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Assessment of Polycyclic Aromatic Hydrocarbons and Heavy Metal Pollutants in Soil Around Semi Urban Petrol Stations and Automobile Mechanic Workshops

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Abstract

This study assessed the heavy metals and polycyclic aromatic hydrocarbons (PAHs) pollutant in soil around petrol filling stations and automobile mechanic workshops. Samples of soil were acquired from the depth range of 0–15 cm. Toxic heavy metals were analyzed with atomic absorption spectrophotometry. The PAHs were analyzed using phytochemical chromatographic analysis by the Soxhlet extraction method. The soil tested was weakly acidic (6.12–6.81). The trend of the heavy metals’ mean levels in soil followed the order: lead (Pb) > nickel (Ni) > vanadium (V) > cadmium (Cd). The mean levels of PAHs were in the order: 1,2-benzanthracene pyrene > anthracene > fluorene > benzo(b)fluoranthene > 1,1,2-benzopyrelene (BghiP) > naphthalene (Naph) > Dibenz(a, h)anthracene > 1, 2 benzanthracene > benzo(k)fluoranthene > phenanthrene > pyrene > xylene > acenapthylene. Pearson correlation and principal component analysis (PCA) revealed the heavy metals were generated from automobile exhaust and parent rocks. Soil pollution index and Numerov composite pollution index revealed that the soil is safe, clean, and unpolluted with heavy metals. The mean levels of heavy metals were below the European Union (2006) permissible values for uncontaminated soil. The PAH mean values were within permissible standards for unpolluted agricultural, forest, and residential soils. The diagnostic ratios of PAHs, supported by PCA, showed that PAHs in soil were produced by pyrogenic and internal combustion of gasoline and kerosene. This method of soil contamination assessment by heavy metals and PAHs is invaluable for pollution assessors in Nigeria and another area in the world.

Keywords: auto mechanic workshops, numerov composite pollution index, petrol filling stations, polycyclic aromatic hydrocarbons, soil contamination, toxic heavy metals

Introduction

Mine tailings and emissions from rapidly expanding industrial areas are possible sources of heavy metal pollution in soil [1]. In addition, the release of toxic metal wastes, leaded gasoline, paints, land applications of fertilizers, pesticides, coal combustion residues, and spillage of petrochemicals to the environment degrade soil quality [1]. Heavy metals, such as Cd, V, Zn, and Pb, constitute a group of inorganic chemicals commonly found in crude oil and drilling fluids in oilfields and contaminated sites [1]. Heavy metals are natural constituents of geological formations that host crude oil and drilling fluids consisting of salts, namely barium sulfate, and chemical components. Several organic materials, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls are commonly found in sites contaminated by petroleum products. Organic contaminants can be oxidized to carbon(IV) oxide by microbial action, whereas most inorganic metals do not go through microbial chemical degradation. Metal pollutants are more persistent in contaminated environments compared with other organic pollutants [2]. Notably, heavy metal speciation and bioavailability can be possibly determined. Inorganic and organic constituents of soil may cause risk and threats to human being and the ecosystem by means of ingestion of contact with contaminated soil and the food chain directly (Figure 1). Such a phenomenon can cause reduction in food quality, phytotoxicity, and reduction in land

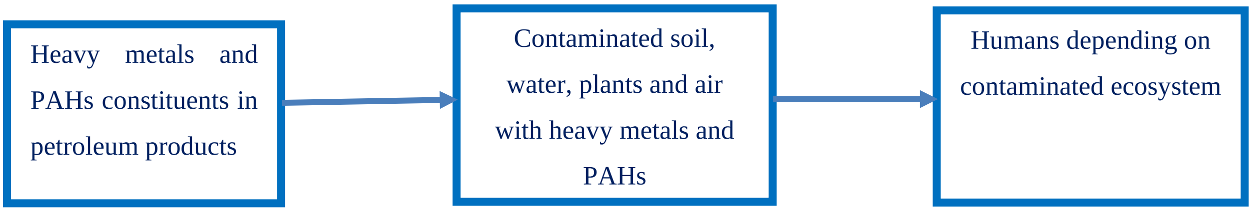

Figure 1. Schematic Showing the Contamination of the Ecosystem with Organic and Inorganic Constituents Consumed by Humans

suitable for agricultural production, resulting in food insecurity and land tenure problems. Soil acts as a sink for PAHs due to the high affinity of such compounds to soil organic matter [3].

Petroleum products exist as complex mixtures of chemicals, essentially hydrocarbons that consist of hydrogen and carbon atoms. Small amounts of constituents, such as PAHs, can be found in certain petroleum products. PAHs are loaded into the environment through the transportation and refining of petroleum [4]. The different types of petroleum products include gasoline, diesel oil, aviation fuel, and heating oil [5]. Soil contamination by petroleum substances has negative effects on plant production and puts people and animals health at risk because most of these compounds are toxic to living organisms. In 2006, the European Environmental Agency [6] declared around 34% of polluted areas in Europe were due to mineral oil. Petroleum substances, namely PAHs, and volatile aromatic hydrocarbons, including benzene, toluene, ethyl benzene, and xylene (Xyl), increase the risk of soil contamination by up to 53% [5; 7]. PAHs are primary pollutants given their potential toxicity, mutagenicity, and carcinogenicity [8; 9]. Thus, the study of these compounds has attracted global attention.

Oil exploration sites, pipelines, or leakages from underground surface tanks and improper removal of petroleum wastes cause environmental pollution by petroleum hydrocarbon. Carr [10] attempted to research the pollution caused by leaking pipeline fractures. Subsequent research focused on the effects of crude oil hydrocarbon as potential amendments on the stimulation of agricultural production through increased nitrification. The presence of hydrocarbons in soil changes its properties, such as acidity, metal mobility, and electrical conductivity. PAHs are natural constituents of fossil fuel and parts of thousands of petroleum product components. They are produced by the incomplete combustion of gasoline and diesel oil. PAHs distributed in the environment may emerge from numerous resources consist of gasoline and diesel oil combustion [4]. The soil contaminated with petroleum products is incompatible for crop growth for several months or years. Environmental pollution with petroleum and petroleum products denotes a disruption to the environment because of their persistent characteristic and spreading tendency into soils [4].

Mustafa *et al*. [1] established the trend of heavy metals that are frequently detected in hydrocarbon during oil spill (Pb > Ni > V > Zn > Cd). These metals exhibit adverse impacts on human's healthiness and are particularly carcinogenic [1]. PAHs originate from pyrogenic and petrogenic sources. Petrogenic sources including crude oil and refined crude oil products, namely gasoline, heating oil, asphalt, and coal. Meanwhile, fires, internal combustion engines, and furnaces produce pyrogenic PAHs [11].

