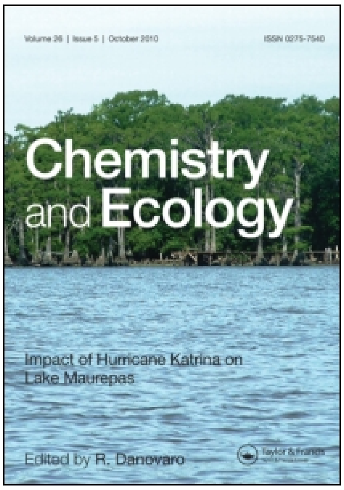

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Characterisation of the petroleum hydrocarbons-contaminated soils around a petroleum products depot

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Oil-impacted soils around a refined petroleum products depot were analysed for physicochemical parameters (pH, Cl^-, CO_3^{2-}, electrical conductivity and organic matter), elemental (Na, K, Fe, Mn, Zn, V, Cr, Cu, Ni and Pb) concentrations and total hydrocarbon content to determine their levels in the soils. Comparison of the values of the elements and physico-chemical parameters in the oil-impacted soils with the control soils and their standard permissible levels showed that their values in oil-impacted soils were excessive; this was corroborated with their t-test values. The geoaccumulation index values of the elements confirmed that with the exception of Na, K and Fe, which *moderately polluted* the soils, the soils were *very heavily polluted* with all other elements. This was corroborated with their pollution index and enrichment factor values. The overall results showed that the soils had been contaminated by refined petroleum oils.

Keywords: metals; petroleum hydrocarbons; physico-chemical; polluted soils

1. Introduction

Petroleum oil is the life blood of our modern industrial society. It fuels the machines and lubricates the wheels of the world's production; but when this vital resource is mishandled, it can ravage the environment and economy of a whole region [1].

In a natural ecosystem, metals and hydrocarbons are present in low levels, usually at μg/kg to ng/kg levels. Recently, the occurrence of metal and petroleum hydrocarbon contaminants, particularly heavy metals and polycyclic aromatic hydrocarbon compounds, has been found in excess of conventional levels and this is a cause for concern.

Production of petroleum hydrocarbons has been in existence in Nigeria for decades now, and their adverse effects on the communities in the area of production and communities in which refineries and depots are located have been challenging. These actions, even though in stages, have brought forth varieties of impacts, ranging from bearable to absolutely catastrophic effects. For instance, the activities are known to have ruined terrestrial and aquatic biota, which make up the major source of livelihood for people residing in these areas [2,3].

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The harmful effects of pollution exceed those happening around the exploration, mining and processing zone but contamination remote from these zones may have resulted from operations involved in petroleum product storage, transportation, marketing and end-user handling [2,4]. The most commonly marketed refined petroleum products – kerosene, gasoline, diesel and lubricating oils – contaminate the environment through spillage accidents involving transportation, overflow leaks in motor vehicles, poor handling, pipeline leakages and vandalisation and leakage of storage tanks. Petroleum hydrocarbons are also known to be included in vehicular emission [5,6]. Naturally, crude oil from which petroleum products are fractionated contains some elements, most especially some transition metals, viz. V, Ni, Zn, Fe, Cu, Mn and Cr, which are known to associate with hydrocarbon formation [7,8]; Na from sea salt intrusion [9]; and Pb as tetraethyl lead, an antiknock additive [10].

Petroleum products composed mainly of hydrocarbons of different types and traces of some potential toxic elements can contaminate soils and leach into ground and surface waters, which are major sources of water for drinking and domestic use, and can further get into the food web, becoming accumulated by plants and animals, including man. This can result in ill health effects for the residents of the area.

