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Quality Assessment and Levels of Polycyclic Aromatic Hydrocarbons in Oil Contaminated Soils in Parts of Rivers State Nigeria

Ideriah T.J.K.[1], Ndokiari Boisa[2], Sadiq Bazamfare[2]

[1]Institute of Pollution Studies, Rivers State University Port Harcourt, Nigeria
[2]Department of Chemistry, Rivers State University Port Harcourt, Nigeria

Abstract The levels of Polycyclic Aromatic Hydrocarbons, Physicochemical Properties and Heavy Metals in Lube and Diesel Oil contaminated soils around automobile mechanic workshops in parts of Rivers State were assessed using standard methods recommended by APHA, Loganathan and EGASPIN for physiochemical parameters, Chromatograph (HP5890 Series II) for PAHs and Atomic Absorption Spectrophotometer for heavy metals. The spill or discharge of spent lube oil on soil was simulated and the results showed mean values of 6.64 ±0.336 pH, 507 ±72.054µS/cm electrical conductivity, 14.733±7.37meq/100g CEC,. 3.357 ±2.34% TOC, 2.375 ±2.12% TON, 0.1975 ±0.056mg/kg Available Phosphorus, 63.08 ±52.694mg/kg potassium, 501.13 ±138.407mg/kg Magnesium, 39.303±4.991mg/kg Manganese, 81.505±19.524mg/kg Total Hydrocarbon content, 0.147 ±0.134mg/kg Polycyclic aromatic hydrocarbons, 90.11 ±1.14% sand, 1.66±0.87% silt. The texture of the soil was predominantly sandy.The concentrations of PAH in unpolluted soil ranged from 5.9995×10^{-6}ppm (chrysene) to 1.8095×10^{-3}ppm (phenanthrene) with mean of 0.00038±0.0005. The PAH concentrations in polluted soil ranged from 1.0705×10^{-4} ppm(2-methyl naphthalene) to 2.0684×10^{-2}ppm (benzo(b)fluoranthene) with mean of 0.0052±0.0054. The mean PAH concentrations in soils was 0.0199±0.0373ppm at Ibeto, 0.0095±0.0162ppm at Ogubolo and 0.0080±0.0153ppm at Ikoku. The levels of pH measured indicate that the soils are moderately acidic.The concentrations of toxic and carcinogenic PAHs such as Benzo(b)fluoranthene, Benzo(k)fluoranthene and Indeno(1,2,3-c,d)pyrene exceeded their permissible limits. The simulation with lube oil discharged on soil showed the contribution of used or spent lube oil to the levels of pollutants measured in soils at the study areas. The concentrations of all the toxic and carcinogenic PAHs in soils at the study areas except Benzo(a)pyrene and Indeno(1,2,3-cd) pyrene at Ibeto exceeded their permissible limits and therefore pose grave environmental and health concerns in the areas. There should be awareness campaign and local crude oil refining (Artisanal Refinery) activities and indiscriminate location of auto mechanic shops close to residential and farm lands should be discouraged.

Keywords Lube oil, Artisanal Refinery, unpolluted soil, carcinogenic PAHs, Physicochemical parameters

Introduction

Polycyclic aromatic hydrocarbons are ubiquitous environmental contaminants occurring naturally in crude oil or created and released into the environment through natural events (e.g., volcanic eruptions, forest fires) and anthropogenic activities (e.g., burning of fossil fuels). Human exposure to mixtures of PAHs can occur through consumption of PAH-containing foods (e.g., contaminated seafood, char-grilled meat), non-dietary ingestion (e.g.,

house dust), inhalation of polluted air (e.g., cigarette smoke, diesel exhaust), or dermal contact in an occupational setting (e.g., road paving, roofing). Polycyclic aromatic hydrocarbons are extensively studied components in air, water, soil and food stuffs as a result of PAH having been shown to be carcinogenic and mutagenic to laboratory animals as well as man [1].

