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Chemical Evaluation of Petroleum Sludge Impacted Soils from Itsekiri Communities around Warri Refinery, Delta State, Nigeria

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Authors' contributions

This work was carried out in collaboration between both authors. Author DMS designed the study, performed the statistical analysis, wrote the protocol, first draft of the manuscript. Authors UMU and DMS managed the analyses of the study. Author UMU managed the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

Effluents from petrochemical operations are generally considered to be harmful to the environment particularly due to their accumulated levels of petroleum hydrocarbons which distort the properties of the habitat immediate to such facilities. This study was undertaken to compare and appraise the petroleum hydrocarbon constituents from oily sludge discharge as well as changes in the physicochemical composition of soils within an 8.5 km radius from Warri refinery in Delta State, Nigeria. Data obtained revealed an almost identical acidic soil environment (5.31 – 5.54) to that of the contaminating sludge (5.25) unlike that of the control (7.81). The overall levels of sulphate (412.73 – 465.13 mg/l), electrical conductivity (0.44 – 0.57 µs/cm), organic carbon (10.02 – 18.22%), oil and grease (96077 – 587642 mg/kg) were observed to be higher across all tested soil samples in comparison to that of the control sample; 56.73 mg/l, 0.26 µs/cm, 4.25%, 1032 mg/kg in that order while that of the total nitrogen (0.08 – 0.44%) and phosphorus (8.72 – 12.40%) were low

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compared to the control (0.87, 15.62)% respectively. The total petroleum hydrocarbon (TPH) content ranged from 48063 – 293846 (mg/kg) across the 5 tested sampling sites with the sludge sample having 686615.6 mg/kg whilst that of the control was found to be averaging 651 mg/kg as detected via GC-FID. The Polycyclic aromatic hydrocarbon (PAH) values ranged from 189.93 – 4255.87 (mg/kg) across the 5 tested sites with that of the sludge being 13648.33 mg/kg while the control site exhibited a 68.06 mg/kg PAH concentration as detected via GC-MS. Dibenzothiophene was also detected with values ranging from 3167.31 – 19001.84 mg/kg which was very high compared to other hydrocarbons. The risk assessment of the soil quality conducted indicated that all the studied sites were seriously contaminated but the level of contamination was a function of proximity of each site to the refinery. The presence of oily sludge due to the operational activities at the refinery resulted in change of known physicochemical properties of the soil which undoubtedly distorted the natural fauna and flora in the affected sites.

Keywords: Soil; total petroleum hydrocarbons; polycyclic aromatic hydrocarbons; physicochemical properties.

1. INTRODUCTION

Prior to the discovery of crude oil in the Niger Delta region of Nigeria in 1956, agriculture (before 1970) was the mainstay of the Nigerian economy. The oil boom witnessed in the 1970s led to a tremendous increase in industrial activities [1]. World's attention shifted to the Niger Delta as oil rigs, wells and exploration activities eroded the territory. But when the issues of oil spill emanated, the initial euphoria that greeted the discovery of oil in commercial quantities in the modest communities soon died down [1,2]. Whilst petroleum products in its refined or crude stage serve the needs of mankind, they pose major environmental constraints. Refined petroleum products are more toxic compared to crude due to alteration in the matrix during refining process.

Incidences of neglected oil spills prevail the region, thus resulting in the perseverance of large reservoirs of petroleum sludge which spilled over and leached within the affected habitats. These culminated in the dilapidation of the environment and the devastating level of ecological biota [3]. One of the major problems faced by oil refineries is the safe disposal of this petroleum sludge. Amongst the array of organic contaminants in the environment, oily sludge represents the most challenging one as it is an extremely complex hydrated mixture of waste oils including petroleum hydrocarbons [total petroleum hydrocarbons (TPHs) comprising mainly the aliphatics and polycyclic aromatic hydrocarbons (PAHs)]. PAHs refer to a ubiquitous family of several chemically related environmental importunate organic compounds of various structures and with different levels of toxicity. TPH is a generally accepted term which described a wide variety of derived petroleum compounds and it's by products. This parameter TPH measures the gross quantity of these petroleum hydrocarbon products present in an environmental media rather than seeking to measure individual component separately which could be tedious and non-practicable. Many of the constituents of the sludge are carcinogenic and potent immunotoxicants [1,4,5]. In addition to the highly viscous nature of petroleum sludge, studies revealed that this complex hydrocarbon also possesses a high concentration of heavy metals resulting from the wearing of mechanical parts during refining operations [6]. Improper disposal of this petroleum sludge leads to environmental infectivity, particularly soil contamination, and poses a serious threat to ground water [7,8]. There is a high possibility of accumulation of these contaminants in the food chain by their consumption in drinking water, fish and crops, which could pose a risk to human and other living organisms [9,10,11]. Reports suggest that such patterns have been directly linked with the upsurge of kidney disease, liver problems, possible damage to the bone marrow and even increase the risk of cancer within affected regions [9,11,12,13].