The analysis of soil in urban fuel stations in Hemedan City, Iran showed that the total petroleum hydrocarbon (TPH) values in all stations were more than 2000 mg/kg, which was recognized by Mosaed *et al*. [7] as the standard level in soil. The study concluded that spillage in urban fuel stations has a distinct effect on the content of TPH in soil. Hu *et al*. [12] studied the PAH contents of soil in Taizhou, East China. The research showed that PAHs in fluvo-aquic soils were higher compared to those in paddy soils outside naphthalene (Naph). Fluoranthene and pyrene (Pyr) dominated other PAHs concentrations, accounting for 19.7% and 13.3% of the total mass of PAHs, respectively. The research showed that PAHs levels in soil increased with anthropogenic activities. Increased activities, such as those of fuel stations and mechanic workshops, might have resulted in significant levels of PAHs in soil. The published literature lacks explanation regarding the concentrations of PAHs and heavy metals in soil in the study area in Onueke, Nigeria. Heavy metal assessments of soils around filling stations in Benue state, Nigeria by Dau and Odor [13] showed a high degree of contamination by metals, for example Pb, Cd, and Zn. In addition, Mn and Ni manifested low degrees of contamination [13].

Rabajczyk and Swiercz [14] examined soil samples for contamination study near petrol stations in the city of Kielce, Poland and reported the exchangeable cation contents of $CaCO_3$ and PAHs. The soil parameters varied based on the soil quality, location and degree of exploitation of petrol stations. Samimi *et al*. [15] studied PAH contamination of soil along a highway in Tehran city, Iran. The study showed that the soil samples contained high levels of PAHs (154 mg/kg to 2886 mg/kg). Alharbi *et al*. [16] assessed soil contamination by underground fuel leakage from a gas station in Riyadh, Saudi Arabia. Their study investigated the possibility of applying volatile organic compounds, TPH, EC, and pH to assess pollutions come from the leaking underground fuel storage tanks. The measured TPH levels were indicative of subsoil contamination mostly at the 1–6 m depth range. The pH caused no observable release nor impact. Cocarta *et al*. [17] evaluated carcinogenic PAHs and heavy metals in Romania for environmental pollution studies. The results were assessed based on Romanian regulations on the assessment of environmental pollution. The quantitative risk calculation revealed an individual risk of 1.07×10^{-5} for children and 6.89×10^{-6} for adults.

Aigberua *et al*. [8] assessed an oil spill-contaminated site in Rumuolukwu Niger Delta in Nigeria for PAHs contamination of soil. Soil analysis showed that the diagnostic ratios of PAHs and total hydrocarbon content levels were higher in the wet season than in the dry season, and this finding may be due to a sorption phenomenon. Diagnostic ratios and PAHs sources present in the oil-contaminated soil reflected the predominance of mixed pyrogenic activities. Petrogenic activities were close to the source [9]. Mosaed *et al*. [7] researched the contaminated soil by TPH around urban fuel stations in Hemedian, Iran. The results showed that TPH values exceeded the 2000 mg/kg standard level for uncontaminated soil.

PAHs have been inserted in the list of priority organic substances by the United States Environmental Protection Agency (USEPA) [18]. Hence, they are among the substances subjected to frequent monitoring [14]. International Organization for Research on cancer identified1,2-benzanthracene pyrene (BaP) as the main carcinogen in humans. Therefore, this compound is the most often tested PAH in environmental studies [18].

The sources of Cr, Zn, Cd, and Pb in the environment mostly include vehicular traffic and the application of chemical fertilizers to soil [19]. Combustion of leaded gasoline, wet cell batteries, corroded metals, and discarded plumbing installations are sources of Pb in the environment [20]. Human exposure to Pb in high doses causes abortion, cardiovascular issues, brain damage, erectile dysfunction, and metabolic poisoning [21, 22]. Inordinate Pb intake is vulnerable to fetal damage, toxicity, interference with efficient coordination of the central nervous system, and damage to hemoglobin synthesis [23]. A high dose of Pb in children triggers convulsion, renal failure, and fatality, whereas the consumption of Cd in small dose causes food poisoning [23]. Excess Pb in the human body leads to the persistent degeneration of the central nervous system, headaches, and blood pressure increase [24]. Rajappa *et al*. [25] reported that kidney damage is traceable to Cd, which causes harmful effects on the human kidney. Cd has no beneficial role in biological species. Pb consumption is toxic to human health, such as the itai-itai reported in Japan [21]. Cd can substitute Zn in the body and cause elevated blood pressure [25]. Protracted subjection to Ni causes cell damage, loss of body weight, liver and heart damage, and malfunction of the central nervous system [21, 26]. Excessive Mn intake induces nervous deterioration [27], meanwhile persistent Cu intake predisposes the victim to increase anemia and liver and kidney injuries [27]. Consumption of Zn salts by humans causes stomach cramps and purulent diarrhea [28]. Excess nickel intake causes dermal toxicity in super sensitive humans [29]. Zn, cobalt (Co), and copper (Cu) in minor doses are essential to the body, but minor levels of Cd and Pb are toxic to humans and aquatic species [26]. Cr in excess induces liver and kidney failure, skin ulcer, and impairment of the central nervous system [26]. A high dose of Cu triggers vomiting, purulent diarrhea, and weakness of the body [21]. Although Fe and Mn are beneficial for hemoglobin synthesis, high levels of Fe result in liver, kidney, and cardiac tissues. The excess intake of Mn causes neurological disorders and muscle damage in the human body [26]. In general, the excess intake of toxic metals by animals and plants causes cancers in humans and physiological and morphological alterations and chlorosis in plants [21].

The USEPA recorded the 16 most regularly found hazardous PAHs, known as primary pollutants, and classified them into carcinogenic and noncarcinogenic types. The probable carcinogenic PAHs include chrysene, benzo(a)fluoranthene (BaF), BaP, benzo(b)fluoranthene (BbF), benzo(k)fluoranthene, dibenzo(a, h)anthracene (Dba), and indeno(1,2,3-c, d)pyrene [30]. Hence, the pollution of soil with PAHs is a challenge of utmost concern [31]. The contamination of arable soil by PAHs translates to their bioaccumulation in crops, which has potential adverse effects on human health [32]. Analysis and health risk assessment of PAHs in soil are crucial for the characterization of their fate and transport in the environment. These actions help in developing strategies for the prevention or remediation of their adverse effects [33, 34, 12].