Human health effects from environmental exposure to low levels of PAHs are unknown. Large amounts of naphthalene in air can irritate eyes and breathing passages. Workers who have been exposed to large amounts of naphthalene from skin contact with the liquid form and from breathing naphthalene vapor have developed blood and liver abnormalities. Several of the PAHs and some specific mixtures of PAHs are considered to be cancer-causing chemicals [2]. There is large contribution of PAH in absorbed lubricating oil to PAH in exhaust emission [3].

Petroleum hydrocarbons are environmental pollutants. Pollution from these sources emanates from two major routes, release of the hydrocarbons into the atmosphere from combustion processes and direct spill of the hydrocarbons into the environment. Various potentially toxic elements such as heavy metals are present in crude oil and elevated concentrations of these compounds are known to affect soil and associated components. [4].

Waste oil are usually generated during servicing of engines, damaged engine parts e.g. damaged seal, faulty crank seal, damaged filter [5]. Waste lubricating oil have been contaminated with impurities in the course of usage and handling which may contain toxic and harmful substances such as benzene, lead, cadmium, polycyclic aromatic hydrocarbon (PAHs), Zinc, Arsenic, polychlorinated biphenyls (PCBs) e.t.c. which are hazardous and detrimental to soil and water surrounding the environment. Increase and demand for cars, heavy duty automobiles, generators etc, throughout the years led to increase in demand of lubricating oils and this has resulted to a large generation of waste oils in Nigeria. Disposal of used engine oil into the environments has created series of health problems. [6].

[3] reported large contribution of PAH in absorbed lubricating oil to PAH in exhaust emission. [7] reported high concentrations of heavy metals in soil and water receiving used engine oil. [5] reported waste engine oil are usually generated during servicing of engines, damage engine parts e.g damaged seal, faulty crank shaft, damaged filter etc. [8] worked on the effect of soil contamination with diesel oil and petrol on the nitrification process and reported that fertilizer nitrogen was subject to strong immobilization in soil contaminated with diesel and petrol. Diesel oil reduced ammonium cation oxidation by 99% and petrol by 88%. Soil ecosystem harbours an enormous biodiversity and is increasingly being recognized that this diversity is essential for the maintenance of the function of other ecosystems. [9].

Adulteration of petroleum products has many effects on both the engine and the human health. There is need for the determination of quality of lube and diesel oil in the market. Used engine oil disposed into the environment in Pakistan creates series of health problems [6].

Heavy metal is any relative dense metal or metalloid that has potential toxic ability especially in the environment. [10]. Heavy metals found naturally on earth become concentrated as a result to human or anthropogenic activities and can enter plant, animal, and human tissues via inhalation, diet, and manual handling. [7] reported high concentrations of heavy metals in soil and water receiving used lube oil (engine oil).

The aim of this study is therefore to assess the concentrations of xenobiotics such as Polycyclic Aromatic Hydrocarbons, heavy metals and Physicochemical parameters contained in soil contaminated with used (spent) and unused lube and diesel oils.

Materials and Methods

The methods recommended by APHA, Longanathan and EGASPIN were used to determine physiochemical parameter in soil such as

Sample Collection

Soil samples from different mechanic workshops at Ibeto, Ikoku and Ogu-Bolo were collected into polythene bags using soil auger. A simulation of polluted soil by used engine oil and fresh soil or non impacted soil within the same area not more than twenty meters apart were collected using a soil auger and stored in labeled polythene bags.

Analytical methods

PAHs

Concentrated aromatic extract of water transferred into labeled glass vials with Teflon or rubber crimp caps for GC analysis. 1µL of the concentrated sample was injected by means of a hypodermic string through a rubber septum into a column of Gas Chromatograph(HP5890 Series II). Separation occur as the vapour constituent partition between the gas and liquid phases

Heavy Metals

1g of the sieved composite soil sample was weighed into a conical flask and digested with 3ml HCL and 1ml HNO_3(Aqua Regia) method. The content were filtered through whatman No. 42 filter paper into 50ml volumetric flask made up to the mark with de ionized water. The concentration of Ni, Cr, Mn, Pb in the digested soil sample were determined by Atomic Absorption Spectrophotometer.