Prior research indicated that petroleum sludge contaminated sites in the Niger Delta region immediately adjacent to an active refinery, particularly, Itsekiri communities around Warri Refinery and Petrochemical Company (WRPC) are poorly and most often never investigated to know the full extent of petroleum hydrocarbon contamination [1,9,14]. The rate at which Itsekiri communities are being impacted with petroleum sludge as a direct result of refining operations has become alarming, which warranty close attention in recent times, thereby necessitating

the need for thorough assessment of the soils within, as one of the primary sources of livelihood.

It is conceivable that the devastating effects of oil spill on the impacted communities around WRPC could be attributed to the scarce information pertaining to qualitative scientific baseline data that would serve as an essential tool in impact assessment and aid in a rapid response to such environmental mishaps. An understanding of the characteristic features of a contaminated environment is key to the successful strategies employed towards its remediation [1]. This paper focused on the chemical evaluation of petroleum sludge impacted soils from Itsekiri communities around WRPC. Studied analytes include physicochemical parameters, TPHs and PAHs. The assessment was carried out on real samples to ascertain the level of contamination caused by the petroleum sludge.

2. MATERIALS AND METHODS

2.1 Description of Sampling Sites

Delta State which is being nicknamed "The Big Heart of the Nation" lies approximately between Longitude 5˚00 and 6˚.45' East and Latitude 5˚00 and 6˚.30' North of the equator. It is located in southern Nigeria with an area of 17,698 km^2 (6,833 sq mi) and a population of 4,112,445 as at 2006 [15,16,17]. The oil spill impacted communities (Itsekiri) are situated between Latitudes 5˚30'N and 5˚33'N of the Equator and Longitudes 5˚45'E of the Prime Meridian, in Warri South Local Government Area of Delta State.

2.2 Sample Collection, Handling and Preservation

US EPA (SW-846) guidelines were applied, using composite sampling for collecting sediment samples where sub-samples were collected from randomly selected locations in an area. Five (5) oily sludge samples were collected from the discharge pit of WRPC with core sampler in a 500 mL wide-mouth glass jar and pooled. Also, fifty (50) soil samples were randomly collected using soil auger from the depth of 0-15 cm from five selected oil-impacted communities (Ubeji – 500 m, Ekpan – 1.5 km, Aja-Etan – 2.5 km, Ifie-Kporo – 3.0 km, Ijala-Ikenren – 3.8 km from WRPC and were coded A, B, C, D and E respectively) and stored in sealed polyethene bags (Fig. 2, Table 1). There were ten (10) replicates for each sampling site and the sub-samples were thoroughly mixed to obtain a representative sample of each. A control sample was also collected 8.5 km away from WRPC. These were stored in well-labelled amber glass bottles with Teflon-lined screw cap, held at 4°C immediately in a cooler of ice and transported to the laboratory for pre-treatment and analyses [1,18]. The soil samples were air-dried for two weeks, rolled manually, mixed and sieved with 2 mm mesh to remove stones and debris. These were properly stored in well-labelled air-tight containers until analysis. All analyses were carried out in triplicates to minimize error.

2.3 Reagents

All solvents and reagents used were of trace analysis (TA), chromatographic or ACS grade. Aliphatic standard, 1000 ppm (Catalog Number: DRH-008S-R2) containing 35 aliphatic hydrocarbon components [C_8–C_{40}, Pristane & Phytane] and Stock solutions of 1000 ppm (Catalog Number: H-QME-01) PAH standards containing 23 environmental PAHs components were purchased from AccuStandard, Inc., New Haven, CT.

2.4 Determination of Soil Physico-chemical Properties

pH was determined for all samples by using 1:2 slurry of 10 g sediment samples with 20 ml deionised water. After 10 minutes, pH was determined using a digital pH meter (Jenway model 3015) with a glass-calomel electrode combination. Conductivity measurements were determined on fresh sediment samples using a conductivity meter (Systronics-304) at 25°C. The moisture content was determined by the gravimetric method.

Soil organic carbon was determined using a modified dichromate wet oxidation method (Walkley-Black (WB) procedure) which measures the active, or decomposable organic matter in the soil samples. The organic matter content in the soils was determined by multiplying the organic carbon content from the procedure above by 1.729 (using the assumption that organic matter contains approximately 58% carbon) [21]. The apparatus for "0 Bar" water holding capacity method was used to determine the water holding capacity. Sulphate was determined by a gravimetric method which involved the use of an excess amount of barium

chloride solution. Total nitrogen in the soil samples was determined using the macro Kjeldahl's method. Available phosphorus was determined by Bray No. 1 method. Sodium and Potassium were determined using a flame photometer (Sherwood Model 410) after due calibration. Oil and grease by gravimetric method also. All these were done following the standard protocols and methods of American Public Health Organization (APHA) [19,20,21].