Principal component analysis (PCA) shows the effective factors that has an impact on soil and importance of the relationship among the components and variables of data. The positive or negative correlation between factors and a variable is displayed by a high factor loading close to 1 or −1, respectively [35]. The Kaiser [35] criterion was used to determine the total number of factors for the data set in this analysis. Applying this criterion, only factors with eigen values larger than or equal to 1 were acceptable as possible sources of variance in the data. The highest priority was attributed to the factor that possessed the highest eigen vector sum. Loading values >0.40 were considered for interpretation [2003].

This study is the maiden attempt to characterize organic and inorganic pollutants in the soil of Onueke community in southeastern Nigeria. This research examined heavy metal- and PAH-contaminated soil around fuel filling stations and automobile service points. Usually, petrol stations consist of buildings with automobile service points, carwash, petrol pumps, and chambered underground fuel tanks. Toxic metals and PAHs are environmental pollutants. Toxic metals and PAHs are carcinogenic to human health. Cancer is the leading cause of deaths around the world. Humans depend on plants that thrive on soil. Therefore, contaminated soil serves as a channel for passing hazardous organic and inorganic pollutants to man. The cultivation of farmlands and gardening are the common occupations by residents of Onueke community in southeastern Nigeria. The residents cultivate on garden soil susceptible to contamination with PAHs and heavy metals, which are human carcinogens. The risk assessment of soils around petroleum product-handling facilities is needed to avert soil pollution. Petrol stations, carwash, and mechanic workshops are sources of soil contamination with heavy metals and PAHs. The evaluation of the concentration of heavy metals and PAHs in soil in the study area will help in the monitoring of these pollutants. This step will safeguard the residents from contaminated crops and vegetables cultivated in this soil. This study will form the basis of urban geochemistry for the benefit of humanity.

This study aimed to evaluate the contamination of arable topsoil by toxic heavy metals and PAHs around petrol filling stations and mechanic workshops. This aim is feasible with the following specific objectives: (1) Determine the level of potentially toxic elements (Cd, V, Ni, and Pb) commonly found in gasoline and other refined petroleum products. (2) Evaluate PAHs in soil used for gardening around fueling stations and mechanic workshops. (3) Assess the source of PAHs in soil using diagnostic ratios, Pearson correlation (PC), and PCA to determine the source of heavy metals in soil. (4) Compare heavy metal and PAHs contamination in soil around petroleum product-handling facilities with world standard values.

Materials and Methods

Study area description. The study area was located between latitudes N06° 10’ 23.0” to N06° 07’ 27.0” and longitude E08° 02’ 20.6” to E08° 01’ 33.3” (Figure 2).

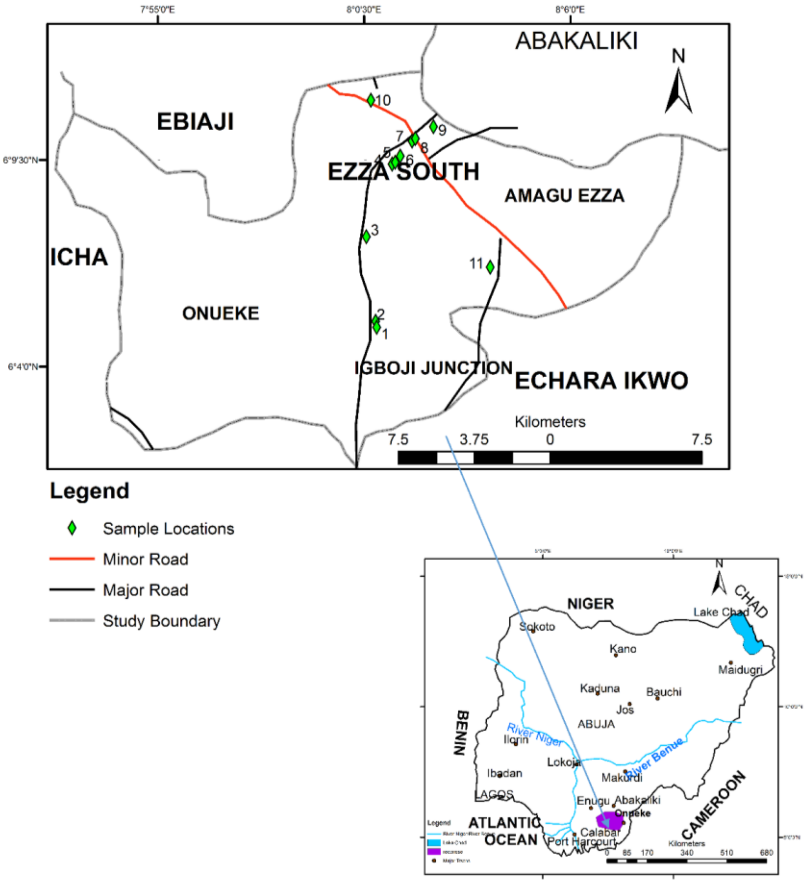

Figure 2. Study Area and Sample Locations

Onueke is in Ezza South Local Government area of Ebonyi state, Nigeria, where people sell their rich agricultural produce. The main occupation of inhabitants is farming yam, cassava, rice, cocoyam, and numerous other crops. The drainage pattern is dendritic as a function of lithology. The drainage runs eastward to join the Cross River channel. The slope is gentle, and runoff is high during the rainy season. Surface water bodies are ephemeral, and floods occur during the rainy season.

The vegetation is luxuriant and common in the tropical rainforest and densely interspersed with grasses and trees of different heights. The area is marked by the 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 400 ft and the lowest at 100 ft above the sea level.

The area is located in the tropical rainforest belt of Southeast Nigeria and signified by an average rainfall of 1750–2000 mm per annum [36]. The mean monthly rainfall varies from 50 mm to 300 mm, whereas August has 180 mm to 200 mm. The two main seasons that dominate the climate of the area are rainy and dry seasons. The rainy season normally starts in late April and ends in October. The dry season occurs from November to April. The mean annual temperature is 31.2 °C and ranges from 33 °C in dry season to 28 °C in wet season [37]. The seasonal climatic conditions are due to the north–south fluctuation of a discontinuity zone between the dry continental (Saharan) air and humid coastal air.

Geology of the study area. Although the area lacks proper and full documentation, the geology of the area within Onueke has been previously examined but mainly on a regional scale. The geology of Onueke and environs is documented in Farrington [38], Reyment [39],

Murat [40], Simpson [41], Kogbe [42], and Olade [43]. The rocks within Onueke common include shale, sandstone, limestone, mudstone, and ironstone. According to studies, shale is mainly rusty brown colored and dominant in the areas within Amagu, Idembia, Amaezekwe, Achara, and Umueze Akwa. Beneath the rusty brown colored shale are dark, gray-colored shale deposits. The shale indicates a great level of fissility with a high degree of lamination, is well jointed, and with minor occurrence of iron fillings.

