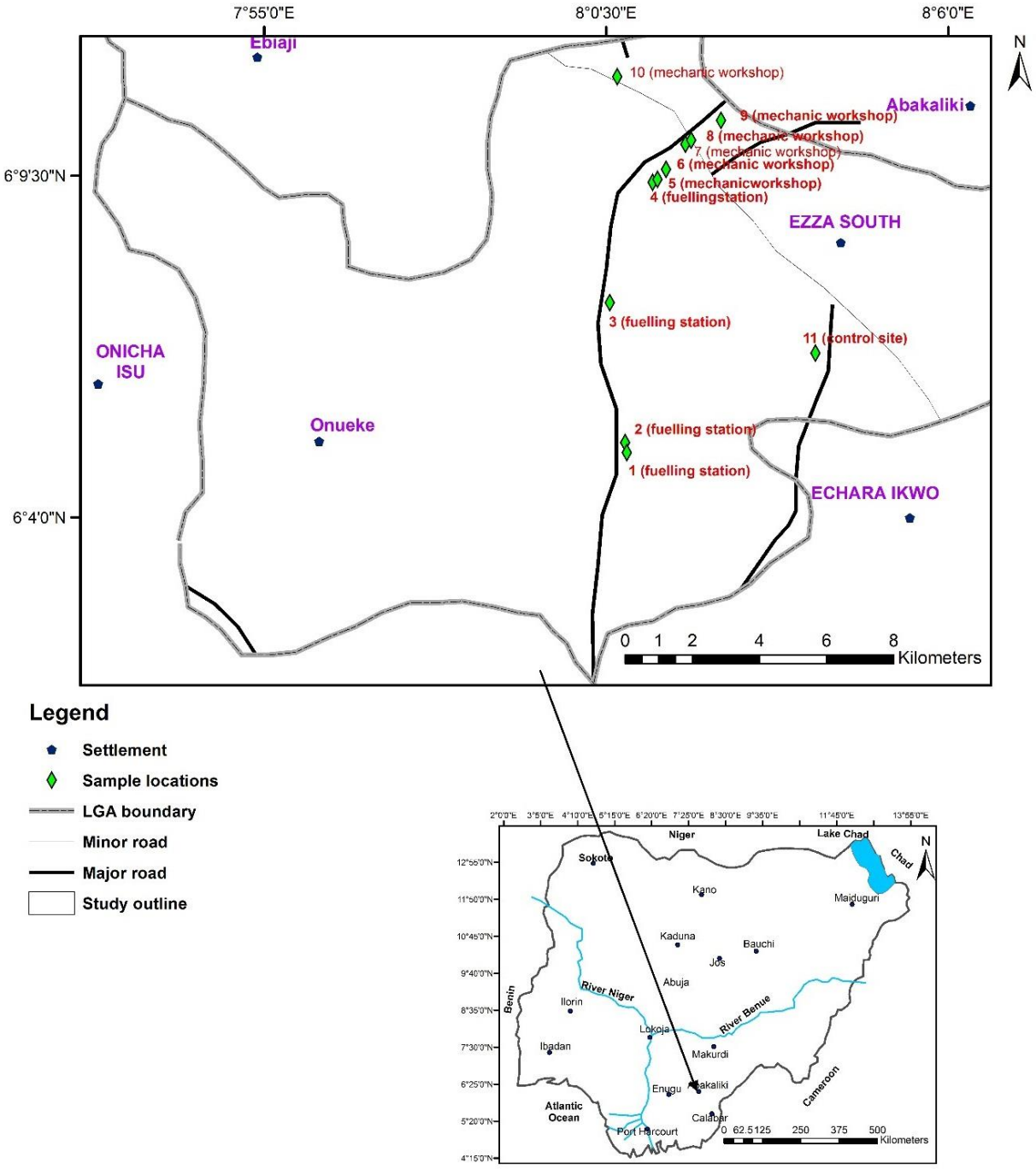


Fig 1. Showing study area and sample locations

The various lithology units as envisaged in the Lower Benue Trough (Fig 2) though with a rare case of tectonic activity, characterize the area within Onueke. There are two major divisions of Abakaliki Anticlinorium and Afikpo Syncline in the Lower Benue Basin. Onueke area forms part of the Abakaliki Anticlinorium seen to flank at the lower end of the formation, very close to the Afikpo syncline. The Abakaliki area forms the key part of the Albian Asu river group sediments, which are predominantly shale with intermittent occurrence of sandstone, siltstone and limestone intercalations (Fig 2).

**2.3. Sample collection**

Plastics were used for collection of samples for heavy metal determination, while samples for PAHs analysis were collected using stainless steel hand trowel. The stainless steel hand trowel plastics were thoroughly cleaned to avoid cross contamination. Soil samples were collected from a depth of 0-15cm. Sample 1 was collected in a vegetable farm about 50m to a fueling station while sample 2 was collected in cassava farm 46m from a fueling station. Sample 3 was obtained from a cassava farm 65m away from a fueling station.