2.5 Hydrocarbon Analysis

A test portion of 10 g ± 0.05 g of homogenized sediment sample each was weighed into 100 ml glass scintillation vials. About 5 g of anhydrous Na_2SO_4 was added to the samples in each vial in order to eliminate aqueous portions if any. 20 ml of 1:1 acetone: dichloromethane was added and the vials were sealed with a foil-lined cap and shaken on a reciprocating platform shaker (Eberbach 6010, Fisher Scientific, St. Louis, MO) at 120 cycles/min for 1h. The extraction procedure was repeated thrice for each sample giving ~60 ml of final extracting solvent for each. Blanks were prepared following the same procedure without adding sediment sample. The extracts were centrifuged for 10 min at 2000 rpm and the organic layer containing the extracted compounds was siphoned out with a Pasteur pipette, into a round-bottom flask, further dried with Na_2SO_4 and clean-up procedure using silica gel column carried out according to ISO Method 16703. The sample extract was then concentrated to ~2 ml using a rotary evaporator and stored at 4°C until analysis.

2.5.1 Preparation of calibration standards

Five (5) point serial dilution calibration standards (2, 6, 10, 50, 1000 ppm) was prepared from TPH stock standard and used to calibrate the GC-FID and (1, 5, 10, 50, 100 ppm) was prepared from PAH standard and used to calibrate the GC-MS prior to analysis. For the TPH, the integration event timetable was programmed to calculate the TPH in the C_{10}-C_{36} ranges. After calibrating with TPH standards, study was carried out using the GC preset temperature and eluting conditions. For the PAH, prior to calibration, the MS was auto-tuned to perfluorotributylamine (PFTBA) using already established criteria to check the abundance of *m/z* 69, 219, 502 and another instrument optimal & sensitivity conditions. Determination of the levels of PAHs in the sample was carried out using GC-MS by operating MSD in selective ion monitoring (SIM) and scan mode to ensure low-level detection of the target constituents.

2.5.2 Instrumentation and conditions

TPH was determined using Agilent 7890 Series GC (Agilent J&W DB-UI G3440A) equipped with an FID detector (340°C). A Supelcowax-10 DB fused silica capillary column (30 m, 0.32 mm ID with 1µm film thickness) was used with helium as the carrier gas and the column head pressure was maintained at 10 psi to give a flow rate of 1.0 ml/min. The injector and detector temperature were maintained at 200°C and 340°C respectively throughout the run. The initial temperature was kept at 45°C for 1 min, ramped to 110°C at 10°C/min, to 270°C at 3°C/min, and to 275°C at 15°C/min and held at that temperature for 10 min. A 1 µg*/l* aliquot was introduced by direct injection with a 1-min purge-off.

GC-MS analysis for the PAH was performed on an Agilent 7820A Series gas chromatograph (Agilent J&W DB-UI 8270D) coupled to 5975C inert mass spectrometer with EI source, HP-5 capillary column coated with 5% Phenyl Methyl Siloxane (30m length x 0.32mm diameter x 0.25 µm film thickness) (Agilent Technologies). The carrier gas was Helium used at a constant flow of 1.48 mL/min at an initial nominal pressure of 1.49 psi and average velocity of 44.22 cm/sec. 1µL of the samples were injected in splitless mode at an injection temperature of 300°C. Purge flow to spilt vent was 15.0 mL/min at 0.75 min with a total flow of 16.67 mL/min; gas saver mode was switched off. Oven temperature was initially programmed at 40°C for 1 min then ramped at a rate of 12°C/min to 300°C for 10 min and held at that temperature. Runtime was 32.67 min with a 3 min solvent delay. The mass spectrometer was operated in EI mode at 70eV with ion source temperature of 230°C, quadrupole temperature of 150°C and transfer line temperature of 300°C. HP MS-ChemStation (DOS series) was used to program the data acquisition and analysis.

2.5.3 Identification and quantification

The quantification of TPH in a sample from the GC run was conducted through total chromatographic area counts after appropriate baseline integration based on the reference standard and calculated by adding all petrogenic analytes and unresolved complex mixtures (UCMs) excluding solvent peak.

The PAHs in the samples were identified by a combination of a retention time match and mass spectra match against the calibration standards. Quantification of PAHs was carried out by the method of external standardization to check matrix interferences that affect detection.

2.5.4 Blank determination

A procedure blank was analyzed periodically for each batch of 10 samples. It was prepared using the entire analytical procedure as well as the same reagents and solvents as for the samples. The purpose of the analytical blank is to check the absence of contamination by interfering compounds, which cause quantification mistakes.

2.5.5 Limit of detection

Limit of detection (LoD) is the minimum concentration of analyte that can be detected but not necessarily quantified with an acceptable uncertainty. LoD was determined from analysis of seven replicates of method blanks which were treated in the same procedure as the actual samples.

LoD was calculated as: $LoD = 3 \times S_b$

Where, S_b is the standard deviation of the method blank.

2.5.6 Limit of quantification

The limit of quantification (LoQ) is the lowest concentration of an analyte in a sample which can be quantitatively determined with acceptable uncertainty. LoQ was obtained from triplicate analysis of seven method blanks which were treated in the same procedure as the actual samples.

The LoQ was calculated as $LoQ = 3 \times S_b$

Where, S_b is the standard deviation of the method blank.