The known volume of sample was ashed at 775 ºC. This is dissolved with minimum volume of conc. HNO_3. The solution is filtered, diluted to mark with deionized water. The sample (filtrate) was taken to the laboratory for AAS.

Determination of soil physicochemical properties

Standard methods were used to analyze the physicochemical parameters in the soil. The parameters determined in the soils collected are the total concentration and the chemical form of Pb, Cr, Ni, Mn. The physicochemical parameters of soil determined are:

1. Soil pH

The soil pH was determined in a 1:2.5 soil to water ratio using a glass electrode pH meter 4g of air-dried and sieved (2mm sieve) soil sample were weighed into a beaker. 10ml of distilled water was added stirred and allowed to stand for 30 minutes before measurement of pH [11].

2. Available Phosphorus

Bray no.1 method as modified by [12] was used in as 1 g of air dried soil sample was weighed into a 15ml centrifuge tube, 7ml of extracted solution was added while the percentage transmittance was measured at 660nm wavelength, the optical density of standard solution was plotted against the concentration p and the content of the extractable P in soil was obtained from the calibration curve.

3. Potassium

To 5g of the soil sample, 30ml of 1M ammonium acetate (NH_4OAC) solution was added and shaken for two hours on a mechanical shaker and was finally determined using a flame photometer

4. Total Nitrogen

Total nitrogen concentration was determined using the regular macro- Kjeldahl method, in this method the sample (5g) was digested and distilled. The distillate was titrated with 0.01M standard sulphuric acid, the percentage total nitrogen was then determined by calculation [11].

5. Total Hydrocarbon Content (THC)

The total hydrocarbon content was determined by refluxing 100g of soil sample with 100ml of methanol containg 3g of KOH for 2.5 hours (2hrs 30miutes).

6. Cation Exchange Capacity (CEC)

The effective cation exchange capacity was determined by calculating the sum of the total exchange acidity and total exchange bases

7. Exchangeable Cations Ca^{2+}, Mg^{2+}, K^{+}

These cations were determined using standard method involving EDTA titration [11].

8. Organic Carbon (OC)

10 ml, 1M potassium dichromate was added to 5g of soil sample and swirled. 20ml of concentrated H_2SO_4 were added to the mixture and swirled the after 30 minutes, 100ml distilled water added followed 3-4 drops of ferrion indicator and was titrated with 0.5M ferrous solution

Results

The results of physiochemical parameters and polycyclic Aromatic Hydrocarbons in soils around automobile mechanic workshops in Port Harcourt are presented in Tables 1-3 and Figs 2–4c.