Several studies have been conducted on the environmental impacts of petroleum in Nigeria; these works were concentrated on crude oil spillages and air quality in oil-producing areas of the Niger Delta, Nigeria [11–13], but there is little or no literature/work on the impact of petroleum on the environments which were accountable to a refined petroleum products depot. This study thus aimed to determine the impact of petroleum hydrocarbons on the soils around a petroleum product depot. The soils were collected using standard analytical procedures [14]. Potential toxic elements (Na, K, Fe, Mn, Zn, V, Cr, Cu, Ni and Pb) were determined using bulk scientific atomic absorption spectrometry/atomic emission spectrometry techniques, while total petroleum hydrocarbons and physicochemical parameters: pH, Cl^-, $CO3^{2-}$, electrical conductivity and organic matter content were determined using standard analytical techniques. The Misimi Petroleum Products and Marketing Company (PPMC) depot located at Shagamu, Southwestern Nigeria was used as the case study. The depot, which is one of the biggest in Nigeria, receives refined petroleum products mainly from Warri refinery and Atlas Cove Jetty in Lagos, Nigeria through pipelines, stores them and distributes them to marketers from Ogun, Lagos and some northern states of Nigeria. A good number of the inhabitants of the area are peasant farmers, who carry out their farming activities around the depot and depend on ground and surface waters as sources of domestic water. It is therefore imperative to evaluate the extent of the damage the anthropogenic activities could pose to the soil system of the area.

2. Experimental

2.1. *Sample collection and treatment*

Ten oil-impacted soil samples were collected from different locations within the depot area at a depth of 0–5 cm using a hand trowel after the decomposing materials had been removed, and were wrapped in aluminium foils to prevent contamination. Sub-samples for total petroleum hydrocarbon (TPH) determination were preserved at a temperature of -4 to $0\,^{\circ}C$ and were immediately taken to the laboratory for analysis.

Soil samples for physicochemical and elemental analyses were air-dried at room temperature but well covered with white paper to prevent air particulate contamination. After drying, the soil samples were crushed to 2 mm mesh size using an agate mortar and mixed thoroughly; these sub-samples served as composite and representative samples for the various analyses [14]. Four control samples were similarly collected from different locations about 1 km away from the depot and were pretreated in the same way as the above-described procedures for physicochemical, elemental and TPH analyses.

2.2. *Quality assurance and quality control*

For quality control, all instruments used were operated as per the manufacturer's instructions. Calibration of AAS/AES was done using mixed calibration standard solutions prepared from the pure BDH Analar grade salt of each element. The % recovery ranged from 90–95. A blank determination was also made following the same procedure. All reagents used were of BDH Analar grade and the solvents (methanol, n-hexane, water) used were triply distilled. All the glassware and sample bottles were cleaned using the procedure of Laxen and Harrison [15]. Only glassware was used in the TPH determination. Three replicate measurements of each of the test samples were carried out.

2.3. *Determination of physicochemical parameters*

The physicochemical parameters pH, Cl^-, electrical conductivity (EC), CO_3^{2-} and organic matter of the soils were determined using the following appropriate standard analytical methods. The pH of the soil samples was measured using a standardised digital pH meter model Jenway 4330. A 1:2 ratio of soil to H_2O was used in the determination of the soil samples. Each test solution (soil suspension) was thoroughly stirred in a magnetic stirrer for 30 min before pH measurement. The pH measurement was taken at 25 °C [16]. The accuracy of the pH value was assured by calibrating the pH meter used with standard pH 4 (potassium biphthalate) and pH 10 (carbonate) buffers. The pH of the buffers was also confirmed with a hand-set glass electrode pH meter model CD 70 (WPA).

After pretreatment of the soil samples following Bailey [16], the EC of the soils was measured using a pH/conductivity meter (Denver Instrument Model 20) at 25 °C after calibration with 0.001 M KCl.

The Mohr method (titrimetry method) was used for chlorinity or Cl^- ions determination. The method employs silver nitrate as titrant and potassium chromate as the end point indicator [16,17].

Carbonate (CO_3^{2-}) content of the soil samples was determined by the gravimetric method for loss of CO_2 [18], while the soil organic matter level was determined by oxidation with a solution of standard 0.067 M $K_2Cr_2O_7$; concentrated H_2SO_4 was used to generate heat and barium diphenylamine sulphonate reagent was employed as the indicator. Excess dichromate was determined by titrating with standard 0.4 M ferrous sulphate, $FeSO_4$, solution [18].

2.4. *Determination of elemental concentrations*

The soil samples were digested using the *aqua regia* procedure of the International Standard Organization (ISO) [19]. The elemental concentrations of the soil samples were determined using atomic absorption/atomic emission spectrometry (AAS/AES).