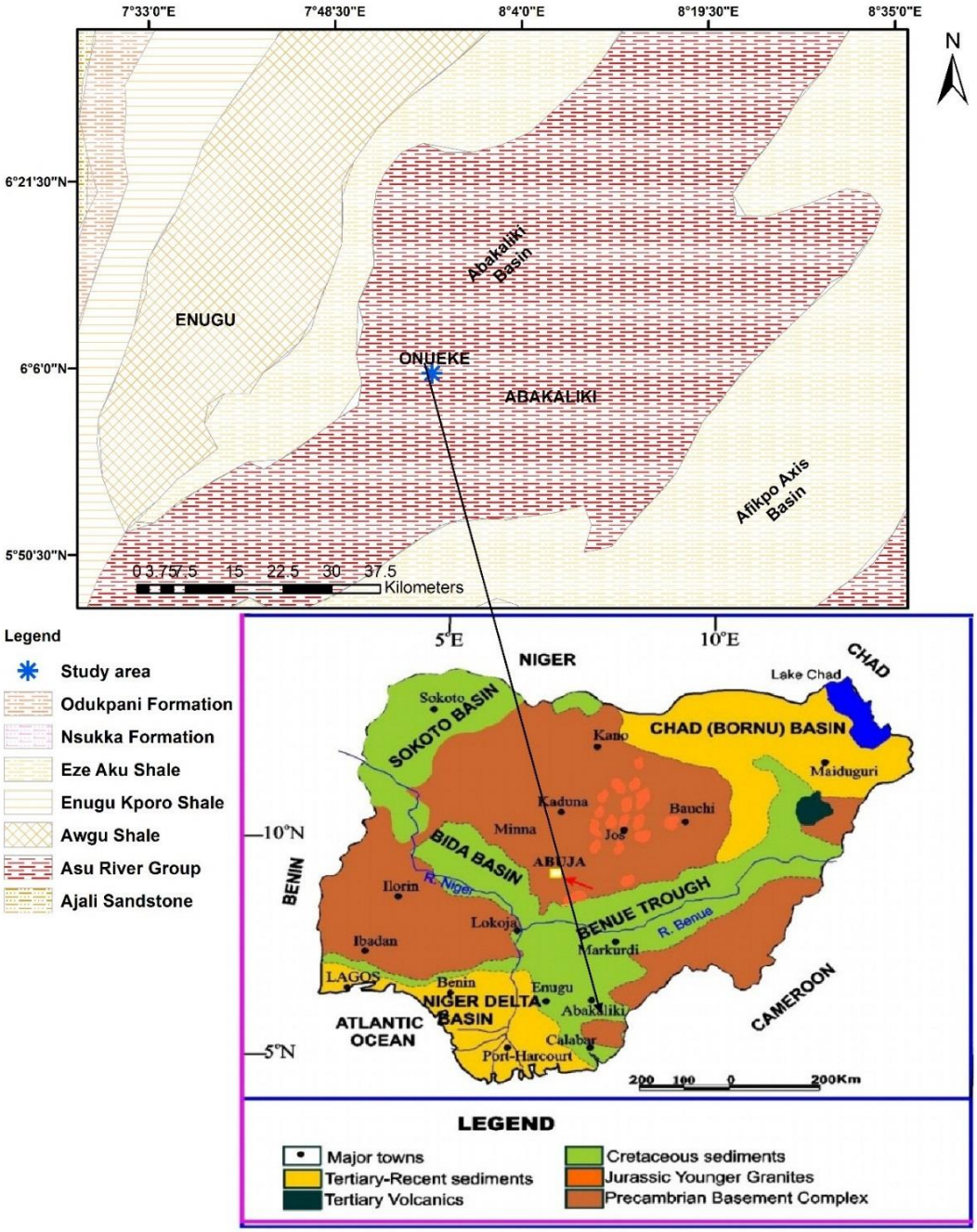


Fig 2. Geological map of Ebonyi and environs showing Ezza the study area (modified from Agumanu 1989)

Coarse fine soil in sample 4 gotten in cassava farm is 50m away from a fueling station. Samples 5 and 6 were collected at 55m and 60m, respectively away from mechanic workshops not in a farmland. Samples 7 and 8 were collected 65m and 70m, respectively away from mechanic workshops, not in a farmland. Furthermore, samples 9 and 10 were collected in cassava farms at distances of 57 and 75m, respectively away from mechanic workshops. The control site sample collected at location 11 was from cassava farm neither close to mechanic workshop nor a fueling station (Fig 2). The study area covered an estimated area of about 543.55 $m^2$ Samples for PAHs were packed in prewashed solvent rinsed aluminum foil. The samples were air dried at $80^0$C. Polyethylene bags were used for packing soils for heavy metals determination. Samples for metals and soil physical properties were air dried in the laboratory after manual removal of stones, twigs and other large materials, then ground in a porcelain mortar and passed through a 2mm sieve. Prior to analyses, PAHs samples were preserved by keeping them in the refrigerator.

**2.4. Sample analysis**

***Heavy metals***

For sample digestion approximately 2g of the dried sample was weighed in a digestion flask and added 20 mL of the acid mixture (650 mL concentrated $HNO_3$; 80 mL perchloric acid; 20mL concentrated $H_2SO_4$). The flask was heated until a clear digest formed. The digest was diluted with distilled water to the 100 mL mark. The sample was mixed thoroughly by shaking, and 100 mL of it transferred into a glass beaker of 250 mL volume. Then 5 mL of concentrated nitric acid was added and heated to boil until the volume was reduced to about 15-20 mL. Concentrated nitric acid was added in increments of 5 mL until the entire residue was completely dissolved. The mixture when cooled was made up to 100 mL using metal free distilled water. The sample was aspirated into the oxidizing air-acetylene flame. When the aqueous sample was aspirated, the sensitivity for 1% absorption was observed (Adrian 1973). The samples were analyzed for Ni, Pb, Cd and V using Agilent FS240AA Atomic Absorption Spectrophotometer (AAS) according to the method of American Public Health Association (APHA 1995). AAS's working principle operates based on aspiration of the sample into the flame and atomized when the AAS's light beam is directed through the flame into the monochromatic. The detector then measures the amount of light absorbed by the atomized element in the flame. Metals have their own characteristic absorption wavelength. Based on this principle we used a source lamp composed of that element, making the method relatively free from spectral or radiation interferences. The amount of energy of the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample.

A series of standard metal solutions in the optimum concentration ranges were prepared. The reference solutions were prepared daily by diluting the single stock element solutions with water containing 1.5 mL concentrated nitric acid/liter. A calibration blank was prepared using all the reagents except for the metal stock solutions. Calibration curve for each metal was prepared by plotting the absorbance of standards versus their concentrations. Metal recovery was by spiking 1g of the soil sample with known concentrations of each metal. Concentrations of each of the metal in the samples not spiked was deducted from that of the spike sample and divided by concentrations of the metals used for spiking, then multiplied by 100.