Various lithologic units are found in the Lower Benue Geology. Rare cases of tectonic activity also characterize the study area. The Onueke area forms a part of the Abakaliki Anticlinorium, which flanks the lower end of the formation, very close to the Afikpo syncline (Figure 2). The Abakaliki area forms the key part of the Albian Asu River group sediments, which are predominantly shale with intercalations of sandstone, siltstone, and limestone. Abakaliki and its environs are geologically important due to their position in the Benue Trough and the tectonic activities witnessed in the area. Abakaliki formation is underlain with shale of the Albian Asu River Group. This study was conducted on a part of the Southern Benue Trough in the southeastern region of Nigeria. The Southern Benue Trough is part of the Benue depression, mainly comprises the Abakaliki Anticlinorium and Afikpo Syncline to the east and the Anambra Basin to the west (Figure 3).

Reyment [39] also described the lithostratigraphy and biostratigraphy of the Asu River Group with its type locality along Asu River, which features lower shale. A middle Albian age was assigned to the group by Reyment [39] on the basis of ammonites, such as *Oxytropidocerashausa* and *Oxytropidocerasmanuanicer as* sp. Deposition occurred under marine conditions, giving rise to deposits of alternating shale, siltstones, and sandstones.

A sequence of mafic lavas, pyroclastic flows, tuffs, and agglomerates forms a part of the Cretaceous succession within the Benue Trough of Nigeria [39]. These volcanic rocks are best exposed in the area around the different rock types encountered. The features are utilized to reconstruct and interpret their depositional environments and paleogeography using various lithofacies, stratigraphic relationship, structures, sedimentological characteristics, and paleontology. In addition, they help in the interpretation of the hydrogeology, engineering geology, and land use significance of the different rock types, minerals, and geological features.

The sediments later became folded, creating rise on the two major structural features, namely, the Abakaliki anticlinorium and the related Afikpo Synclinorium. The Eze–Aku Shale Formation of the Turonian age contains shale, siltstones, sandstones, and limestone.

Sample collection

Global Positioning System (GPS), measuring tape, geologic hammer, sample bags, field notebook, topographic map, digital camera, and hand trowel were used in sample collection. Ten (10) soil samples were collected in different locations, and one was used as the control, which add up to 11 samples. The samples were collected around auto mechanic workshops and petrol (fueling) stations. Six sample locations were from mechanic workshops (locations 5, 6, 7, 8, 9, and 10, with one sample obtained from each). The remaining locations were fueling stations (locations 1, 2, 3, and 4). Meanwhile, the control was sampled from a farmland, which is distant from any of the petroleum-handling site (Figure 2).

This field exercise lasted for 2 days. The first day was the reconnaissance survey, which was performed with the help of a topographic map, and the second day was used for sample collection. Before each sample was collected, the longitude, latitude, and elevation of the place were obtained using the GPS. Soil samples were acquired from the depth of about 0–15 cm using a geologic hammer and a hand trowel. The samples were collected in cleaned polyethylene bags.

Sample Location 1 comprised shale with dark to very light brown color. The sample was collected in a vegetable farm very close to a fueling station. A part of the farm has very light brown shale, whereas another has very dark shale. Location 2 **(**Chiezugo Petroleum Ltd: Sacred heart) is predominantly light brown colored shale, and a cassava farm is proximate to the fueling station. Traces of sand were observed on the surface of this location, at about 5 cm deep. Location 3 (Deweb Oil, Idembia) features light to dark brown color shale. The samples were obtained from a cassava farm. Very fine sand was observed on the surface of about 0–2 cm. The farm is very close to a fueling station. Location 4 (Eastern Int’l Oil, Sacred Heart) predominantly consists of coarse to fine sand grains. The surface is coarse but becomes finer with depth, that is, fine downwards and coarse upwards. In this location, a sample was obtained from a cassava/okro farm very close to a fuel station. In certain portions of the farm, shale is mixed with sand particles. Location 5 **(**mechanic workshop, Onueke Junction) is predominantly shale of dark brown color.