2.5. *Determination of total petroleum hydrocarbons (TPHs)*

The total hydrocarbon oil content was determined by the IOC method [20]. About 100 g of soil was refluxed with a mixture of 3 g KOH and 100 cm^3 methanol for about 2.5 hours using a Soxhlet extractor. This was then filtered and the filtrate extracted twice with 25 cm^3 doubly distilled n-hexane using a separating funnel. The combined extract was evaporated to about 4.0 cm^3 and then subjected to clean-up with a short silica column. After elution with purified n-hexane, the oil was isolated by evaporation of the n-hexane and concentration of the extract using a rotary evaporator to a constant weight to determine the TPHs.

2.6. *Treatment of data*

2.6.1. *Enrichment factor (EF)*

The elemental concentrations of the soil samples were subjected to statistical analysis to determine the enrichment factor (EF) of the elements. The EF is the quotient of the ratio of the concentration of element x to the concentration of reference element f in the sample to the same ratio in the crust [21]. EF is expressed as $(C_x/C_f)_{\mathrm{sample}}/(C_x/C_f)_{\mathrm{crust}}$, where C_x and C_f are the concentrations of the element x and reference element f in the soil and reference samples [21–23].

2.6.2. *Geoaccumulation index (I-$_{geo}$)*

Geoaccumulation index (I-$_{\mathrm{geo}}$) values for the elements was also calculated using the equilibrium equation $\{\mathrm{I\text{-}}_{\mathrm{geo}} = \mathrm{Log}_2(C_n/1.5B_n)\}$ according to Diatta et al. [24] and background levels of elements in non-contaminated soils as reported by IUGS/IAGC [25]. Here, C_n is the measured mean concentration of the element in the soil samples, B_n is the background value, and 1.5 is the background matrix correction factor due to lithogenic effects.

2.6.3. *Pollution index (PI)*

The elemental concentrations of the soils were also subjected to statistical analysis to determine the PI of the elements. The PI is the quotient of the concentration of the element x in the sample to the maximum permissible level of the element: $\mathrm{PI}_{(x)} =$ Concentration in the sample/Tolerable limit.

It is agreed in principle that if the PI value of an element is greater than 1, it implies that the contamination of the sample by the element is high and may be toxic at the level it is present in the sample [26].

3. Results and discussion

3.1. *Total petroleum hydrocarbons analysis*

The percentage composition of the TPHs in the oil-impacted soils ranged from 1.67–2.65%, with a mean concentration of 2.05% and a standard deviation of 0.45, while hydrocarbons were not detected in the control soils (Figure 1). The low value of the standard deviation from the mean showed that the hydrocarbons were moderately distributed in the area of study. The level of TPHs obtained in this study was much higher than values obtained in studies of similar settings by Onianwa [27], viz. rail tracks (0.0355%), refuse dumps (0.0403%), high traffic density areas (0.1950%), auto mechanical workshops (0.0923%) and petrol stations (0.1950%). The high TPH values in the soils indicated that the anthropogenic activities in the depot area had resulted in a high hydrocarbon burden.

3.2. *Elemental analysis*

Figure 2(a) and (b) presents and compares the concentrations of the analysed elements (K, Na, Pb, Mn, Zn, Cu, Fe, Ni, Cr and V) in the oil-impacted soils with the control soil samples. It is observed

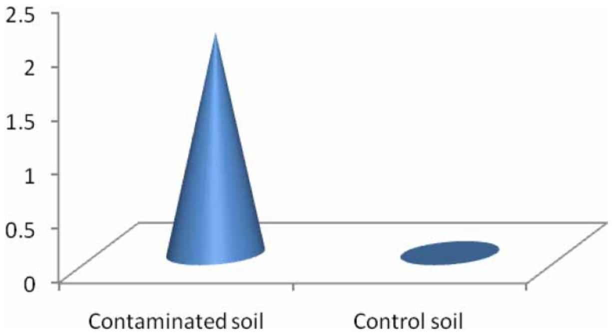

Figure 1. Frequency distribution of TPHs concentrations of the soils (%).