***PAHs***

Thirteen PAHs fluorene (Fluo), naphthalene (Naph), phenanthrene (Phen), benzo (ghi) pyrelene (Bghi), Benzob, acenaphthylene (acen), Diben, benzo (k) fluoranthene (Benzo k), BaP, xylene (Xyl), anthracene (Ant), BaA and pyrene (Pyr) were analyzed. Using soxhlet extraction method, 20g of the homogenized sample was mixed with 60g of anhydrous sodium sulphate ($Na_2SO_4$) in agate mortar to absorb moisture. The homogenate was placed in a 500mL beaker. The extraction was carried out with 300 mL of n–hexane for 24 hours. The crude extract obtained was evaporated to dryness using a rotary vacuum evaporator at $40^0$C. The residue was transferred with n–hexane onto a 5 mL florisil column for cleanup.

During clean up the florisil (magnesium silicate) was heated in an oven at $130^0$C overnight, then transferred to a 250 mL size beaker, and placed in a desiccator. A 0.5g anhydrous $NaSO_4$ was added to 1.0g of activated flosiril (60–100nm mesh) on an 8 mL column plugged with glass wool. Packed columns were filled with 5 mL n–hexane for conditioning. The stopcock was opened to allow n–hexane run out until it just reached the top of sodium sulfate into a receiving vessel. The top of the column was tapped gently until the florisil settled well in the column. The extract was transferred onto the column with disposable Pasteur pipette from an evaporating flask. Each evaporating flask was rinsed twice with 1mL portion of n–hexane added to the column. The eluate was collected into an evaporating flask and the rotary evaporated to dryness. The dry eluate was dissolved in 1mL n–hexane for Phytochemical Chromatographic analysis (APHA1998).

In fixed setting, we adjusted gas flows to the columns, the inlets, the detectors, and the split ratio. In addition, the injector and detector temperatures were set. The detectors were held at the high end of the oven temperature range to minimize the risk of analyte precipitation. All of these parameters were set to the correct values, and double-checked the entire instrument. Buck 530 GC was equipped with an on–column, automatic injector, Mass spectroscopy, HP 88 capillary column (100m x 0.25µm film thickness, CA, USA.

Detector temperature A and Injector temperatures were $250^0$ C and $22^0$C, respectively. The integrator chart speed was 2cm/min, and the oven temperature was set to $180^0$ C and the GC allowed warming up. While it was warming

the temperature, condition was set. The not ready light on the instrument was turned off when the instrument was ready and we began the run. 1-microliter sample was injected onto column 'A' using proper injection technique. The concentration of each analyte was determined by calculating the amount of analyte injected from the peak response in area ratio.

2.5 Data analysis

Descriptive statistics (mean, standard deviation; kurtosis, skewness) and multivariate statistical analysis of heavy metals and PAHs data were calculated using SPSS version 20. Pearson correlation (PC) and PCA of heavy metals and PAHs were determined using SPSS software. PC and PCA were used to identify sources of heavy metal contamination in soil. Diagnostic ratios of PAHs (Phen/Ant, Ant/ (Ant + Phen), Fluo/Pyr, BaP/ (BaP + Pyr), Fluo / (Fluo + Pyr) and BaA/ (BaA + Pyr) were computed to identify the sources of PAHs in soil. Diagnostic ratios and PCA help to decipher sources of PAHs in soil (Ilic et al. 2021; Aigberua et al. 2016; Yunker et al. 2002).

Soil pollution index (SPI) and Numerov composite pollution index (NCPI) were computed using the equations developed by CEPA (2004). SPI is given by

$$P_i = \frac{C_i}{S_i} \quad (1)$$

Where Pi represents single pollution index, Ci is content of heavy metal in soil and Si stands for threshold value of heavy metal.

The Numerov composite pollution index is given by the equation

$$NCPI = \frac{\sqrt{P(Max)^2 + (P)^2}}{2} \quad (2)$$

Where NCPI represents Numerov Composite Pollution index, $Pi_{max}$ is the maximum value of single pollution index and P is the mean value of SPI.

## 3. Results

### 3.1. Effects of mechanic workshops and filling stations on heavy metals content of the soil

Table 1 shows the summary statistics of the result of chemical analysis performed on soil where petroleum products handling activities are taking place. Mean values of chemical constituents were compared with permissible world standards for soil quality (Table 1). The trend of heavy metals concentrations in soil is presented in Fig 3. Tables 2 and 3 show the summary statistics of PAHs measured in soil samples and their classification, respectively. The pH levels ranged from 6.3-6.8 with a mean and standard deviation of 6.6 $\pm$ 0.2 with negative skewness and kurtosis. EC achieved a mean of 50.6 µs/cm and a standard deviation of 16.3 with a negative skewness and kurtosis. Pb recorded the highest concentration of 3219 µg/kg in location 6 (mechanic workshop) and the least concentration of 0.0 µg/kg in location 2 (fueling station) and location 11(control site) (Fig 3). Pb possessed a mean of 1379µg/kg and standard deviation of 1105 with a negative kurtosis (Table 1). Ni obtained the highest level of 849 µg/kg in location 5 and the least value of 434 µg/kg in location 4. At location 11, Ni recorded a value of 486 µg/kg (Fig 3). Ni possessed a mean of 636 µg/kg and standard deviation of 136.1 with a positive skewness but negative kurtosis. The mean value is below world bodies (EU 2006, DPR 1991, DPS 2000 and CCME 2007) limits of 50, 35, 35 and 45 mg/kg for unpolluted soil (Table 1). Cd and V obtained highest values of 79 and 46 µg/kg in locations 7 and 6, respectively. Cd and V obtained the least values of 0.0 and 3µg/kg, respectively at location 11. Ni, Pb and V obtained values at the site of activities significantly higher than their corresponding values at the control site. Cd values were 0.0 µg/kg in most locations including the control site (Fig 3). Cd attained a mean value of 12 µg/kg and a standard deviation of 25.2 (Table 1). V achieved a mean of 18 mg/kg and standard deviation of 0.01mg/kg. The mean levels of all toxic metals was below approved limits by world standards for unpolluted soil. The mean concentrations of heavy metals trend as Pb > Ni > V > Cd.