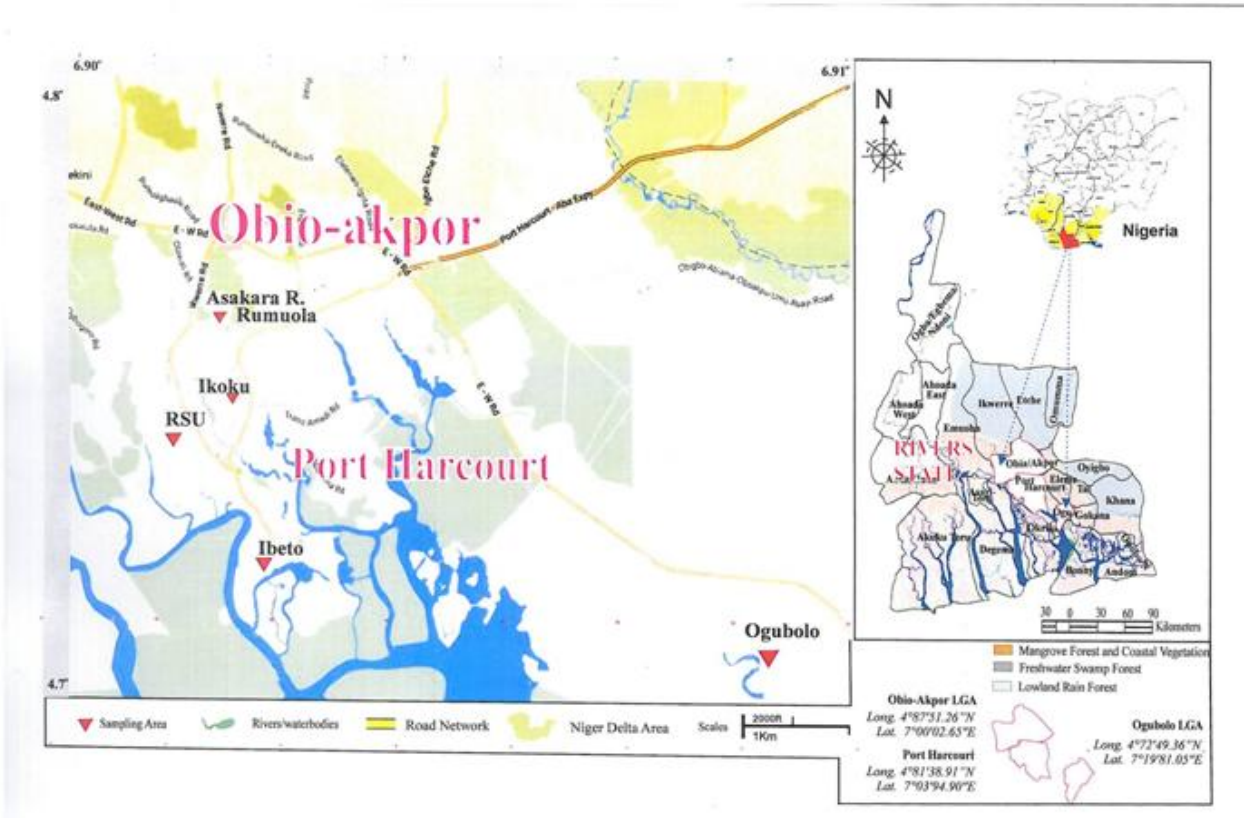

Figure 1: Map of Rivers State showing the Study area

Physicochemical Parameters

The mean pH of the soils in the area ranged from 6.2±0.01 at Ibeto to 6.68±0.012 at Ogubolo with a total mean of 6.64 ±0.336. The electrical conductivity in the area ranged from 225±1.10µS/cm in unpolluted soil to 1365±2.45µS/cm at Ibeto with total mean of 507 ±72.054µS/cm. The CEC of the soils in the areas ranged from 6.777±0.05meq/100g in Polluted soil to 22.384±1.00meq/100g at Ibeto canal with total mean of 14.733±7.37meq/100g.The mean TOC of the soil in the area ranged from 2.34±0.61% at unpolluted to 1.29±0.011% at Ogubolo with total mean of 3.357 ±2.34%. The mean TON of soils in the area ranged from 0.111±0.001% at Ogubolo to 5.11±1.13% in Polluted soil with total mean of 2.375 ±2.12%. The Available Phosphorus concentrations in soils in the areas ranged from 0.14±0.01mg/kg at polluted soil to 0.25±0.01mg/kg at Ogubolo with total mean of 0.1975 ±0.056mg/kg.The concentrations of potassium in soils in the area ranged from 32.25±1.0mg/kg at Ogubolo to 141±5.29mg/kg at Ibeto with total mean of 63.08 ±52.694mg/kg.The concentrations of Magnesium in soils from the areas ranged from 238.50±0.41mg/kgin Polluted soils to 996.81±2.48mg/kg at Ibeto with total mean of 501.13 ±138.407mg/kg.Manganese in soils in the areas ranged from 39.64±0.62mg/kg at Ibeto to 44.28±1.10mg/kgin unpolluted soil with total mean of 39.303±4.991mg/kg.The Total Hydrocarbon content of the soils in the areas ranged from 3.49±0.24mg/kgin unpolluted soil to 191.33±3.21mg/kgin Ibeto soil with total mean of 81.505±19.524mg/kg. The Polycyclic aromatic hydrocarbonsin the soils of the area ranged from 0.006±0.001mg/kg at unpolluted site to 0.319±0.02mg/kg in Ibeto soil with total mean of 0.147 ±0.134mg/kg. The sand content of the soil in the area ranged from 88.48±0.01% in polluted soil to 91.12±0.01% in Ogubolo soil with total mean of 90.11 ±1.14%. The silt content in the area ranged from 0.36±0.001% in Ogubolo to 2.16±0.001% in unpolluted soil with total mean of 1.66±0.87%. The Texture of the soil in the study areas was predominantly sandy.