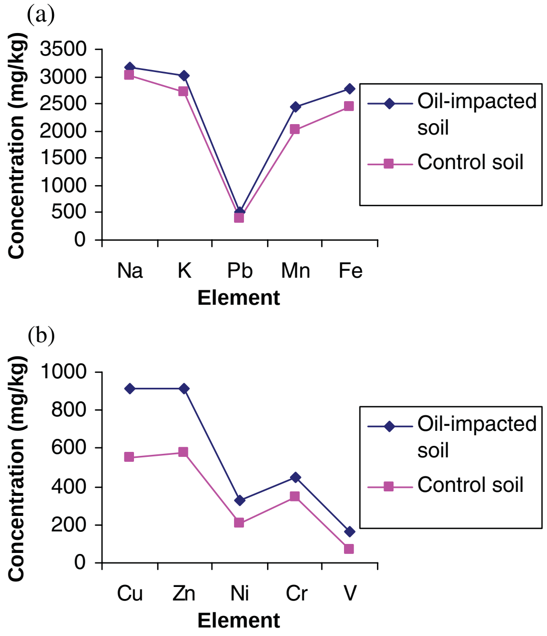

Figure 2. (a & b). Frequency distributions of the elemental concentrations of the soil samples.

that all the elements had higher concentrations in the oil-contaminated soils than in the control soils. This was due to the contamination of the oil-impacted soils by refined petroleum oils. It was reported that naturally, crude oil from which petroleum products are fractionated contains some elements, most especially transition metals, viz. V, Ni, Zn, Fe, Cu, Mn and Cr, which are known to associate with hydrocarbon formation [7,8]; Na from sea salt intrusion into the crude oils [9]; and Pb (tetraethyl lead, an antiknock) as an additive during crude oil processing [10]. The t-test values of the analysed elements in Table 1 indicate that statistically, Pb, Mn, Zn, Cu, Cr and V showed *significant* differences in their values between the oil-impacted soils and control soils as a result of high concentrations of the elements in the oil-impacted soils.

3.3. *Physicochemical parameters analysis*

The results of the physicochemical parameters are presented in Figure 3. The oil-impacted soils had pH values ranging from 6.18–7.51 with a mean value of 6.57, while those of the control

Table 1. Results of t-tests comparing the physico-chemical properties of the oil-impacted and control soil samples.

	t-test		
Parameter	t_c	Observation	Remark
pH	1.871	$t_c < t_t$	NSD
E.C	1.514	$t_c < t_t$	NSD
Cl^-	3.799	$t_c > t_t$	SD
CO_3^{2-}	1.947	$t_c < t_t$	NSD
Organic matter	2.489	$t_c < t_t$	NSD
Na	3.176	$T_c < T_t$	NSD
K	3.054	$T_c < T_t$	NSD
Pb	4.963	$T_c > T_t$	SD
Mn	5.586	$T_c > T_t$	SD
Zn	3.650	$T_c > T_t$	SD
Cu	5.521	$T_c > T_t$	SD
Fe	3.484	$T_c < T_t$	NSD
Ni	3.195	$T_c < T_t$	NSD
Cr	4.901	$T_c > T_t$	SD
V	7.025	$T_c > T_t$	SD

Note: T_c = T-calculated; T_t = T-tabulated = 4.032 at α level = 0.01, 99% Confidence limit; Degree of freedom = 5; NSD = Not significantly different, SD = Significantly different.

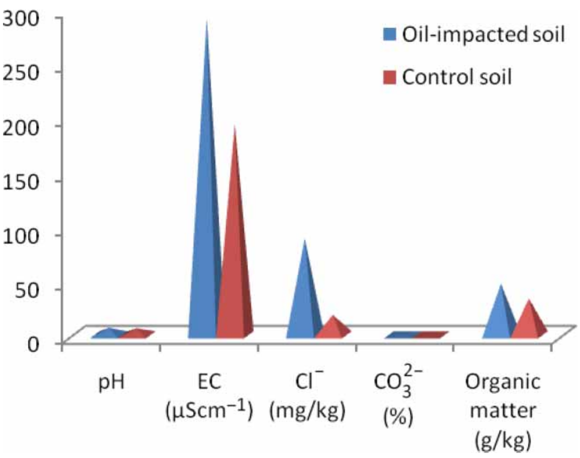

Figure 3. Frequency distribution of the concentrations of the physicochemical properties of the soil samples.

soils ranged between 5.85 and 6.21 with an average value of 6.03. The mean pH value of oil-impacted soils was comparatively higher than that of the control soils, though the difference was *not significant* according to statistical logic. This was in agreement with the study of Hajira and Zehra [28] on the soils from Clifton beach analysed after the oil disaster of Tasman Spirit. Oiling must have discouraged the leaching of basic salts which were responsible for raising the pH of the oil-impacted soils. The comparatively higher mean content of CO_3^{2-} in oil-impacted soils (1.21%) than in that of the control soils (0.75%) attested to the observed difference in the pH values. The binding of the oil with soil particulate matters in the affected area probably posed a major resistance to the removal and leaching of the basic ions, thereby resulting in their accumulation and higher concentrations in the oil-impacted soils than in the control soils.