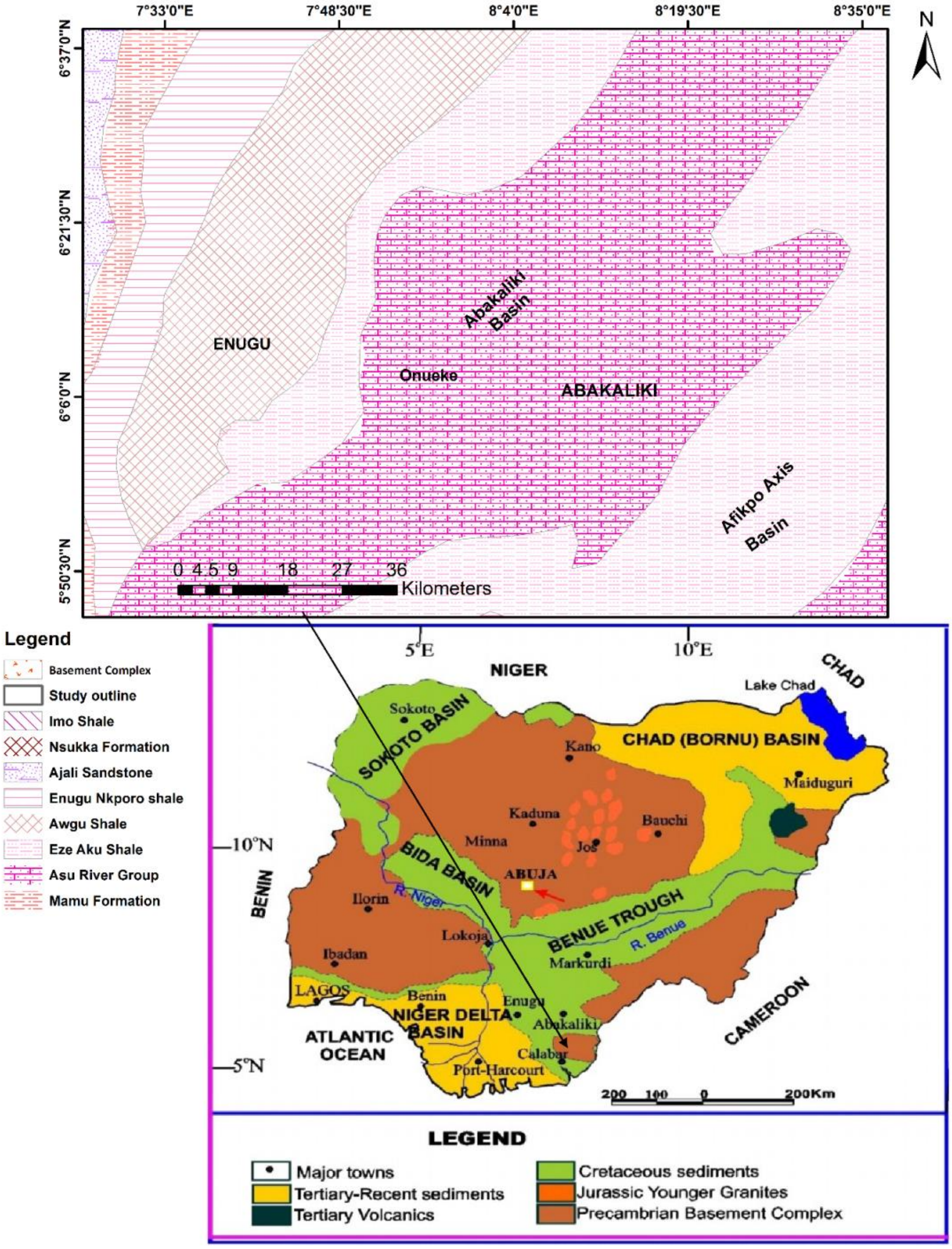

Figure 3. Geological Map of Ebonyi and Environs Showing the Study Area in Onueke (Modified from Agumanu [44])

The sample location is close to an auto mechanic workshop at Onueke junction. No farmland exists around the mechanic workshop. At Location 6 (mechanic workshop, Onueke), the sample was obtained from a mechanic workshop. No farm exists around this location. The location is predominantly dark brown shale. Sand particles were observed at this location. At Location 7 (mechanic workshop, Nwafia Ogna; Umuomo Ohiuzor), the sample was acquired close to a mechanic workshop with no farm observed nearby. This location is predominantly dark brown colored shale. At Location 8 (mechanic workshop, Amudo), the sample was obtained close to a mechanic workshop with no proximal farmland. The location is dominantly light to dark brown color shale. At Location 9 (mechanic workshop, Amudo), which features dark gray sand, the sample was collected from a mechanic workshop very close to a cassava farm. At a depth of 0–4 cm, the sand is coarse grained but becomes fine grained at 5–15 cm depth. At Location 10 (mechanic workshop, Sacred Hearts), the sample was obtained from a cassava farm close to a mechanic workshop. The site is dominantly clayey and dark brown shale. At Location 11 (Control), the control was neither from a mechanic workshop nor a fueling station or any petroleum-handling site. Instead, the sample was collected from a farm featuring clay soil noticed (shale).

Sample preparation. The samples were sundried for about five days and disaggregated with an agate mortar and pestle. The disaggregated samples were further sieved using an 80-mesh nylon sieve and later transferred to the laboratory for the analysis of heavy metals (Cd, Ni, V, and Pb). PAHs, namely, fluorene (Fluo), Naph, phenanthrene (Phen), benzo(g, h, i)perylene (BghiP), benzo(b)fluoranthene (BbF), acenaphthylene (Acen), Dibenz, benzo(k)fluoranthene (Benzok), BaP, Xyl, anthracene (Ant), 1,2-benzanthracene (BaA), and Pyr were analyzed.

Laboratory analysis aspect. Adopting the procedure developed by [45] and using the Soxhlet extraction method, 20 g homogenized sample was blended with 60 g anhydrous sodium sulfate (anhydrous $NaSO_4$) in an agate mortar to absorb moisture. Then, the homogenate was placed in a 500 mL beaker. The extraction was conducted with 300 mL n-hexane for 24 h. The crude extract result was evaporated using a rotary vacuum evaporator at 40 °C to dryness. The residue was transferred with n-hexane onto a 5 mL florisil column for cleanup.

Florisil (magnesium silicate) was heated in an oven at 130 °C overnight during clean up, transferred to a 250 mL beaker, and placed in a desiccator. A total of 0.5 g anhydrous $NaSO_4$ was added to 1.0 g activated florisil (60–100 nm mesh) on an 8 mL column plugged with a glass wool. Packed columns were filled with 5 mL n-hexane for conditioning. The stopcock was opened to allow n-hexane to run out until it reached the top of sodium sulfate in a receiving vessel, whereas the top of the column was tapped gently until florisil settled well in the column. The extract was transferred to the column with disposable Pasteur pipette from an evaporating flask. Each evaporating flask was rinsed twice with 1 mL portions of n-hexane and then added to the column. The eluate was collected into an evaporating flask and rotary evaporated to dryness. The dry eluate was dissolved in 1 mL n-hexane for phytochemical chromatographic analysis [45].

Fixed Setting: In general, the operator must adjust gas flows to the columns, inlets, detectors, and split ratio. 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 these parameters were fixed to correct values, and the entire instrument was double checked. Buck 530 gas chromatograph (GC) was equipped with an on-column, automatic injector, mass spectroscope, and HP 88 capillary column (100 m × 0.25 μm film thickness; CA, USA).

The detector temperature A and injector temperatures were 250 °C and 22 °C, respectively. The integrator chart speed was 2 cm/min, the oven temperature was set to 180 °C, and the GC allowed warming up. Conditions were set at the warming temperature. The not-ready light on the instrument was turned off when the instrument was ready, and we began running the equipment. Then, 1 µl sample was injected onto column "A" using the proper injection technique [45].

Heavy metals were analyzed by an atomic absorption spectrophotometer (AAS; Agilent FS240AA), in accordance with the method of American Public Health Association [46]. The working principle of the AAS operation is based on the aspiration of the sample into the flame and atomization when the light beam of the AAS is directed through the flame into the monochromator. The detector then determines the amount of light absorbed by the atomized element in the flame. Metals have their own characteristic absorption wavelength. Based on this principle, a source lamp consists of a certain element was applied, generating the method relatively free from spectral or radiation interferences. The amount of energy of the characteristic wavelength absorbed in the flame was proportional to the concentration of the element in the sample [47].

For sample digestion, around 2 g dried sample was weighed into a digestion flask and added with 20 mL acid mixture (650 mL concentrated HNO_3, 80 mL perchloric acid, and 20 mL concentrated H_2SO_4). The flask was heated until a clear digest was produced. The digest was diluted with distilled water to the 100 mL mark. The sample was then thoroughly mixed by shaking, and 100 mL of it was transferred to a 250 mL glass beaker. Then, 5 mL 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. After cooling, the mixture was then diluted 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 [48].