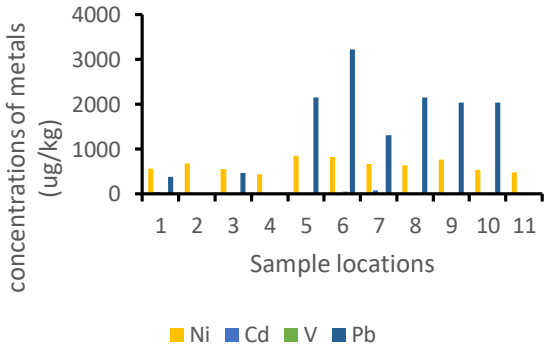


Fig 3. Showing spatial distribution of heavy metals in the study area

### 3.2. Statistical summary of PAHs concentrations in soil of the study area

In Table 2, Fluo obtained a mean value of 2.01µg/kg with a standard deviation of 1.64 with negative skewness and kurtosis. The minimum values of all the PAHs was 0.0 mg/kg. Fluo, BghiP, Benzob and BaP, possessed mean values more than 1 µg/kg. The rest of the PAHs had mean values below 1 µg/kg. PAHs mean values were below standards prescribed for uncontaminated soils (Table 2). Mean values of PAHs (Table 2) show that BaP > Ant> Flou > Benzo (b) > Bghip > Naph > Ant > Diben > BaA > Benzok > Phen > Pyr > Xyl >Acen.

Table 1. Summary statistics of heavy metals in soil of the study area

| Variable | unit | N | Min | Max. | Mean | Std Dev. | Skewness | Kurtosis | CV % | EU (2006)[a] | DPR (1991)[b] | Dutch target (VROM 2000)[c] | CCME (2007)[d] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EC | µs/cm | 11 | 23.6 | 70.9 | 50.6 | 16.3 | -0.3 | -1.5 | 2.7 | 1500 | NA | NA | NA |
| pH | | 11 | 6.3 | 6.8 | 6.6 | 0.2 | -0.7 | -1.6 | 32.2 | 6.5-8.5 | NA | NA | NA |
| Ni | µg/kg | 11 | 434 | 849 | 636 | 136.1 | 0.3 | -1.0 | 21.4 | 50 | 35.0 | 35.0 | 45.0 |
| Cd | µg/kg | 11 | 0.0 | 79.0 | 12.0 | 25.2 | 2.3 | 5.2 | 210.4 | 1 | 0.80 | 0.80 | 10.0 |
| V | µg/kg | 11 | 2.2 | 46.0 | 18.0 | 13.6 | 0.7 | 0.1 | 75.6 | 100 | NA | NA | NA |
| Pb | µg/kg | 11 | 0.0 | 3219 | 1379 | 1105 | 0.1 | -1.2 | 80.1 | 60 | 85.0 | 85.0 | 140.0 |

[a] EU European Union (2006), [b] DPR Department of Petroleum Resources (1991), [c] DPS Duch Pollutant Standard (2000), [d] CCME Canadian Council of Ministers of the Environment (2007)

Table 2. Summary statistics of PAHs (µg/kg) concentration in soil of the study area

| Variable | N | Minimum | Maximum | Mean | Std. Dev | Skewness | Kurtosis | CV % | PC PAHs soil* |
|---|---|---|---|---|---|---|---|---|---|
| Fluo | 11 | 0.00 | 3.90 | 2.01 | 1.64 | -0.37 | -1.87 | 81.59 | NA |
| Naph | 11 | 0.00 | 2.80 | 0.84 | 0.70 | 2.37 | 7.17 | 83.33 | 0.1 |
| Phen | 11 | 0.00 | 1.80 | 0.36 | 0.49 | 2.92 | 9.21 | 136 | 0.1 |
| BghiP | 11 | 0.00 | 3.80 | 1.12 | 1.48 | 1.01 | -0.41 | 132.1 | 0.1 |
| Benzob | 11 | 0.00 | 7.10 | 1.14 | 2.55 | 2.02 | 2.74 | 223.6 | NA |
| Acen | 11 | 0.00 | 0.10 | 0.01 | 0.03 | 3.32 | 11.00 | 300 | NA |
| Diben | 11 | 0.00 | 4.30 | 0.69 | 1.55 | 2.01 | 2.70 | 129.6 | NA |
| Benzok | 11 | 0.00 | 2.00 | 0.42 | 0.61 | 1.88 | 4.14 | 145.2 | NA |
| BaP | 11 | 0.00 | 12.20 | 2.04 | 3.95 | 2.08 | 4.13 | 193.6 | 0.03 |
| Xyl | 11 | 0.00 | 0.80 | 0.07 | 0.24 | 3.32 | 11.00 | 342.8 | NA |
| Ant | 11 | 0.00 | 4.10 | 0.75 | 1.48 | 1.85 | 2.15 | 197.3 | 0.1 |
| BaA | 11 | 0.00 | 1.60 | 0.45 | 0.64 | 0.83 | -1.29 | 142.2 | 0.1 |
| Pyr | 11 | 0.00 | 0.50 | 0.12 | 0.21 | 1.40 | 0.18 | 175 | NA |

PC–permissible concentration; PAHs – polycyclic aromatic hydrocarbons; NA– not available

Table 3. Classification of PAHs contamination in soil (µg/kg) (after Maliszewska-Kordybach, et al. 2008).

| PAH contamination in soil | Degree of pollution | Assessment of soil contamination |
|---|---|---|
| <200 | 0 | Not contaminated (natural content) |
| 200-600 | 1 | Not contaminated (increased content) |
| 600-1,000 | 2 | Weakly contaminated |
| 1,000-5,000 | 3 | Contaminated |
| 5,000-10,000 | 4 | Heavily contaminated |
| >10,000 | 5 | Very heavily contaminated |

Comparison of PAHs mean values obtained in this study (Table 2) with their standard of classification for agricultural purposes (Table 3) shows that the soil falls under not contaminated with PAHs and reflect their natural content in soil.