The Cl^- ions were generally higher in the oil-impacted soils (88.9 mg/kg) than in the control soils (18.4 mg/kg). The use of chloride compounds such as sodium hypochloride (as a sweetener) and $CuSO_4/NH_4Cl$ slurry (as a catalyst) in the refinery might have resulted in the accumulation of the Cl^- ions in refined petroleum oils and, hence, in the oil-impacted soils (relative to the uncontaminated control soils) [29]. It was also reported by NALCO [30] that mineral salts such as NaCl, $MgCl_2$ and sulphates of Ca and Mg are usually found in crude oils as the result of long contact of H_2O and crude oils with salt substrates and soils. If crude oil was not desalted well, the inorganic salts could increase the Cl^- ion content of the soils via contamination of the soils by oils; this would eventually elevate the EC of the soils. The EC of the oil-impacted soils ranged from 188–358 μScm^{-1} with mean concentration of 291 μScm^{-1} while, the values of the uncontaminated control soils ranged from 88.7–235 μScm^{-1} with a mean average of 194 μScm^{-1} but the values for the two set of soils were *not significantly* different from a statistical point of view. The higher mean value of EC for oil-impacted soils was due to the reason explained earlier.

The mean organic matter content of the oil-impacted soils (47.2 g/kg) was also higher than that of control soils (33.4 g/kg), but the difference was *not significant* from the statistical point of view. Higher organic matter content of the oil-impacted soils was due to the contamination of the oil-impacted soils by the crude oil products which were composed mainly of hydrocarbons (carbon and hydrogen compounds) and hence resulted in elevated organic carbon/matter content.

Table 2 compares the results of the analysed elements with their background levels as reported by Jones et al. [31]. It is observed that the concentrations of all the elements exceeded their background levels. The $I\text{-}_{geo}$ values of the elements in the soils were calculated using the equation according to Diatta et al. [24] and their background levels as reported by Jones et al. [31]. With reference to the report of Diatta et al. [24], it is observed that based on the values of the $I\text{-}_{geo}$ of the elements in the oil-impacted soils, with the exception of Na (0.74), K (0.89) and Fe (0.42) which *moderately polluted* the soils ($0 < I\text{-}_{geo}$value < 1), the soils were *very heavily polluted* with respect to all the elements ($I\text{-}_{geo}$value > 5). This was corroborated with their values for the enrichment factor of the elements: Cr (31.3), Pb (254), Zn (76.1), Ni (28.5), Cu (128) and Mn (18.0), viz. EF $>$ 10.

Table 2 also compares the average concentrations of the analysed elements in the oil-impacted soils with their risk reduction standards, viz. value limits that pose no significant risk for residential use [32]. It is observed that potential toxic elements – Cr (451.3 mg/kg), Pb (512.1 mg/kg), Zn (910 mg/kg), Ni (329.1 mg/kg), V (163.1 mg/kg) and Cu (917.7 mg/kg) – were excessive. This was supported by the calculated PI values of the elements – Cr (4.51), Pb (6.83), Zn (9.11), Ni (6.58), V (1.63) and Cu (9.18) – viz. PI $>$ 1; indicating that the soils were contaminated with the elements [26].

4. Conclusion

Selected physicochemical parameters (pH, Cl^-, electrical conductivity, CO_3^{2-} and organic matter contents), elements (Na, K, Pb, Mn, Zn, Cu, Fe, Ni, Cr and V) and TPHs in soils around one of the biggest petroleum products depot in Nigeria were determined using standard analytical techniques. The oil-impacted soils were loaded with these potential environmental pollutants due to the fact that their values were higher than their tolerable limits, the values in the control soils, and possessed high EFs which were corroborated with their high PI and $I\text{-}_{geo}$ values.