2.6 Individual Risk Assessment or Soil Quality Standards (SQSs)

Individual risk assessment criteria were conducted for the substances under study, distinguishing between not seriously and seriously contaminated sites. An individual index (I_i) was applied to dimensionless TPH and PAH concentrations. The parameter is defined as the ratio between the individual concentration (C_i) and the Intervention value (IV) for the substance under study, given in the equation as follows:

$I_i = C_i/IV_i$

Where;

I_i = Individual index
C_i = Individual concentration of the substance under study
IV_i = Intervention value for the substance under study

The IVs applied to obtain I_i values are adopted as 5000 mg/kg and 40 mg/kg for TPH and PAH respectively [22].

2.7 Multivariable Assessment

A multivariable index (I_{MV}) was defined for the individual compounds which have an IV based on toxicological studies. The I_{MV} represents the sum of the I_i for PAH and TPH.

$I_{MV} = I_{PAH} + I_{TPH}$

The application of the I_{MV} homogenises the different variables, establishing for all the cases the same maximum acceptable value of 1.0. A comparison between I_{TPH} and I_{PAH} was performed by looking for any interaction among these substances. The study of the individual indices for the selected substances gives unacceptable contaminated sites individually, but it does not offer information about the total number of seriously contaminated sites. The addition of variables determines the total number of contaminated sites by any substance. If a sample is considered to be seriously contaminated in the first criterion, it is not included when applying the second or the third one.

2.8 Gravimetric Determination of TPH

TPH was also determined gravimetrically to compare the results. 20 g of sediment samples were consecutively soxhlet- extracted with n-hexane, dichloromethane and chloroform (l00 ml each). The sample was mixed with 10 g of anhydrous Na_2SO_4 prior to extraction and quantitatively transferred to extraction thimble. All the three extracts were pooled and clean-up procedure using silica gel column carried out to remove biogenic polar materials. The sample extract was then evaporated in a rotary vacuum evaporator to about 2 ml. The distilling head was removed, and dried in vacuum, cooled, and weighed [23,24].

The concentration of TPH in the original sample was calculated as:

TPH (mg/kg dry weight) =

$$\frac{\text{Gain weight of the flask (mg)}}{\text{Weight of solid (g)}} \times 1000$$

3. RESULTS AND DISCUSSION

3.1 Physicochemical Analysis

The physicochemical parameters of the studied samples are recorded in Table 1. Evaluation of the soil samples surrounding the refinery in this study is an important physical factor in the determination of the toxicity levels which would otherwise contaminate the food chain by way of useful microorganisms, plants and marine organisms. Data obtained showed that the pH of the studied samples ranged from 5.31 ± 0.25 to 5.54 ± 0.01 which were lower than that of the control counterpart, 7.81 ± 2.01. The pH range of oil-contaminated environments generally tends to be acidic with a reduced level of porosity [25]. Run-offs from the refining activities would account for the reduction in pH observed in the samples. pH regulates the ion solubility and availability, thereby influencing plant and microbial activities and dispersion of nutrients [26]. Furthermore, the pH level is a good indicator of the contaminating elements end-point, leachability and decomposition which in effect affects the physical, chemical and biological properties of the environment [27].

There was no significant change in the pH across the soil samples, however the electrical conductivity was higher (0.48 to 0.56 µs/cm) in the oily sludge impacted soil samples, which may be due to the presence of heavy metals or other ions. As expected due to hydrocarbons from the petroleum, the organic carbon content in all the contaminated soil samples was significantly higher (5.29±0.16% to 7.22± 0.13%) compared to the control soil (3.25±1.04%) sample while that of the oily sludge was the highest, 10.86±0.05%. Pathak et al., [28] also carried out the physicochemical analysis of two PHC contaminated soils and reported high carbon content of 4.96% and 4.33% for each soil sample as compared to 0.56 and 0.65% for uncontaminated soils. A decrease (30 to 70%) in the total nitrogen and available phosphorous (AP) contents were also seen in the PHC polluted soils. This may be attributed to oily sludge contamination in the soil which could increase the carbon concentration that might affect the equilibrium of nutrients in the soil.

Microbes in soils, which utilize PHC as a carbon source, could utilize considerable amounts of AP when they degrade the hydrocarbons. Secondly, phosphorus solubility is maximized at pH 6.5 [29] and consequently, the lower pH values in the oily sludge impacted sites could also lower the AP concentration compared with the concentration in the control site. Lower concentration of nitrogen, phosphorous and other mineral nutrients have been reported as limiting factors for the growth of