### 3.3. Spatial distribution of PAHs concentrations in sample locations

Fig 4. Shows Fluo recorded very low values of PAHs in locations 2, 3, 4 (petrol fueling stations), 5, 6, 7, 8 and 9 (mechanic workshops). Flou values were nil in locations 6 and 11. Benzob obtained high concentrations at locations 2 and 3 but nil in other locations including control site (Fig 4). Diben obtained the highest value of 0.0043 µg/kg in location 1 and the least value of 0.0033 µg/kg in location 7 but nil in other locations including the control site. Acen achieved a mean value of 0.0001µg/kg in location 1 but nil in other locations including control site. Naph recorded concentrations of 0.0028 µg/kg in location 1, 0.009 µg/kg in locations 2 and 3, 0.005, 0.0007 and 0.001 µg/kg in locations 4, 5 and 7, respectively. Naph also recorded values of 0.0006 µg/kg in locations 8, and 9 then 0.0005 and 0.0008 µg/kg in locations 10 and 11. Bghi attained values of 0.0036, 0.0038 and 0.0011 µg/kg in locations 2, 7, and 8, respectively. Bghi also recorded 0.0019 µg/kg in locations 3 and 6 but obtained zero concentration in locations 1, 9, 10 and 11. Phen attained 0.0004 mg/kg in location 1, 0.0003 µg/kg in locations 2, 3, 6 and 7, 0.0002 µg/kg in locations 8 and 9 then 0.0007 and 0.0018 µg/kg in locations 10 and 11.

The highest value of Phen was at the control site and the least value in locations 8, 9 and 10. Phen concentration was nil in locations 4 and 5. Benzok obtained values of 0.002 mg/kg in location 1, 0.0006 µg/kg in locations 4 and 5, 0.0007 µg/kg in locations 10 and 11 but nil in locations 2, 3, 6, 7, 8, and 9 (Fig 4). Naph was present in almost all the locations except location 6. Sample location 6 was collected 60m away from a mechanic workshop. Phen was present in nine locations but was not present in locations 4 and 5. Locations 4 and 5 were sampled 50 and 55 m away from petroleum handling sites, respectively. Bghi was present in five locations. Xyl was present in location 1 and 6 only.

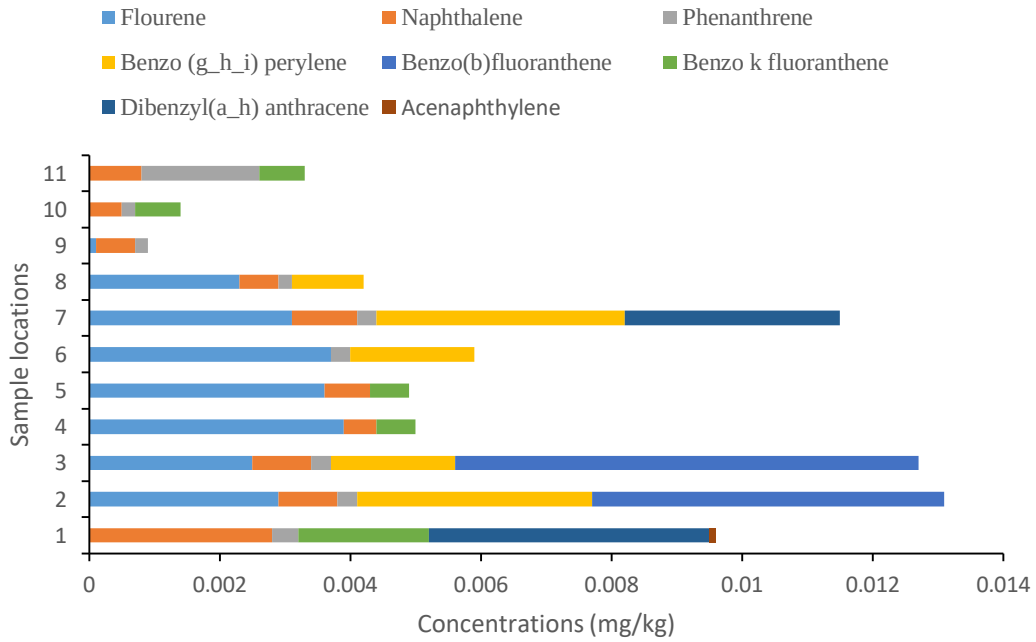


Fig 4 Bar chart of selected PAHs

### 3.4. Multivariate statistical analysis of data

In Table 4, the pH had significant negative correlation with EC. EC possess negative significant correlation with Cd. Ni and Pb. V and Pb recorded significant correlation. In Table 5, PCA shows two distinct principal components (PCs) due to homogenous geology of the study area. The PCA explained a total variance of 77.62%. PC 1 contributed 40.72% of the total cumulative percentage of 77.62% with significant constituents of pH, EC, Cd and V. PC 2 contributed 36.90% of the total variance. PCA of toxic metals in Table 5 shows two distinct PCs. PC 1 consist of positive significant constituents of pH, Cd and V while PC 2 consist of significant constituents of Ni, V and Pb.

PCA of PAHs (Table 6) shows four distinct components with a total variance of 84.26%. PC 1 exhibited significant constituents of Flou, Naph, Acen, Diben, Benzok and BaP. PC 2 contributed 19.96% of the total variance with significant constituents of Flou, Phen and Bghip, PC 3 contributed 15.19% of the total variance with significant constituents of BghiP, Benzob and Ant. PC 4 contributed 12.81% of the total variance with significant constituents of Xyl, Ant and BaP (Table 6).

Table 4. Pearson correlation matrix of physicochemical parameters in soil

| | PH | EC | Ni | Cd | V | Pb |
|---|---|---|---|---|---|---|
| **PH** | 1 | | | | | |
| **EC** | -0.766** | 1 | | | | |
| **Ni** | -0.054 | 0.256 | 1 | | | |
| **Cd** | 0.490 | -0.618* | 0.083 | 1 | | |
| **V** | 0.302 | -0.488 | 0.461 | 0.268 | 1 | |
| **Pb** | 0.026 | -0.015 | 0.710* | -0.059 | 0.704* | 1 |

**. Correlation is significant at the 0.01 level (2-tailed). *. Correlation is significant at the 0.05 level (2-tailed).

Table 5. Principal Components Analysis of heavy metals

| Variable | PC1 | PC2 | Communalities |
|---|---|---|---|
| pH | 0.804 | -0.323 | 0.751 |
| EC | -0.854 | 0.426 | 0.911 |
| Ni | 0.190 | 0.843 | 0.746 |
| Cd | 0.649 | -0.391 | 0.574 |
| V | 0.682 | 0.572 | 0.793 |
| Pb | 0.381 | 0.858 | 0.882 |
| Total | 2.443 | 2.214 | |
| % of Variance | 40.720 | 36.904 | |
| Cumulative % | 40.720 | 77.624 | |