The excessive levels, high EF, $I\text{-}_{geo}$ and PI values obtained for these potential toxic elements and the comparatively high amount of TPHs in the soils are bothersome due to their possible adverse effects on the health of living organisms, including human beings, and can also alter the ecosystem components of the area: for instance, when the oils are washed into the ground and surface waters of the area by run-off or are emitted and pollute the ambient air or are ingested by young children. The pollutants can also get into the food web as a result of their bioaccumulation by food crops via the contaminated soils as a result of farming activities around the depots by

Table 2. Comparison of the analysed elements in the soils with their standard permissible levels (mg/kg).

Element (mg/kg)	This study (range and mean)	Maximum permissible level (FMEnv [38])	Excessive level (Domy [39])	Threshold level (EEC [40])	Geochemical minimum baseline (IUGS/IAGC [24])	Enrichment factor (EF)	Geoaccumulation index (I_{geo})	Tolerable limits (Sonon and Gaskin [32])	Pollution index (PI)
Na	3155–3338 (3274)	N.A	NA	NA	400	0.99	0.74	NA	–
K	2886–3167 (3025)	N.A	NA	NA	260	1.0	0.89	NA	–
Pb	488.6–520.4 (512.1)	50.0	200	500	3.00	**254**	6.83	75.0	**6.83**
Mn	2368–2549 (2456)	N.A	1500	NA	10.0	**18.0**	7.36	NA	–
Zn	836.9–1018 (910.8)	N.A	250	300	4.00	**76.1**	7.27	100	**9.11**
Cu	831.4–1050 (917.7)	N.A	100	130	1.00	**128**	9.26	100	**9.18**
Fe	2656–2940 (2777)	N.A	NA	NA	700	0.47	0.42	NA	–
Ni	268.7–368.7 (329.1)	N.A	100	70	2.00	**28.5**	6.78	50	**6.58**
Cr	413.8–465.9 (451.3)	50.0	100	600	1.00	**31.3**	8.23	100	**4.51**
V	148.6–185.1 (163.1)	N.A	NA	NA	1.00	7.06	6.76	100	**1.63**

Note: Mean values are in brackets, NA = Not available, PI values > 1 and EF values > 10 are in bold type.

the villagers (residents) of the area who are, mostly, peasant farmers. The overall results showed that the physicochemical properties of the components of the ecosystem had been altered due to contamination of the soils by refined petroleum oils and that the pollutants from the refined petroleum oils might be toxic to flora, fauna and humans at the levels at which they were present in the soils.

It has been reported that extreme levels of Cr can result in dermatitis, ulceration of the skin, perforation of the nasal septum, chronic catarrh and emphysema; Cu can have an effect on erythrocytes and the liver and is also a skin and mucous membrane irritant [33]; while Mn can reduce Fe absorption and affect the central nervous system [33]. It has also been reported by Filby and Berkel [33] that Pb can cause brain damage, convulsions, behavioural disorders and death; Ni can cause dermatitis, respiratory disorders, lung and nose cancers; while Zn can cause dermatitis and hypertension as well as atherosclerotic and heart diseases.

It has been reported that polyaromatic hydrocarbons (PAHs) which are known to be significant components of petroleum hydrocarbons have moderate to high acute toxicity to aquatic life and birds, while some of them can cause damage and death to agricultural and ornamental crops [34]. The United States of America Environmental Protection Agency (EPA) has classified some PAHs as carcinogens [35,36]. Epidemiologic studies have reported an increase in lung cancer in humans exposed to coke oven emissions, roofing tar emissions and cigarette smoke. Each of these mixtures contains a number of polyaromatic organic matter (POM) compounds [37]. Polyaromatic hydrocarbons are promutagens, and nitro derivatives of certain PAHs are strong direct mutagens [37].

Since it has been established by this study that the oil-impacted soils have extreme levels of the potential toxic elements and high content of TPHs that can cause different kinds of ill-health, it is recommended that removal of these elements be done well; addition of Pb derivatives as anti-knocking agents should be discouraged and substituted with other mild anti-knocking agents such as ethanol; hydrogen fuel should be encouraged; indiscriminate discharge of petroleum oils and petrochemicals should be discouraged; siting of petroleum products depots close to human settlements should be discouraged and farmers should not be allowed to carry out any farming (crop production and/or animal husbandry/rearing) activities around petroleum depots. The environmental regulatory bodies should be active to avoid environmental degradation because these pollutants may be hazardous not only to the workers, the local residents, fauna and flora, but can also alter the ecology of an area.