Polycyclic Aromatic Hydrocarbons (PAHs)

The concentrations of PAH in unpolluted soil ranged from 5.9995×10^{-6}ppm (chrysene) to 1.8095×10^{-3}ppm (phenathrene) with mean of 0.00038±0.0005. The PAH concentrations in polluted soil ranged from 1.0705×10^{-4}ppm(2-methyl naphthalene) to 2.0684×10^{-2}ppm(benzo(b)fluoranthene) with mean of 0.0052±0.0054.

The PAH concentrations in soils at Ibeto varied from 1.2893×10^{-5}ppm (naphthalene) to 1.4823×10^{-1}ppm (fluoranthene) with mean of 0.0199±0.0373ppm. In Ogubolo soil the PAH concentrations varied between 2.5428×10^{-4}ppm (benzo(k)fluoranthene) and 6.4056×10^{-2}ppm(anthracene) with mean of 0.0095±0.0162ppm. The PAH concentrations in Ikoku soil ranged between 2.5828×10^{-4}ppm(benzo(k)fluoranthene) and 6.2988×10^{-2}ppm(anthracene) with mean of 0.0080±0.0153ppm.

The mean concentrations of the individual PAHs in soils from the study areas were 0.00099±0.00124ppm naphthalene, 0.00022±0.00019ppm 2-methylnaphthalene, 0.00353±0.0043ppm acenaphthylene, 0.00138±0.00058ppm for acenaphthene, 0.00614±0.03816ppm fluorene, 0.01589±0.01739ppm phenanthrene, 0.02927±0.0318ppm anthracene, 0.03686±0.06247ppm fluoranthene, 0.0092±0.0157ppm pyrene, 0.01468±0.01442ppm Benz(a)anthracene, 0.00744±0.00593ppm chrysene, 0.00654±0.00909ppm benzo(b)fluoranthene, 0.00144±0.002116ppm benzo(k)fluoranthene, 0.0016±0.00292ppm benzo(a)pyrene, 0.00119±0.00119 indeno(1,2,3-cd)pyrene and 0.00098±0.0010332 dibenz(a,h)anthracene.

Table 1: Mean Levels of Physicochemical Parameters in Soils at the Study Areas

STATIONS	TOC (%)	TOM (%)	TON (%)	pH	EC(µS/cm)	Av.P (mg/kg)	PAH (mg/kg)	THC (mg/kg)	Mg (mg/kg)	K (mg/kg)	Mn (mg/kg)	CEC (meq/100g)	Sand (%)	Silt (%)	Clay (%)	Texture
Unpolluted soil	2.34 ±0.61	4.02 ±0.80	1.26 ±0.02	6.64 ±0.01	225 ±1.10	0.16 ±0.01	0.006 ±0.001	3.49 ±0.24	414.01 ±2.10	41.84 ±1.21	44.28 ±1.10	9.276 ±0.07	90.36 ±0.01	2.16 ±0.01	7.48 ±0.01	Sandy
Polluted soil	6.68 ±1.20	11.50 ±2.30	5.11 ±1.13	6.68 ±0.02	210 ±1.50	0.14 ±0.01	0.088 ±0.001	52.98 ±1.12	238.50 ±0.41	37.23 ±1.06	40.87 ±1.00	6.777 ±0.05	88.48 ±0.01	2.08 ±0.01	9.44 ±0.01	Sandy
Ibeto soil	3.12 ±0.12	5.37 ±0.40	3.02 ±0.22	6.2 ±0.01	1365 ±2.45	0.24 ±0.01	0.319 ±0.02	191.33 ±3.21	996.81 ±2.48	141 ±5.29	39.64 ±0.62	22.384 ±1.00	90.48 ±0.01	2.04 ±0.01	7.48 ±0.01	Sandy
Ogubolo soil	1.287 ±0.01	2.25 ±0.03	0.111 ±0.01	7.02 ±0.02	228 ±1.11	0.25 ±0.01	0.174 ±0.01	78.22 ±1.51	355.2 ±1.01	32.25 ±1.0	32.42 ±0.33	18.256 ±0.24	91.12 ±0.01	0.36 ±0.01	8.52 ±0.01	Sandy