A series of standard metal solutions in the optimum concentration range was 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. The calibration curve for each metal was constructed by plotting the absorbance of standards versus their concentrations [48].

Data analysis. Descriptive statistics was performed on heavy metal and PAHs data using SPSS version 20 [49]. Using SPSS package, the mean, standard deviation; kurtosis, skewness, and coefficient of variance were computed.

Soil pollution index (SPI) and Numerov composite pollution index (NCPI) were computed using the equations developed by CEPA [44]. SPI is given by the following:

$$P_i = \frac{C_i}{S_i} \tag{1}$$

where Pi represents the SPI, Ci is the content of heavy metals in soil, and Si stands for the threshold value of heavy metals.

The NCPI is given by the following equation:

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

where NCPI represents the Numerov composite pollution index, Pi_{max} refers to the maximum value of SPI, and P is the mean value of SPI.

PC is applied to assess the degree of interrelation between two variables [50]. PCA produces a subset of uncorrelated variables known as components, which informs the variance obtained in the original data [51; 52]. PC and PCA were applied to identify the sources of heavy metal contamination in soil. Diagnostic ratios of PAH concentrations were used to characterize the sources of PAHs. To identify the PAH sources in soil, we computed the ratios of Phen/Ant, Ant/(Ant + Phen), Fluo/Pyr, BaP/(BaP + Pyr), Fluo/(Fluo + Pyr), and BaA/(BaA + Pyr) in this study. In addition, PCA was applied to decipher sources of PAHs in soil in the study area.

Results

Statistical summary of results. Table 1 shows the statistical summary of physical parameters and heavy metal levels (mg/kg) in soil. Tables 1, 2, and 3 show the summary statistics of heavy metals, PAHs, and PAH classification in soil, respectively.

The pH levels ranged from 6.32 to 6.81 with a mean and standard deviation of 6.62 ± 0.19 with negative skewness and kurtosis. The soil EC achieved a mean of 50.50 µs/cm and a standard deviation of 16.30 with a negative skewness and kurtosis. Ni possessed a mean of 0.64 mg/kg and standard deviation of 0.14 with a positive skewness but negative kurtosis. The mean value was below the European Union (EU) standard limit of 35 mg/kg for unpolluted soils. Cd attained a mean value of 0.012 mg/kg and a standard deviation of 0.03. V achieved a mean of 0.02 mg/kg and standard deviation of 0.01 mg/kg. Pb possessed a mean of 1.25 and a standard deviation of 1.13 with a negative kurtosis (Table 1). The mean concentrations of heavy metals had the following trend: Pb > Ni > V > Cd.

PAH concentrations of soil in the study. In Table 2, the mean value of PAHs showed that Fluo had a mean value of 2.01 µg/kg with a standard deviation of 1.64 with negative skewness and kurtosis. The minimum value of all the PAHs was 0.0 mg/kg. Fluo, BghiP, Benzo(b), and BaP possessed mean values of more than 1 µg/kg, whereas the remaining PAHs had mean values below 1 µg/kg. The PAH mean values were below the standards prescribed for uncontaminated soils (Table 2). The mean concentrations of the PAHs were below the values prescribed for permissible concentrations (<200 µg/kg) for agricultural, forest, bush soils, wasteland, and residential and urban areas [14].

Figure 2 displays the spatial distribution of PAH concentrations in sample locations. Fluo, BbF, and Dibenz exhibited higher concentrations. The mean values of PAHs in this study showed the following trend: BaP > Ant > Fluo > BbF > BghiP > Naph > Ant > Diben > BaA > Benzok > Phen > Pyr > Xyl > Acen.

Table 3 shows the classification of PAHs in soil in the range of <200 (not contaminated) to >10,000 (very heavily contaminated).

Multivariate analysis of data. The PC in Table 4 revealed the significant negative correlation of pH with EC. The EC exhibited a significant negative correlation with Cd. Ni and Pb correlated significantly. V and Pb recorded a significant correlation. In Table 5, which shows the PCA of heavy metals, two distinct principal components (PCs) were due to the homogenous geology of the study area. The PCA explained a total variance of 77.62%. PC1 contributed 40.72% of the total cumulative percentage of 77.62%, with positive significant constituents consisting of pH, EC, Cd, V, and a negative EC. PC2 contributed 36.90% of the total variance and incorporated significant constituents, such as Ni, V, and Pb.

Table 1. Summary Statistics of Physical Parameters and Heavy Metals in Soil of the Study Area

Variable	unit	N	Minimum	Maximum	Mean	Std. Dev.	Skewness	Kurtosis	CV%	EU[53]
pH		11	6.32	6.81	6.62	0.19	-0.66	-1.58	2.71	6.5-8.5
EC	µs/cm	11	23.60	70.90	50.60	16.30	-0.27	-1.49	32.21	1500
Ni	Mg/kg	11	0.43	0.85	0.64	0.14	0.25	-1.00	21.87	50
Cd	Mg/kg	11	0.00	0.08	0.012	0.03	2.33	5.24	210.41	1
V	Mg/kg	11	0.00	0.05	0.02	0.01	0.67	0.13	55.55	100
Pb	Mg/kg	11	0.00	3.22	1.25	1.13	0.26	-1.32	90.04	60

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

	N	Minimum	Maximum	Mean	Std. Dev	Skewness	Kurtosis	CV %	PC PAH 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

NA- Not Available

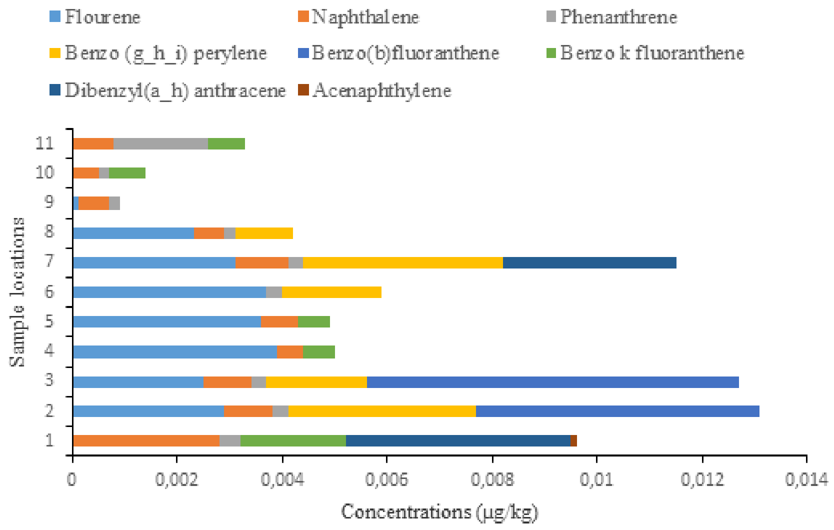

Figure 4. Bar Chart of Several Selected PAHs

Table 3. Classification of PAH Contamination in Soil (µg/kg) (After Maliszewska-Kordybach, *et al*. [2])