References

[1] N.E. Max, *Oil Pollution and the Law*, The Bureau of National Affairs, Inc., Washington, DC, 1969.

[2] C.O. Oyibo, and E.A. Agbola, *Pollution control in petroleum product marketing operations in Nigeria*, in *The Petroleum Industry and the Nigeria Environment*, Nigerian National Petroleum Corporation, Lagos, 1983, pp. 65–70.

[3] R.L. Siegrist, T.J. Phelps, N.E. Korte, and D.A., *Pickering characterization and biotreatability of petroleum contaminated soils in a Coral Atoll in the Pacific Ocean*, Appl. Biochem. & Biotech. 45 & 46 (1994), pp. 757–773.

[4] O. Osibanjo, S. Abumere, and F. Akintola, *Disposal of used oil from motor garages and petrol stations in some Nigerian coastal towns. Field survey study on environmental sector plan for Nigeria*, Nigerian National Petroleum Corporation, Lagos, 1983.

[5] J. Borneff, and H. Kunte, *Carcinogenic substances in water and soil. XVII. About the origin and evaluation of the PAH in water*, Arrh. Hyg. Bakt. 149 (1965), pp. 226–243.

[6] H.E. Mc Kee, and W.A. Mc Mahon, *Polynuclear aromatic contents of vehicle emissions*, Am. Petrol. Inst. Tech. Report, No. 1, 1967.

[7] B.P. Tissot, and D.H. Welte, *Petroleum Formation and Occurrence*, 2nd ed., W.H. Freeman and Co., New York, 1984.

[8] T.F. Yen, *The role of trace metals in petroleum*, Ann Arbor Sci. (1975), pp. 126–130.

[9] Kittiwake Developments, *Vanadium and sodium*, 2008. Available at: http://www.kittiwake.com/default.aspx/page/KB/KB33, 2008.

[10] O.I. Milner, *Analysis of petroleum for trace elements*. International Series of Monographs on Analytical Chemistry, Pergamon Press, Oxford, 1963, pp. 61–68.

[11] L.C. Osuji, and I. Nwoye, *An appraisal of the impact of petroleum hydrocarbons on soil fertility: the Owaza experience*, Afri. Jour. Agric Resear. 2(7) (2007), pp. 318–324.

[12] L.C. Osuji, and C.M. Onojake, *Field reconnaissance and estimation of petroleum hydrocarbon and heavy metal contents soil affected by the Ebocha-8 oil spillage in Niger Delta, Nigeria*, Jour. Environ Mgt. 79 (2006), pp. 133–139.

[13] L.C. Osuji, and S.O. Adesina, *The Isoko oil pipeline leakage. Total organic carbon/organic matter contents of affected soil*, Cem. Biodiv. 2 (2005), pp. 1075–1085.

[14] International Atomic Energy Agency, *Quantitative X-ray Analysis System (QXAS). Users Manual*, IAEA-TECDOC, Vienna, 1996.

[15] D.P.H. Laxen, and R.M. Harrison, *Cleaning methods for polythene containers prior to determination of trace metals in fresh water samples*, Anal. Chem. 53 (1981), pp. 345–530.

[16] S. Bailey, *The analysis of agricultural materials*, in *A Manual of the Analytical Methods used by Agricultural Development and Advisory Services*, 3rd ed., London, 1986, pp. 66–241.

[17] Association and Water Pollution Control Federation, AWPCF, *Standard Method for the Examination of Water and Waste Water*, 18th ed., E.G. Arnold, S. Lenor, and D.E. Andrew, eds., EPS Group Incorporation Handover, Maryland, USA, 1992, pp. 3–5.

[18] C.A. Black, D.D. Evans, J.L. White, L.E. Ensminger, and F.E. Clark, *Methods of Soil Analysis (Chemical and Microbiological Properties), Part 2,* American Society of Agronomy, New York, 1965, pp. 914–926.

[19] International Standard (IS), *Soil Quality-Extraction of Trace Elements Soluble in* Aqua Regia, ISO 11466, Geneva, 1995.