Table 2: Mean Concentrations (mg/kg) of Heavy Metals in Soils at the Study Areas

Station	Mn	Pb	Cr	Ni
Unpolluted soil	44.14±0.9	0.01±0.01	4.22±0.05	0.675±0.02
Polluted soil	40.55±0.4	2.03±0.02	5.02±0.01	1.2±0.01
Ibeto soil	39.22±0.5	10.32±0.01	9.65±0.07	3.15±0.07
Ogu	11.49±0.07	11.15±0.07	10.69±0.12	3.9±0.01
Ikoku	10.11±0.01	13.01±0.01	10.60±7.0	4.25±0.07
RSMEnvR	NS	2-20	10-200	5-500

NS = Not Stated

Table 3: Mean Concentrations (ppm) of PAHs in Soils from at the Study Areas

S/No.	PAHs	UNPOLLUTED	POLLUTED	IBETO	OGUBOLO	IKOKU	USEPA
1	Naphthalene	1.4911×10^{-4} $\pm1.22\times10^{-5}$	1.0352×10^{-4} $\pm1.00\times10^{-5}$	1.2893×10^{-5} $\pm1.36\times10^{-6}$	2.4490×10^{-3} $\pm1.03\times10^{-4}$	2.2491×10^{-3} $\pm1.09\times10^{-4}$	4.0×10^{-2}c
2	2-Methylnaphthalene	7.605×10^{-5} $\pm2.12\times10^{-5}$	1.0705×10^{-4} $\pm1.23\times10^{-5}$	7.3113×10^{-5} $\pm2.23\times10^{-6}$	4.3482×10^{-4} $\pm1.41\times10^{-4}$	4.1488×10^{-4} $\pm1.21\times10^{-5}$	4.0×10^{-2}c
3	Acenaphthylene	2.4267×10^{-4} $\pm1.11\times10^{-5}$	7.6584×10^{-4} $\pm3.22\times10^{-5}$	2.1323×10^{-4} $\pm1.00\times10^{-4}$	8.7201×10^{-3} $\pm1.70\times10^{-4}$	7.7201×10^{-3} $\pm2.15\times10^{-3}$	2.0×10^{-1}b
4	Acenaphthene	1.1672×10^{-3} $\pm1.02\times10^{-4}$	1.0038×10^{-3} $\pm1.02\times10^{-4}$	9.6344×10^{-4} $\pm1.31\times10^{-4}$	2.3732×10^{-3} $\pm1.30\times10^{-4}$	1.3732×10^{-3} $\pm0.31\times10^{-3}$	2.0×10^{-1}b
5	Fluorene	7.8187×10^{-4} $\pm2.22\times10^{-5}$	3.4818×10^{-3} $\pm1.33\times10^{-4}$	8.1788×10^{-3} $\pm2.33\times10^{-4}$	9.6246×10^{-3} $\pm2.24\times10^{-3}$	8.6246×10^{-3} $\pm3.42\times10^{-4}$	2.0×10^{-1}b