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

Table 4. Pearson Correlation Matrix

	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 shows the PCA of PAHs in four distinct components with the following total variance: PC1, 36.303%; PC2, 56.261%; PC3, 71.451%; PC4, 84.26%. PC1 exhibited significant constituents, including Fluo, Naph, Acen, Diben, Benzok, and BaP. PC2 contributed 19.96% of the total variance with significant constituents comprising Fluo, Phen, and BghiP, PC3 contributed 15.19% of the total variance with significant constituents consisting of BghiP, Benzo(b), and Ant. PC4 contributed 12.81% of the total variance with significant constituents, such as Xyl, Ant, and BaP (Table 6).

Diagnostic ratios of PAHs. The diagnostic ratios of Ant/Ant + Phen in Location 6 obtained a value of 0.769. Phen/Ant recorded a ratio of 0.3. This result proves that the source of PAHs in this location is pyrogenic. Ant/Ant + Phen > 0.10 indicated pyrogenic PAH. Phen/Ant < 10.0 is pyrolytic [11; 53]. The ratios for the other PAHs were as follows: 0.3 for Phen/Ant in Location 3; 7.67, 0.94, and 0.88 for Fluo/Pyr, BaP/BaP + Pyr, and Flu/Flu + Pyr, respectively, in Location 8; 0.67 for BaA/BaA + Pyr in Location 103.5 Evaluation of soil heavy metal pollution.

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	

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 [50])

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

Table 9. NCPI Classification (After CEPA [50])

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

The pH classification pH < 6.5, $6.5 \leq$ pH < 7.5, and pH > 7.5 indicated contaminated, moderately contaminated, and suitable soils, respectively. The soil pH was in the range of 6.32–6.81, which is not within the EU [54] range of 6.5–8.5 for uncontaminated soils (Table 1). The soil was therefore moderately contaminated. The SPI (Table 7) values for each heavy metal (Ni, Cd, V, and Pb) were ≤1.0. Hence, the soil can be classified as safe and clean of heavy metal pollution (Table 8). The computed NCPI value was <0.7, indicating the presence of safe and clean soil (Table 9).

Discussion

Heavy metals and PAHs concentrations in soil. Table 1 presents the range of heavy metal concentrations in soil. None of the mean values of the metals exceeded the threshold value by the EU for unpolluted soils. The range of soil PAHs in Table 2 reveals that all the mean values of PAHs were below the permissible values for unpolluted soils. The comparison of mean PAHs in soil with the standard in Table 3 revealed that the soil was uncontaminated. The spatial distribution of PAHs in soil Figure 4 indicated that high-concentration PAHs included Fluo, Dibenz, and BbF, among which Dibenz and BbF are carcinogenic. The high coefficient of variation (CV)% of heavy metals and PAHs in soil revealed that they were contributed by a nonpoint source and anthropogenic input.

Ni and Pb recorded high concentrations in the study. The values of Cd and V were extremely low. The concentration of Ni ranged from 0.34 mg/kg to 0.849 mg/kg. The lowest value was observed in a cassava and okra farmland near Eastern International Oil, Sacred Heart. The highest value was noted at Location 5, near a mechanic workshop at Onueke junction in a farmland. The least value of Pb was established at Location 1 in a vegetable farmland very close to a fueling station. The highest value of (2.150 mg/kg) was obtained at Location 8 near a mechanic workshop. The sources of Ni include automobile bodies, wires, and parent geological material. The permissible limit of Ni by EU [53] for unpolluted soil is 50 mg/kg. The sources of Pb comprise parent geological material, leaded petrol, smelter, coal combustion, and automobile exhaust. Excess Ni intake causes allergic skin diseases, such as itching, cancer of the lungs, and nose sinuses through continuous inhalation and affects fertility and hair loss [55; 56; 57]. Excessive exposure of children to Pb causes impaired development, reduced intelligence, short-term memory loss, disabilities in learning, and coordination problems and risk of cardiovascular disease [56; 58]. Most studies used CV% to identify heavy metals having anthro-pogenic sources in soil [59; 60]. The high CV% of Pb and Ni in the study indicated their anthropogenic origin. The Cd concentration ranged from 0 mg/kg to 0.008 mg/kg. The highest value of Cd was obtained at Location 7 near a mechanic workshop. The sources of Cd are fuel combustion and vehicle exhaust structures. The high CV% (210) of Cd proved its anthropogenic input. The sources of Cd also include Fe and Mn oxides. The acceptable level of Cd in unpolluted soil is 0.8 mg/kg. Cd is carcinogenic and a mutagenic endocrine disruptor, and it damages the lungs and affects calcium regulation in biological systems [61]. The heavy metals most frequently contained in oil spill are in the order Pb > Ni > V > Zn > Cd [17]. This result conforms with the study results conducted near petrol filling stations and mechanic workshops, with the order of heavy metals being Pb > Ni > V > Cd. No appreciable difference was observed between heavy metals levels at the control site (Location 11) and the affected locations. All the heavy metals tested were below the desirable maximum value level in unpolluted soils recommended by the EU [53].

Most PAHs are a group of hydrocarbons that are contained at relatively high amounts in crude oil, coal, coal tar, and most of their products. PAHs in urban centers originated from petrogenic PAHs from anthropogenic sources, such as asphalt fuels and lubricating oil drips from cars and tank storage of gasoline to heavy oils underground, and coal-heating devices at homes. Petrogenic PAHs also originate from these sources [8]. Given that soil is moved around and with the expansion of urban centers, the concentrations and locations of petrogenic PAHs in urban centers are difficult to predict [11].

PAHs, such as Fluo, Naph, and Phen, exhibited an even spatial distribution compared with the others (Figure 2). Other PAHs were unevenly detected and unavailable in most locations. The mean levels of Fluo and BaP were 2.01 and 2.04 µg/kg, respectively. The mean values of BghiP, Benzob, and BaP were 1.12, 1.14 and 2.04µg/kg, respectively. Anthropogenic input (nonpoint source) was suspected at high levels of PAHs. The mean values of other PAHs were <1.0 µg/kg. All the priority PAHs tested were below the recommended permissible limits for clean and unpolluted soil for agricultural, residential, and forest areas (Table 2). The findings on PAHs sources using diagnostic ratios showed that the PAHs were produced by pyrogenic and petroleum combustion. This study used Pyr instead of chrysene to compute several of the diagnostic ratios and to obtain reliable information because both are carcinogenic PAHs. The method involved testing the appropriateness of using Pyr in place of chrysene in computing diagnostic ratio.