[20] Intergovernmental Oceanographic Commission (IOC), *The Determination of Petroleum Hydrocarbon in Sediments*, Manuals and Guidelines of the IOC, Paris, 1982, pp. 11–15.

[21] N.C. Brandy, *The Nature and Properties of Soils*, MacMillan Company Inc., New York, 1984.

[22] F.M. Adebiyi, O.I. Asubiojo, T.R. Ajayi, and E.I. Obiajunwa, *Trace element and physico-chemical characteristics of sand and water fractions of Nigerian bituminous sands*, Chem. Ecol. 21(5) (2005), pp. 369–380.

[23] M.K. Fasasi, and E.I. Obiajunwa, *Determination of soil to plant transfer rations of major, minor and trace elements in some vegetables grown around Ile-Ife, Nigeria*, Niger. Jour. Pure Appl. Sci. 15 (2000), pp. 1019–1023.

[24] J.B. Diatta, E. Chudzinska, and S. Wirth, *Assessment of heavy metal contamination of soils impacted by a zinc smelter activity*, J. Elem. 13(1) (2008), pp. 5–16.

[25] IUGS/IAGC, *Annual Report for the International Union of Geological Sciences (IUGS)/International Association of Geochemistry (IAGC) Task Group on Global Geochemical Baselines*, 2008. Available at: http://www.ugs.org/PDF/AR07_IG_GGB.pdf.

[26] P.C. Onianwa, and J.O. Adoghe, *Heavy metal content of roadside gutter sediments in Ibadan, Nigeria*, Environ. Inter. 23(6) (1997), pp. 873–877.

[27] P.C. Onianwa, *Petroleum hydrocarbon pollution of urban topsoil in Ibadan city, Nigeria*, Environ. Inter. 21(3) (1995), pp. 341–343.

[28] T. Hajira, and M. Zehra, *Assessment of the soil samples after the disaster of Tasman Spirit near the Clifton beach, Karachi, Pakistan*, Electron J. Environ. Agric. Food Chem. 4(6) (2005), pp. 1094–1101.

[29] G.C. Ofunne, *A closer look at crude oil*, Afr. Rev. (2008), pp. 34–39.

[30] NALCO, *Crude oil desalting*, 2008. Available at: http://www.coopg.org/potter_SAT_Feb_2007.pdf.

[31] K.C. Jones, J.A. Stratford, and K.S. Waterhouse, *Polynuclear aromatic hydrocarbons in UK soils: Long-term temporal trends and current levels*, Trace Subst. Environ. Health 2 (1987), pp. 140–148.

[32] L.S. Sonon, and J.Gaskin, *Metal concentration standards for land application of biosolids and other by-products in Georgia*, 2009. Available at: http://pubs.caes.uga.edu/caespubs/pdf/B1353.pdf.

[33] R.H. Filby, and G.I. Berkel, *Geochemistry of metal-complexes in petroleum, source rock and coal*, in *Metal Complexes in Fossil Fuel*, R.H. Filby and J.F. Branthaver, eds., ACS Symposium Series, Washington, DC, 1987, pp. 2–39.

[34] Australian Government Department of the Environment, Water, Heritage and the Arts, (AGDEWHA), *Polycyclic Aromatic Hydrocarbons*, AGDEWHA, Australia, 2004.

[35] United States Environmental Protection Agency (USEPA), *Method 610 – Polynuclear Aromatic Hydrocarbons*, 40 CFR Part 136, 43344; Federal Register 49, No. 209, 1984.

[36] S.O. Back, R. Field, M.E. Goldstone, P.W. Kirk, J.N. Lester, and R.A. Perry, *Review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior*, Water Air Soil Pollut. 60 (1999), pp. 279–300.

[37] Agency for Toxic Substances and Disease Registry (ATSDR), *Total petroleum hydrocarbons (TPH),* US Department of Health and Human Services, Atlanta, USA, 1998.

[38] Federal Ministry of Environment (FMEnv), *Guidelines and Standards for Environmental Pollution Control in Nigeria*, FMEnv, Nigeria, 1991, pp. 33–103.

[39] C.A. Domy, *Biogeochemistry of Trace Metals*, Lewis Publishers, Chelsea, 1992.

[40] EEC Directive 79/531, Annex V, Part C, *Methods for the Determination of Ecotoxicity Levels, Commission of European Communities*, DG X1/127–129/82, 1982.