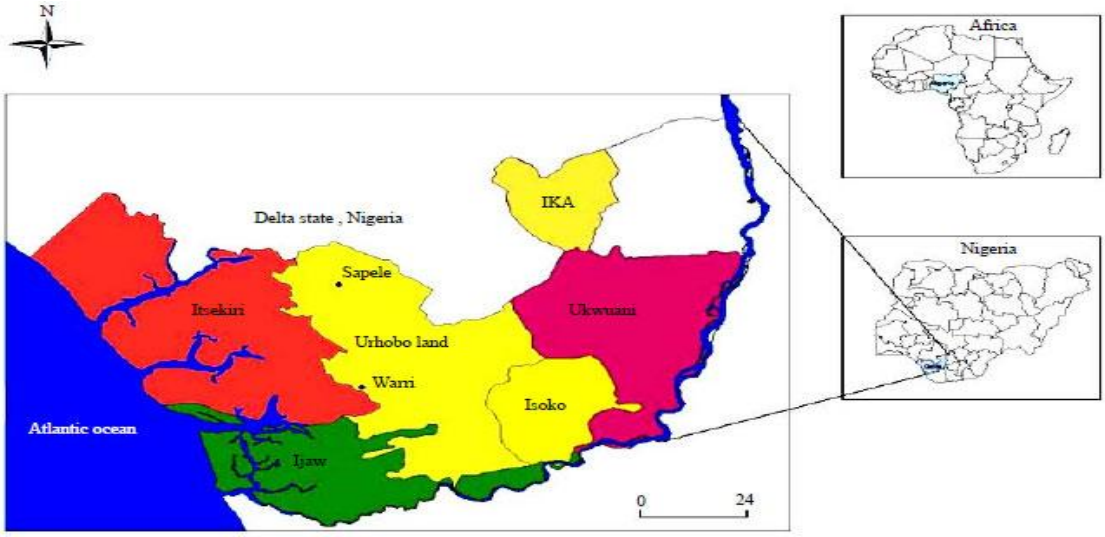

Fig. 1. Map of delta state showing the study area

Table 1. Selected physicochemical parameters of the Sludge and Soil samples

Parameters	Sludge	Site a	Site b	Site c	Site d	Site e	Control
pH	5.25±0.12	5.31± 0.25	5.35±0.62	5.42±0.03	5.47±0.51	5.54±0.01	7.81±2.01
Conductivity (µs/cm)	0.63±0.01	0.57± 0.02	0.56±0.02	0.48±0.08	0.50±0.01	0.44±0.00	0.26±0.03
Moisture content (%)	2.10±0.17	1.85± 0.03	3.22±0.83	2.63±0.01	3.41±0.01	3.75±1.30	5.45±0.02
Organic carbon (%)	32.86±0.05	18.22± 0.13	16.51±0.37	15.53±0.05	13.29±0.16	10.02±1.92	4.25±1.04
Organic matter (%)	56.81±2.11	31.50±0.01	28.55±0.05	26.85±1.41	22.98±0.03	17.32±0.17	7.35±0.02
Sulphate (mg/l)	670.53 ± 2.15	463.94 ± 1.06	465.13±1.25	429.76±0.01	420.65±0.06	412.73±1.00	56.73±1.13
Water holding Capacity (%)	33.00 ± 1.20	38.00 ± 0.15	45.47±0.01	50.28±0.04	57.10±0.26	58.62±1.91	65.10±0.43
Available Phosphorus (%)	6.65± 1.10	8.72± 0.01	10.59±1.33	10.86±0.20	12.28±1.37	12.40±1.85	15.62±1.11
Sodium (mg/kg)	67.10± 2.03	58.39 ± 0.00	54.20 ±1.00	47.65 ±0.01	45.17 ±2.01	36.15 ±0.01	21.76 ±0.01
Potassium (mg/kg)	0.52±0.01	1.36 ± 0.00	1.59 ±0.10	1.84 ±0.01	2.35 ±0.01	2.78 ±0.00	5.00 ±0.20
Calcium (mg/kg)	1.49±0.01	ND	ND	ND	1.62±0.08	ND	3.68±0.01
Magnesium (mg/kg)	288.91±3.01	231.24±0.11	193.62±0.03	158.71±1.00	160.45±1.03	137.28±0.02	65.94.±1.02
Total Nitrogen (%)	0.07±0.00	0.08± 0.00	0.26±0.01	0.35±0.01	0.37±0.02	0.44±0.00	0.87±0.01
Oil and grease (mg/kg)	1373181.2 ± 0.15	587642± 0.27	247698±2.33	194532±0.04	175072.4±1.16	96077.2±0.45	1032.4±0.18

ND = Not detected. The results are means of triplicate determination ± standard deviation

Fig. 2. Cross section of sampling sites. A = Collection of samples in the field, B = Image of one of the sampling sites, C = Soil samples as they arrived at the laboratory, D = Samples air-dried for two weeks

microorganisms in PHC contaminated environments [30]. A field study on the Momoge wetlands showed that the concentration of AP decreased with increasing time of oil exploration and production [31]. However, Liu et al., [32] reported that AP concentration was not significantly affected by oil contamination. Phosphorus and nitrogen are among the most important macro-nutrients for plants and soil microorganisms. The decrease of AP and N concentrations in oilfield marshes could change the structure of vegetation and soil microorganisms, and reduce marsh ecosystem services and values.

The water holding capacity which determines the extent of water retention and aeration in the soil was also less in PHC contaminated soils than that of control soil and this property is important for the growth of biotic components in the soil. This is in agreement with other researchers like Osuji and Nwoye [33] who reported that the presence of PHC in the soil increases the soil hydrophobicity, reducing the water holding capacity of the soil. Accordingly, this confirms why the moisture content of the contaminated soils was observed to be less (1.75±2.30 to 3.41±0.01%) than control soil (5.45±0.02%).