Multivariate analysis. The positive correlation between Ni and Pb and between V and Pb showed the possibly same source of the elements (Table 4). The negative correlation between pH and EC and between EC and Cd implied different sources. The low negative correlation between pH, EC, and Cd with Ni, V, and Pb showed that the concentrations of these elements were derived by different factors [62]. The negative correlation indicated that as one element increased, the other decreased, and vice versa. Automobile exhaust is a possible source of Pb, whereas Ni originates from Ni wires and parent rock weathering. Ni and Pb are most likely to be affected by anthropogenic activities [62]. As shown in Table 5, the PCA of heavy metals unveiled that pH, Cd, and V are significant constituents in PC1. This result implies that a high pH level mobilizes Cd and V at reduced EC. The sources of Cd and V include geological materials and automobile exhaust and leaded petrol combustion. PC2 possessed positive significant constituents of Ni, V, and Pb. Their possible sources are geological weathering and automobile exhaust petrol combustion at reduced pH. The significant negative correlation of Cd and EC showed that different factors control their concentrations in soil. This relationship was buttressed by PCA, in which PC1 contained a significant negative EC and a positive Cd. This result can be interpreted as geogenic and anthropogenic inputs. PC2 reflected gasoline and kerosene combustion as sources. The significant components of PC2 were significantly correlated. This result revealed that they originated from the same source. The components were chalcophillic elements and had affinity for sulfides. The major sources of Pb in soils include automobile exhaust fumes, paint pigment manufacturers, pesticides, and mining, burning of coal, batteries, and less likely from atmospheric deposition [63]. Ni is likely sourced from electroplating and battery industries [63]. The significant negative EC and Cd correlation showed an anthropogenic input. Pb is soluble in soil, but Ni is not [63].

In addition to diagnostic ratios of PAHs, PCA was performed on the PAH data and identified four distinct PCs. The eigen values explained 84.20% of the variance. This result helped in the selection of statistically independent source tracers (Table 6). PC1 consisted of significant constituents (Naph, Acen, Diben, Benzok, Fluo, and BaP). Dibenz, Benzok, and BaP are indications of emissions from internal combustion engines [64; 12]. BaA can be interpreted as the product of the combustion of gasoline and kerosene [12]. Thus, PAHs in soils of Onueke, Nigeria mainly come from the internal combustion of gasoline and kerosene and parent geological materials.

Risk assessment using pollution indices. The mean SPI values of Ni, Cd, V, and Pb fell in class 1 SPI $\leq$ 1.0, interpreted as safe and clean soils (Table 7 and 8). The values of NCPI fell in class 1 NCPI $\leq$ 0.7, representing safe and clean soils (Table 9). NCPI is a comprehensive index used to classify soils in terms of heavy metal pollution. Nwankwoala and Emenu [65] applied Numerov integrated pollution index to analyze the data obtained from topsoil samples from filling stations in Anambra state, Nigeria. The analysis revealed that the soil was heavily contaminated by the activities of fueling stations. The pH in this study ranged from 6.32 to 6.81, indicating that the soil is weakly acidic. The pH correlated significantly with the EC, showing that the soil acidity resulted from weathering and organic matter decomposition. Idugboe *et al.* [66] analyzed soil samples around mechanic workshops in Benin City, Nigeria and established a pH below 6.5 and high conductivity values. This result demonstrates acidity and the existence of soluble salts.

Conclusion

The soil around petroleum product-handling facilities is weakly acidic. Ni, Cd, V, and Pb recorded low concentrations. Pb and Ni recorded low concentrations with a slightly elevated pH in several petroleum product-handling locations. Heavy metals were positively skewed, whereas only Pb had a negative kurtosis. Cd and Pb possessed CV% above 50%, indicating an anthropogenic origin. The mean levels of heavy metals were below the standards prescribed by the EU for clean unpolluted soils. The values for PAHs were below the standards for unpolluted soil. PAHs are standards for uncontaminated soils for agriculture, forest, and residential areas. The comparison of mean values of PAHs with soil standards showed that the soil was uncontaminated. Carcinogenic PAHs (BbF and Dibenz) and non-carcinogenic PAH (Fluo) recorded higher concentrations than the other PAHs. Ni and Pb; V and Pb correlated strongly and probably originated from the same source. From PCA analysis, the heavy metals came from automobile exhaust, petrol combustion, and parent geological materials. The source of PAHs is the internal combustion of gasoline and kerosene. The arable soil used in the study is suitable for the cultivation of tuberous crops and gardening given that it is unpolluted with respect to heavy metals and PAHs.

SPI and NCPI indicated that the soil is safe, clean, and uncontaminated by heavy metals. Diagnostic ratios of PAHs indicated that the source of PAHs in the study is pyrogenic and petroleum product combustion. Unlike existing studies, this research integrated heavy metals pollution with PAHs close to mechanic workshops, fueling stations, kerosene, and diesel dispensing outlets. This integrated approach is overarching and presents soil contamination around petroleum product facilities comprehensively and a guide to regulating soil contamination around petroleum product-handling facilities in the region. No such preceding work is available in the study area.

This study will serve as a guide to assess the soil pollution caused by petroleum products handled in the region. The research information, method, and science can be applied in Nigeria and other parts of the world to assess the environmental degradation caused by crude oil spill and refined petroleum products for the handling of environmentally related problems.

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Appendices

Index of abbreviations and chemical compounds

PAHs	polycyclic aromatic hydrocarbons
Fluo	flourene
Naph	naphthalene
Phen	Phenanthrene
Bghi	Benzo (ghi) perylene,
benzob	benzo (b) fluoranthene,
acen	acenaphthylene
Diben	dibenzyl(a_h) anthracene
benzok	benzo (k) fluoranthene,
BaP	Benzok benzo (a) pyrene
Xyl,	xylene
Ant	anthracene
BaA	1, 2 benzanthracene
(Pyr)	pyrene
PCA	Principal Component Analysis
PC	Pearson Correlation
PCs	Principal Components
NA	not available
EU	European Union
USEPA	United States Environmental Protection Agency
NCPI	Numerov Composite Pollution Index
SPI	Soil Pollution Index

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