Table 6. Principal component analysis of PAHs

| Variable | PC1 | PC2 | PC3 | PC4 | Communalities |
|---|---|---|---|---|---|
| Fluo | -0.638 | 0.646 | 0.235 | -0.102 | 0.890 |
| Naph | 0.933 | 0.313 | -0.158 | -0.001 | 0.993 |
| Phen | 0.213 | -0.558 | -0.473 | -0.140 | 0.600 |
| BghiP | -0.370 | 0.542 | -0.543 | 0.392 | 0.879 |
| Benzob | -0.238 | 0.422 | -0.660 | -0.037 | 0.671 |
| Acen | 0.925 | 0.221 | 0.144 | 0.163 | 0.952 |
| Diben | 0.754 | 0.403 | -0.043 | 0.233 | 0.787 |
| Benzok | 0.875 | -0.043 | 0.257 | -0.250 | 0.671 |
| BaP | 0.839 | -0.104 | 0.207 | 0.330 | 0.857 |
| Xyl | -0.372 | -0.017 | 0.388 | 0.595 | 0.643 |
| Ant | -0.266 | 0.289 | 0.672 | -0.613 | 0.981 |
| BaA | -0.315 | -0.475 | 0.397 | 0.685 | 0.952 |
| Pyr | 0.051 | -0.878 | -0.222 | -0.170 | 0.852 |
| Total | 4.719 | 2.595 | 1.975 | 1.666 | |
| % variance | 36.303 | 19.958 | 15.190 | 12.812 | |
| Cumulative % | 36.303 | 56.261 | 71.451 | 84.263 | |

### 3.5. Diagnostic ratios of PAHs

Diagnostic ratio of Ant / (Ant + Phen), in location 6 obtained a value of 0.769. Phen/Ant recorded a ratio of 0.3. This is evident that the source of PAHs in this location is pyrogenic. Ant / (Ant + Phen) > 0.10 indicating pyrogenic PAHs. Phen/Ant recorded 0.3 in location 3. In location 8, calculated ratios of Fluo/Pyr, BaP/BaP + Pyr, Flu/Flu + Pyr were 7.67, 0.94 and 0.88, respectively. In location 10, the diagnostic ratio of BaA/BaA + Pyr is 0.67.

### 3.6. Heavy metal pollution assessment in soil

SPI (Table 7) for each heavy metal showed values of Ni, Cd, V and Pb were $\leq$1.0, hence the soil can be classified as safe and clean without heavy metals pollution (Table 8). Computation of the NCPI shows that the value is < 0.7 indicating the presence of safe clean soil (Table 9). Using pH classification ranges of pH < 6.5, 6.5 $\leq$ pH < 7.5 and pH >7.5. This shows the soil pH ranged from contaminated to contaminate moderately to suitable (Table 1).

Table 7. Pollution indices of top soil in the study area

| | SPI | | | | NCPI |
|---|---|---|---|---|---|
| | Ni | Cd | V | Pb | |
| **Mean** | 0.012 | 0.012 | 0.0002 | 0.021 | 0.028 |
| **STD** | 0.003 | 0.025 | 0.0001 | 0.019 | 0.025 |
| **Minimum** | 0.019 | 0.000 | 0.000 | 0.000 | 0.000 |
| **Maximum** | 0.020 | 0.080 | 0.0001 | 0.050 | 0.060 |
| **Skewness** | 0.112 | 2.329 | 0.625 | 0.273 | 0.138 |
| **Kurtosis** | -1.108 | 5.241 | -0.009 | -1.304 | -1.866 |

Table 8. SPI classification (after CEPA 2004)

| Class | SPI | Grade | Description of Soil Heavy Metal Pollution |
|---|---|---|---|
| 1 | $\leq 1.0$ | Safety | Clean |
| 2 | $1.0 < SPI \leq 2.0$ | Slight pollution | Slightly clean |
| 3 | $2.0 < SPI \leq 3.0$ | Mild pollution | Soil pollution exceeds background, crops start to be polluted |
| 4 | $3.0 < SPI \leq 5.0$ | Moderate pollution | Soils and crops have been polluted moderately |
| 5 | $SPI > 5.0$ | Severe pollution | Soils and crops have been polluted severely |

Table 9. NCPI classification (after CEPA 2004)

| Class | NCPI | Grade | Description of Soil Heavy Metal Pollution |
|---|---|---|---|
| 1 | $\leq 0.7$ | Safety | Clean |
| 2 | $0.7 < NCPI \leq 1.0$ | Alert | Slightly clean |
| 3 | < NCPI 2.0 | Slight pollution | Soil pollution exceeds background, crops start to be polluted |
| 4 | $2 < NCPI \leq 3.0$ | Moderate pollution | Soils and crops have been polluted moderately |
| 5 | $NCPI > 3.0$ | Severe pollution | Soils and crops have been polluted severely |

## 4. Discussion

The mean values of heavy metals did not exceed their threshold values by world standards for unpolluted soil (Table 1). The mean values of Ni, Pb, Cd and V are lower than standards set by world bodies for soil quality. Abdulrashid et al. (2017) and Ogunbunmi (2014) tested soil around petroleum products handling sites and reported that some of the heavy metals were within limits recommended by WHO (2005) and EU (2006). Ogunbunmi (2014) reported that Cd exceeded permissible limits by WHO for soil quality.