Bundy et al., [34] have also reported that nutrient balance (C and N), pH and moisture content of soil were usually affected as a result of contamination by hydrocarbons. The altered physicochemical properties of PHC contaminated soil makes it unfit for the growth of agricultural crops as well as the normal soil flora.

3.2 Analytical Characteristics for Hydrocarbon Analysis

To validate the analytical procedure for quantitative determination of TPH and PAH in soil samples, the main figures of merit: limit of detection (LoD), limit of quantification (LoQ), working and linear range was evaluated. Calibration curves were constructed with the external standard multipoint calibration for each TPH and PAH. Quantification of the analyzed compounds was performed in the linear range of the calibration curves. A linear response was obtained with coefficients of determination (r^2) ranging from 0.995 to 1.000. At the lower end of the range, the restrictive factor is LoQ, while, at the upper end, limitations are imposed by various effects depending on the instrument response. Linearity was evaluated from the regression function of calibration using 5 standards.

Table 2. Molecular mass, retention time, limit of detection, limit of quantitation and m/z for the PAHs

Compound	Molar mass	Chemical formular	No. of rings	Retention time (min)	LoD (mg/kg)	LoQ (mg/kg)	m/z
Naphthalene	128.00	$C_{10}H_8$	2	7.683	0.05	0.06	128, 127, 129, 102, 87
Acenaphthylene	152.00	$C_{12}H_8$	3	10.466	0.02	0.06	152, 151, 150, 76, 63
Acenaphthene	154.00	$C_{12}H_{10}$	3	10.939	0.02	0.06	154, 152, 102, 76
Fluorene	166.00	$C_{13}H_{10}$	3	11.963	0.02	0.06	166, 165, 82, 83
Phenanthrene	178.00	$C_{14}H_{10}$	3	13.670	0.03	0.09	178, 176, 179, 152
Anthracene	178.00	$C_{14}H_{10}$	3	13.854	0.02	0.06	178, 176, 179, 89
Fluoranthene	202.00	$C_{16}H_{10}$	4	16.086	0.04	0.12	202, 200, 101,203
Pyrene	202.00	$C_{16}H_{10}$	4	16.742	0.04	0.12	202, 200,101, 100
Benzo[c]phenanthrene	228.00	$C_{18}H_{12}$	4	18.449	0.05	0.20	288, 226, 227, 113
Benz[a]anthracene	228.00	$C_{18}H_{12}$	4	18.869	0.06	0.20	228, 226, 229, 114
Chrysene	228.00	$C_{18}H_{12}$	4	19.132	0.06	0.20	228, 226, 229, 227
Benzo[e]pyrene	252.00	$C_{20}H_{12}$	5	21.075	0.10	0.30	252, 250, 126, 253
Benzo[j+k+b]fluoranthene	252.00	$C_{20}H_{12}$	5	21.574	0.15	0.50	252, 250, 253, 126
3-Methylcholanthrene	268.00	$C_{21}H_{16}$	5	22.046	1.95	2.50	268, 252, 253, 267
Indeno[1,2,3-cd]pyrene	276.00	$C_{22}H_{12}$	6	23.386	1.80	2.10	276, 138, 278, 279
Benzo[ghi]perylene	276.00	$C_{22}H_{12}$	6	23.281	0.76	1.50	276, 274, 138, 277
Dibenzo[a,h]pyrene	302.00	$C_{22}H_{14}$	6	26.222	0.10	0.40	302, 300, 150,303
Dibenzo(a,i)pyrene	302.00	$C_{22}H_{14}$	6	27.613	0.20	0.50	302,303, 300, 151
Benzo[a]pyrene	252.00	$C_{20}H_{12}$	5	21.394	0.15	0.40	252, 225, 161, 253
Dibenzothiophene	184.00	$C_{12}H_8S$	3	13.407	0.03	0.09	184, 139, 185
TPH					8.5	26	

The relative standard deviation was mostly below 20%. The lowest LoD was 0.02 mg/kg for lower molecular mass compounds while 3-Methylcholanthrene has the highest at 1.95 mg/kg. Ten standard solutions at the calculated LoQ concentration were prepared and analysed for its confirmation by evaluation of precision and accuracy. The targeted recoveries ranged from 90-105%. These methods enabled the quantification of lower amounts of hydrocarbons than the established alert and intervention values.

3.3 Petroleum Hydrocarbon Content

The petroleum hydrocarbon concentrations of the samples are recorded (Table 2,3). The TPH contents according to GC-FID analysis in the contaminated soils were found to be in the range of 48063.6 to 293846.0 mg/kg of soil which were higher than the control counterpart (651.2 mg/kg) while that of the petroleum sludge was highest (686615.6 mg/kg) although this was in order since the oily sludge was the contaminant. Further, the TPH levels in the soil samples were