6	Phenanthrene	$1.8095x10^{-3}$ $\pm1.00x10^{-4}$	$6.1833x10^{-3}$ $\pm2.00x10^{-4}$	$4.0182x10^{-2}$ $\pm2.25x10^{-4}$	$2.8409x10^{-2}$ $\pm1.48x10^{-3}$	$2.8409x10^{-3}$ $\pm1.22x10^{-4}$	$2.0x10^{-1}$b
7	Anthracene	$5.1875x10^{-4}$ $\pm1.30x10^{-5}$	$2.8544x10^{-3}$ $\pm1.12x10^{-4}$	$1.5920x10^{-2}$ $\pm1.80x10^{-3}$	$6.4056x10^{-2}$ $\pm1.25x10^{-3}$	$6.2988x10^{-2}$ $\pm1.82x10^{-3}$	$2.0x10^{-1}$b
8	Fluoranthene	$1.6412x10^{-4}$ $\pm1.22x10^{-5}$	$1.1260x10^{-2}$ $\pm1.10x10^{-3}$	$1.4823x10^{-1}$ $\pm0.32x10^{-2}$	$1.1333x10^{-2}$ $\pm0.23x10^{-3}$	$1.3336x10^{-2}$ $\pm0.44x10^{-3}$	$2.0x10^{-1}$b
9	Pyrene	$4.6476x10^{-4}$ $\pm1.61x10^{-5}$	$7.8497x10^{-3}$ $\pm1.41x10^{-4}$	$3.7098x10^{-2}$ $\pm1.02x10^{-3}$	$4.5601x10^{-3}$ $\pm1.55x10^{-3}$	$3.5601x10^{-3}$ $\pm1.60x10^{-4}$	$2.0x10^{-1}$b
10	Benz(a)anthracene	$1.1573x10^{-5}$ $\pm1.02x10^{-5}$	$1.0772x10^{-2}$ $\pm2.22x10^{-3}$	$3.8774x10^{-2}$ $\pm1.08x10^{-2}$	$1.0187x10^{-2}$ $\pm0.06x10^{-3}$	$1.3675x10^{-2}$ $\pm0.50x10^{-3}$	$1.0x10^{-4}$b
11	Chrysene	$5.9995x10^{-6}$ $\pm1.22x10^{-5}$	$5.2412x10^{-3}$ $\pm1.38x10^{-4}$	$1.6362x10^{-2}$ $\pm1.02x10^{-3}$	$7.3078x10^{-3}$ $\pm1.68x10^{-4}$	$8.3018x10^{-3}$ $\pm2.94x10^{-3}$	$2.0x10^{-4}$a
12	Benzo(b)fluoranthene	$1.9249x10^{-4}$ $\pm1.51x10^{-5}$	$2.0684x10^{-2}$ $\pm1.21x10^{-3}$	$1.0787x10^{-2}$ $\pm1.35x10^{-4}$	$5.1287x10^{-4}$ $\pm1.18x10^{-4}$	$5.3287x10^{-4}$ $\pm1.398x10^{-5}$	$2.0x10^{-4}$a
13	Benzo(k) fluoranthene	$3.4706x10^{-5}$ $\pm1.00x10^{-5}$	$5.0625x10^{-3}$ $\pm1.13x10^{-4}$	$1.5665x10^{-3}$ $\pm1.35x10^{-4}$	$2.5428x10^{-4}$ $\pm1.03x10^{-5}$	$2.5828x10^{-4}$ $\pm1.55x10^{-5}$	$2.0x10^{-4}$a
14	Benzo(a)pyrene	$2.0433x10^{-5}$ $\pm1.23x10^{-5}$	$6.8216x10^{-3}$ $\pm1.10x10^{-3}$	$1.3845x10^{-5}$ $\pm1.35x10^{-4}$	$6.6042x10^{-4}$ $\pm1.03x10^{-5}$	$6.2042x10^{-4}$ $\pm1.24x10^{-5}$	$2.0x10^{-4}$a
15	Indeno(1,2,3-cd)pyrene	$1.7229x10^{-4}$ $\pm1.10x10^{-5}$	$3.0993x10^{-3}$ $\pm1.00x10^{-3}$	$2.2218x10^{-4}$ $\pm1.35x10^{-4}$	$1.0567x10^{-3}$ $\pm1.03x10^{-5}$	$1.0447x10^{-3}$ $\pm1.24x10^{-5}$	$4.0x10^{-4}$a
16	Dibenzo(a,h)anthracene	$1.8830x10^{-4}$ $\pm1.22x10^{-5}$	$2.7784x10^{-3}$ $\pm0.20x10^{-4}$	$4.0673x10^{-4}$ $\pm1.35x10^{-4}$	$7\pm.1629x10^{-4}$ $\pm1.03x10^{-5}$	$8.1999x10^{-4}$ $\pm1.24x10^{-5}$	$3.0x10^{-4}$a