All the heavy metals in this study recorded values higher than the control site. Concentrations of Ni and Pb were higher in all the locations than those of Cd and V (Fig 3). Both Ni and Pb recorded lower values at the control site compared to locations in petroleum product handling facilities. This is evidence of anthropogenic source of pollution. These findings are in agreement with results obtained in similar studies by Isibor (2016) and Abidemi (2011) in soils around automobile mechanic workshops. Ogunkolu et al. (2019) reported concentrations of Cd, Zn, Pb, Ni and Cr in soil around automobile mechanics workshops higher than the control site samples. In this study, Ni obtained the highest value (849 µg/kg) at location 5 near mechanic workshop in a farmland. The source of Ni is automobile bodies, wires and parent geology. Ni intake in excess causes allergic skin diseases such as itching, cancer of the lungs, nose sinuses. Through continuous inhalation, it affects fertility and also causes hair loss (Salem et al. 2000; Khen et al. 2007).The highest concentration of Pb (3219 µg/kg) near a mechanic workshop is attributable to parent geological materials, leaded petrol, and automobile exhaust. Excessive exposure of children to Pb causes impaired development, coordination problems and risk of cardiovascular diseases (Salem et al. 2000; Wuana and Keiman 2011). Most studies used CV % above 50% to identify heavy metals having anthropogenic sources in soil (Ding et al. 2017; Fan and Wang 2017). In this study, high CV % Cd (210.4) Pb (80.1 and V (75.1) are indicative of their anthropogenic origin. Cd concentrations were generally below world standards for agricultural soil quality. The highest value of Cd (79 µg/kg) recorded at location 7 near a mechanic workshop is traceable to fuel combustion and vehicle exhaust structures. The sources of Cd are Fe and Mn oxides. The mean of Cd (12.0 µg/kg) is below the permissible level of 0.8 mg/kg by EU (2006) for unpolluted soil. Nwaichi et al. (2016) reported significant

levels of Cd that exceeded WHO (2005) limit of 0.1 and 0.05 mg/kg in soil and cassava, respectively in petroleum-contaminated soil. Cd is carcinogenic, a mutagenic endocrine disruptor, damage lungs and causes fragile bones and affects calcium regulation in biological systems (Degraeve 1981). Badowska and Bandzierz (2019) analyzed agricultural soil around service stations and established that petroleum appear in the environment during transportation and storage. Heavy metals most frequently detected in oil spill are in the order Pb > Ni > V > Zn > Cd (Aigberua et al. 2017). This is in agreement with the findings in this study which has the order Pb > Ni > V > Cd. Studies by Abidemi, (2011), Idugboe et al. (2014) and Adu et al. (2012) identified trends of Fe>Pb>Co>Cd, Fe>Zn>Mn>Pb>Cu>Cd>Ni and Zn>Pb>Cr>Cu>Ni>Cd, respectively, in top soil around automobile workshops.

Positive correlation shows the elements are from the same source while negative correlation shows they are from different sources. Positive significant correlation between Pb with Ni and V show they are from the same source. Significant negative correlation between EC with pH and Cd showed they are from different sources (Table 4). Negative correlation also implies that as one element is increasing, the other is decreasing and vice versa. Low negative concentrations between elements show that the elements were derived by different factors (Askari et al. 2020). The possible source of Pb is automobile exhaust, while the source of Ni is Ni wires and parent rock weathering. Ni and Pb are most likely to be affected by anthropogenic activities (Askari et al. 2020). From PCA the PCs show that the possible sources of heavy metals were geological materials, automobile exhaust and leaded petrol combustion. Significant negative correlation of Cd and EC shows that different factors are controlling their concentrations in soil. PCA supports this relationship as PC1 contains significant negative EC and positive Cd depicting geogenic and anthropogenic inputs. PC2 components correlated significantly reflecting gasoline and kerosene combustion, which indicate anthropogenic sources. PC2 component are chalcophillic and have affinity for sulphides. Major sources of Pb in soils include automobile exhaust fumes, mining, burning of coal and less likely from atmospheric deposition. Significant negative correlation of EC and Cd show anthropogenic input. Pb is soluble but Ni is insoluble in soil (Ali et al. 2015). Using renewable energy sources and heavy metals free pesticides instead of fossil fuel can reduce heavy metals concentrations in the environment (Dokmeci 2020).

PAHs are below permissible values for unpolluted soil (Table 2). Daniel et al. (2020) assessed PAHs in soil around auto mechanic workshops and reported PAHs levels lower than their DPR standards in all the locations. The control site values did not show consistent pattern when compared with the test values. PAHs exhibited the same pattern at the control site and test values in this study. Comparison of mean PAHs in soil with the standard in Table 3 shows the soil is not contaminated. PAHs < 200 µg/kg concentrations are recommended for agricultural, forest, bush soils, wasteland, residential and urban areas (Rabajczyk and Swiercz 2018). Figure 3 shows that spatial distribution of Fluo and Diben in soil are of higher concentrations. High CV % of both heavy metals and PAHs in soil showed that they are contributed from a non-point source and of anthropogenic input. Abhulinhen (2016) analyzed PAHs in soil around automobile mechanic workshops and showed that PAHs varied between experimental and control site. The study recommended that mechanic villages be sited away from residential areas and quick intervention deployed in polluted areas. Most PAHs are a group of hydrocarbons that are present at high relative amounts in crude oil, coal, coal tar and many of their products. PAHs in urban centers originate from petrogenic sources as asphalt fuels, lubricating oils drips, tank storage of gasoline coal-heating devices (Mauro and Roush 2008). Expansion of urban centers makes it difficult to predict the concentrations and locations of petrogenic PAHs in such areas (Mauro and Roush 2008).

PAHs (Flou, Naph and Phen) exhibited an even spatial distribution than others (Fig 4). Some PAHs were unevenly detected and in most locations not available. The mean levels of Flou, BaP, BghiP, Benzob and BaP were >1 while other PAHs recorded mean values < 1.0 µg/kg. High levels of PAHs suspect anthropogenic input (non-point source). All priority PAHs were below permissible limits for clean unpolluted soil for agricultural, residential and forest areas (Table 2). Diagnostic ratios of chosen PAHs is a method used in identifying and characterizing their origins (Yunker et al. 2002; Aigberua et al. 2016). Phen/Ant <10.0 is pyrolytic (Aigberua et al. 2016). In this study, Phen/Ant < 0.3 indicates a pyrolytic source. The findings of PAHs sources using diagnostic ratios showed that the PAHs were mostly pyrogenic and of petroleum combustion origin. Hu et al. (2014) used diagnostic ratios of PAHs to identify their sources. This study used Pyr instead of Chrys in computing some of the diagnostic ratios and obtained reliable information because they are both carcinogenic PAHs. PAHs and heavy metals are environmental pollutants around fueling stations, mechanic workshops and automobile service stations (Abhulimhen 2016; Nwankwoala and Ememu 2018; Daniel et al. 2020).