Table 3. Hydrocarbon concentrations of the samples by GC-MS and GC-FID

Comp #	Compound Name	SLUDGE (mg/kg)	SITE A (mg/kg)	SITE B (mg/kg)	SITE C (mg/kg)	SITE D (mg/kg)	SITE E (mg/kg)	CONTROL (mg/kg)
1	Naphthalene	20.26	10.42	9.41	6.85	4.74	2.70	N.D.
2	Acenaphthylene	68.13	20.38	10.39	7.93	3.46	1.75	0.33
3	Acenaphthene	58.98	37.67	30.01	22.37	5.12	2.38	0.31
4	Fluorene	789.84	287.47	143.11	89.04	30.49	19.15	0.91
5	Phenanthrene	935.88	435.89	386.15	118.46	66.44	23.34	1.73
6	Anthracene	554.71	78.32	58.16	41.38	25.61	14.76	1.06
7	Fluoranthene	759.89	94.78	60.78	46.79	15.52	4.11	1.13
8	Pyrene	1447.61	671.29	432.71	268.47	131.96	8.88	1.50
9	Benzo[c]phenanthrene	972.15	554.12	316.57	240.70	94.05	9.01	1.57
10	Benz[a]anthracene	843.04	492.01	388.61	241.28	67.34	16.45	0.86
11	Chrysene	1260.85	594.35	398.53	210.73	107.72	3.69	1.38
12	Benzo[e]pyrene	401.19	82.34	71.18	55.28	34.60	7.11	2.39
13	Benzo[j+k+b]fluoranthene	784.59	118.56	113.35	118.56	82.49	15.20	8.65
14	3-Methylcholanthrene	861.20	282.59	209.34	82.59	51.15	16.43	12.60
15	Indeno[1,2,3-cd]pyrene	382.24	80.22	77.07	80.22	46.74	4.82	4.79
16	Diben[a,h]anthracene	109.43	34.13	29.87	16.03	14.61	17.04	16.61
17	Benzo[ghi]perylene	432.58	177.48	62.45	57.48	52.55	3.18	1.32
18	Dibenzo[a,h]pyrene	810.50	46.57	23.54	16.57	17.10	6.46	3.55
19	Dibenzo(a,i)pyrene	999.23	39.37	27.78	17.00	15.76	5.57	3.13
20	Dibenzo(a,l)pyrene	224.15	32.11	24.81	14.83	14.78	5.13	2.73
21	Benzo[a]pyrene	931.88	85.80	77.21	65.80	45.99	2.77	1.51
	∑PAH	**13648.33**	**4255.87**	**2951.03**	**1818.36**	**928.22**	**189.93**	**68.06**
	TPH	**686615.60**	**293846.00**	**123874.00**	**97291.00**	**87561.20**	**48063.60**	**651.20**
22	Dibenzothiophene	63332.91	19001.84	18345.84	9501.19	8233.33	3167.31	0.00

Table 4. Gravimetric determination of TPH (mg/kg)

Sample	Sludge	Site a	Site b	Site c	Site d	Site e	Control
TPH	718532.4±0.01	342901.5±2.10	125172.0±0.13	98015.2±0.00	88176.0±0.35	48587.0±1.09	802.4±1.12

higher than the global average permissible limit of TPH for soil (1000 mg/kg) [35,36,37], indicating high PHC contamination. Alinnor and Nwachukwu [36] reported that soil samples in Rivers State, Nigeria were contaminated with TPH concentrations of 1534.7, 1438.0 and 1651.0 mg/kg at depths of 0.0 to 0.5 m, 0.5 to 1.0 m and 1.0 to 2.0 m respectively, which were much lower than values obtained in this study. According to Iturbe et al., [38], the soil of coastal Mexican refinery was heavily contaminated with hydrocarbons with detectable TPH concentration of 130000 mg/kg. This value was closer to those recorded at soils from the study site in this work. Pathak et al., [28] observed high concentrations of 11149 mg/kg and 14244 mg/kg TPH in soils contaminated with PHC and engine oil respectively as compared to uncontaminated soils (614 and 700 mg/kg). They suggested the probability of reduced microbial population in these contaminated soil samples.

Uche et al., [39] also reported high TPH concentration (>200 mg/kg) in surface and sub-surface soil samples collected from crude oil contaminated sites which far exceeded the 50 mg/kg compliance baseline limit set for petroleum industries in Nigeria. Further, the TPH contents of all the samples were also determined by gravimetric method (Table 4) to compare the efficacy of the analytical methods. It was found that the TPH values obtained from the gravimetric analysis were relatively higher than the values from a spectrometric method. This could be due to the fact that the extraction efficiency of gravimetric methods, albeit poor, is hugely affected by the type of eluting solvent used.

Hexane has poor extraction efficiency for higher molecular weight petroleum compounds [40] and low polarity, which causes the co-extraction of natural organic matter containing multiple polar functional groups [41]. Consequently, other chlorinated compounds like chloroform as well as toluene have been used as liquid extractant. It is well known that both of them have serious health implications as evident in the risk phrases published in their respective safety data sheets. Additionally, gravimetric methods are non-specific since they give no information about the type of hydrocarbon present. As a result, they are not suitable for assessing PAH compounds. Instead, the method is best suited for screening TPH in very oily sludges or samples containing very heavy molecular-weight hydrocarbons since light hydrocarbons (< C15) are easily volatilized at temperatures below 70 to 85ºC during the evaporation step.