PCA of PAHs data done in addition to diagnostic ratios identified four distinct principal components. This helps to select statistically independent source tracers (Table 6). In PC1, Naph, Acen, Diben, benzok, Flou and BaP. Diben, Benzok and BaP reflect emissions from internal combustion engines (Guo et al. 2003; Hu et al. 2014). The interpretation is that BaP is due to combustion of gasoline and kerosene (Hu et al. 2014). These show that PAHs in Onueke soils are mainly from internal combustion of gasoline, kerosene and weathering of parent geology.

SPI shows that the heavy metals fall in class 1(SPI $\leq$ 1.0). This grade indicates safe and clean soil (Table 7 and 8). NCPI mean falls in the class 1 (NCPI $\leq$ 0.7) which is interpreted as safe and clean soils (Table 9). NCPI is a comprehensive index used to classify soils in terms of heavy metals pollution. Nwankwoala and Emenu (2018) applied Numerov Integrated Pollution Index (NIPI) that has similar interpretation with NCPI. The study reported heavily polluted soils owing to the activities of fueling and service stations. The pH range in this study is from 6.32 to 6.81 indicating that the soil is weakly acidic. The pH correlated significantly with EC showing that the soil acidity is from weathering and organic matter decomposition.

This study determined concentrations of heavy metals and PAHs including human health risks to assess soil pollution around petrol stations and mechanic workshops. Therefore, this is more comprehensive and credible compared to previous studies that in most instances applied either heavy metals or PAHs only. The method of data analysis is more reliable because the study applied various data analytical techniques such as multivariate statistical analysis, SPI, NCPI, diagnostic ratios of PAHs. The above stands the study out relative to previous studies that did not consider all the above for a more credible outcome of their studies. The distance of sample collection varied based on the location of activities and farmlands. The lithology of the study area is homogenously shale. Diagnostic ratios and multivariate statistics showed that sources of PAHs and heavy metals were automobile exhaust, internal combustion of gasoline and lithology. The distance of sampling had an influence because control sample recoded values of heavy metals lower than samples collected from sites of activities. The methods of data analysis used by previous authors cited in the literature involved mostly geo accumulation factor (I-geo), enrichment factor and ecological risk indices. This study applied SPI and NCPI in data analysis for risk analysis. Diagnostic ratios helped in identifying sources of PAHs in soil. Related works elsewhere did not applied all these methods and there is no similar work in the study area. These methods used are comprehensive and had the possibility of unraveling any soil pollutant in the study area.

## 5. Conclusions

The aim of this research was to assess heavy metals and PAHs concentrations in soil and determine their sources and possible environmental and human health risks. Ni and Pb possessed higher ranges of 434-849 µg/kg and 0.0-3219 µg/kg, respectively. Levels of heavy metals were higher at sites of activities than the control site. PAHs such as Bghip, Benzob and BaP attained mean values higher than other PAHs. Flou recorded higher concentrations than other PAHs. There was no regular pattern of PAHs and heavy metals occurrence in sample locations of activity and control site. Some PAHs such as Phen, Naph and benzok were present at control site but absent in some locations of activity. Method of data collection, analysis and distance of sampling from site of activities had some effect on PAHs concentrations. Pearson correlation shows that there is significant correlation between pH and EC indicating that soil acidity is from soil weathering and organic matter decomposition. Ni and Pb and Pb and V correlated significantly showing they are from the same source. From PCA the possible sources of Pb is automobile exhaust and Ni from Ni wires and parent rock weathering. PC1 and PC2 show that sources of heavy metals concentrations in soil are from geological weathering, automobile exhaust, and petrol combustion. Pearson correlation and PCA show that pH and EC control the concentration of heavy metals in the soil. PC1 and PC2 reflects gasoline and kerosene combustion sources. All the components of PC1 and PC2 correlated significantly showing they are of the same source. The conclusion is that the sources of heavy metals in soil were from both geogenic and anthropogenic sources. Diagnostic ratios of PAHs show that they are of pyrogenic and petroleum combustion origin. PAHs analysis shows that PC1 constituents were from internal combustion of gasoline and kerosene and parent geology. Comparison of heavy metals and PAHs with world standards for soil quality show that the soil is unpolluted with heavy metals and PAHs.

Heavy metals pollution indices such as SPI and NCPI show that the soil is safe, clean and not toxic to human health. Diagnostic ratios and multivariate statistics show that sources of PAHs and heavy metals were from automobile exhaust, internal combustion of gasoline and lithology. Some sample locations nearer to the point of activities obtained higher values of PAHs than sites distant from the location of activities.

Combined use of PCA and diagnostic ratios helped to unravel the sources of organic and in organic pollutants in the study area.

The soil is uncontaminated with heavy metals and PAHs. However, this study recommend siting of petroleum products handling facilities away from arable land to avoid contamination. Since the soil is unpolluted with respect to heavy metals and PAHs, it is suitable for cultivation of tuberous crops and gardening. Risk analysis of priority carcinogenic heavy metals and PAHs shows that human health is not at risk owing to the presence of petroleum products handling facilities. Continuous environmental monitoring including air and water samples in future studies will assist to determine their extent of pollution.

These findings are valuable to scientists for a better knowledge of the origin and toxicities of heavy metals and PAHs in the semi urban area of Onueke and elsewhere. This study provides a reliable geochemical data on heavy metals and PAHs pollution management for a cleaner environment.

## Acknowledgements

The authors appreciate the laboratory analyst at Springboard Research Laboratories Awka, in Nigeria for careful handling and analysis of samples. We appreciate the petrol fueling station and farmland owners for permitting us to collect soil samples from their fueling stations and farmlands, respectively. We appreciate Prof Gabriel Egbe of Veristas University Abuja for proof reading the manuscript

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