From Table 3, the results of polycyclic aromatic hydrocarbons (PAHs) in the study sites recorded elevated values which ranged between 189.93 to 4255.87 mg/kg as compared with 68.06 mg/kg obtained at the control site, with that of the oily sludge being the highest as well (13648.33 mg/kg). Total PAHs concentration obtained in this study were higher than the recommended levels of 1 mg/kg, 1.5 mg/kg and 5 mg/kg imposed by soil clean-up guidelines from Denmark, Netherlands and Australia respectively [42,43]. The high PAH contents of soil samples demonstrated high contamination of the study sites. It was also observed that both the TPH and PAH concentrations from each community got reduced as a function of distance from the Warri Refinery and Petrochemical Company (WRPC). That is to say, the closer each community is to the refinery, the higher the health risk of the people. Inhalation, ingestion and dermal contact are the primary routes of exposure of PAHs to humans. PAHs are extremely toxic with the excellent capability to stimulate health effects such as nausea, vomiting, eye irritation, diarrhoea and confusion (short-term effects). Other health effects (long-term) include immune function suppression, cataracts, kidney and liver damage, skin inflammation, asthma amongst others. Generally, mixtures of PAHs are known to cause carcinogenic, genotoxic, teratogenic effects and are potential immunosuppressant.

Further, from Table 3, it was revealed that a hetero – compound, Dibenzothiophene (DBT) was one of the contaminants present in the petroleum sludge. Its values were so high across all the sampling sites except the control site. This could be the reason for the high sulphate contents observed across all the sampling sites (Table 1). Although opinions differ as to whether DBT is a PAH, in one reference, it is listed as a three-ring aromatic PAH [44]. Others say that DBT is an heterocyclic rather than a PAH compound, yet nevertheless, include it with lists of PAHs [45]. It is notable as a very persistent compound compared to most PAHs and other crude oil aromatics [46]. DBT is a sulfur-containing, high molecular weight compound and can be present in significant amounts in petroleum-contaminated samples [45]. Heavier

Table 5. Soil quality standards (SQSs)

Sites	TPH (mg/kg)	PAH (mg/kg)	(I_{TPH})	I_{PAH}	I_{MV} (mg/kg)	Remarks
Site A	293846.00	**4255.87**	58.77	106.40	165.17	Seriously contaminated
Site B	123874.00	**2951.03**	24.78	73.78	98.56	Seriously contaminated
Site C	97291.00	**1818.36**	19.46	45.46	64.92	Seriously contaminated
Site D	87561.20	**928.22**	17.51	23.21	40.72	Seriously contaminated
Site E	48063.60	**189.93**	9.61	4.75	14.36	Contaminated
Control	651.20	**68.06**	0.13	1.70	1.83	Very slightly contaminated

fractions of petroleum also tend to contain the homologous series (alkylated compounds C_1 through C_3) of DBT. DBT and related dibenzothiophenol compounds in expanded scans for PAHs help complete "fingerprinting" for petroleum contamination-source identification [46]. Acute toxicity is rarely reported in humans, fish, or wildlife, as a result of exposure to low levels of a single PAH compound such as this one. It has been reported that DBT were still present after 10 years in sediment experimentally polluted with crude oil, long after most aromatics had disappeared [47].

3.4 Soil Quality Assessment

TPH and PAH indices (I_{TPH} and I_{PAH}) are recorded in Table 5 for all the studied samples. In addition, the dimensionless IV of 1.0 is included to easily establish which substances are mainly above or below the regulation limit. Results indicated that all the studied sites except the control sample (I_{TPH} < 1.0) have unacceptable TPH concentrations. Regarding PAH concentrations, all the studied sites from soil A to soil D were found to be “seriously contaminated” (I_{PAH} > IVs) with soil E being only “contaminated” since the value is close to IV while the control sample (I_{PAH} = 1.70) was very slightly higher than the regulation limit denoting some traces of PAH contamination. Going by the I_{MV}, it was observed that all the studied sites from A to E were seriously contaminated. It is expected that the inclusion of PAH concentrations will improve the soil quality assessment since they complement TPH analysis and include potential risks. In addition, the TPH parameter is considered to pose toxic but not carcinogenic effects.

Focusing on the correlation between TPH and PAH concentrations, all samples presented unacceptable TPH and PAH concentrations unlike the control counterpart. These results suggest a strong correlation between both indices.

According to the individual indices (I_i), the contamination level was a factor of the proximity of each site to the WRPC. When the soil is slightly contaminated, a site-specific assessment is needed to determine if the risks are acceptable or not. In this case, monitoring campaigns must be performed to track the contaminants concentration. In the case of unacceptable high concentration of contaminants (as seen in all the studied sites), the soil can directly be considered contaminated and a remediation procedure should be established.

4. CONCLUSION

Data obtained in this study has shown that the contaminant sludge discharged from the refinery contained petroleum hydrocarbons which leaches into and ended up being translocated into the soil spanning several kilometers over time. Data collated in this study has also showed that the varying concentrations of petroleum products accumulate in the soil whereby it affects soil physicochemical properties which reduces the availability of essential nutrients in each studied sample. The results of the study could be utilized as a baseline towards the development and implementation of both remediation and in situ containment techniques.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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