a=2013, b=2014, c=1996

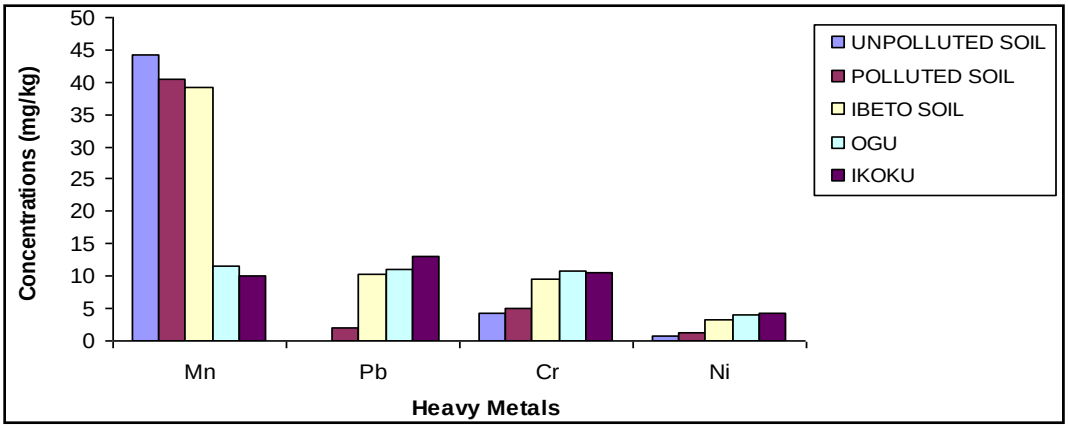

Figure 2: Variations in Concentrations of Heavy Metals in Soils

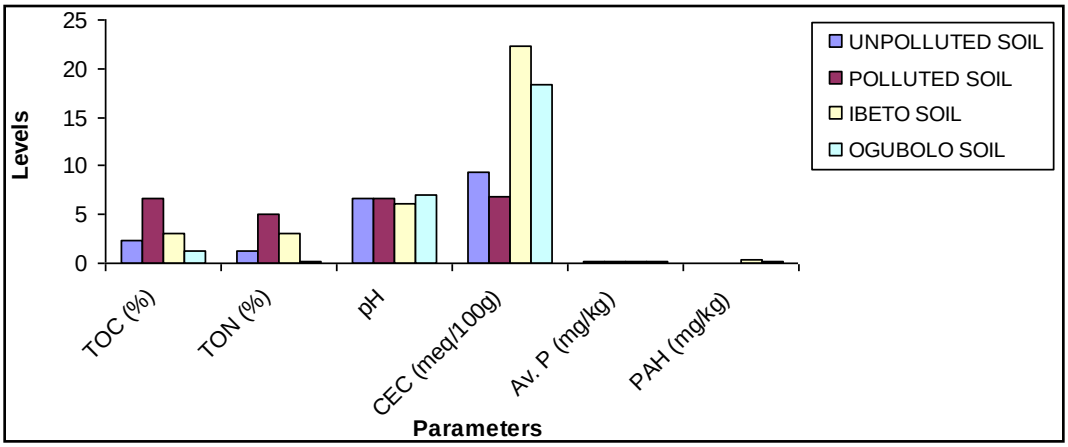

Figure 3a: Variations in Levels of some Parameters in Soils

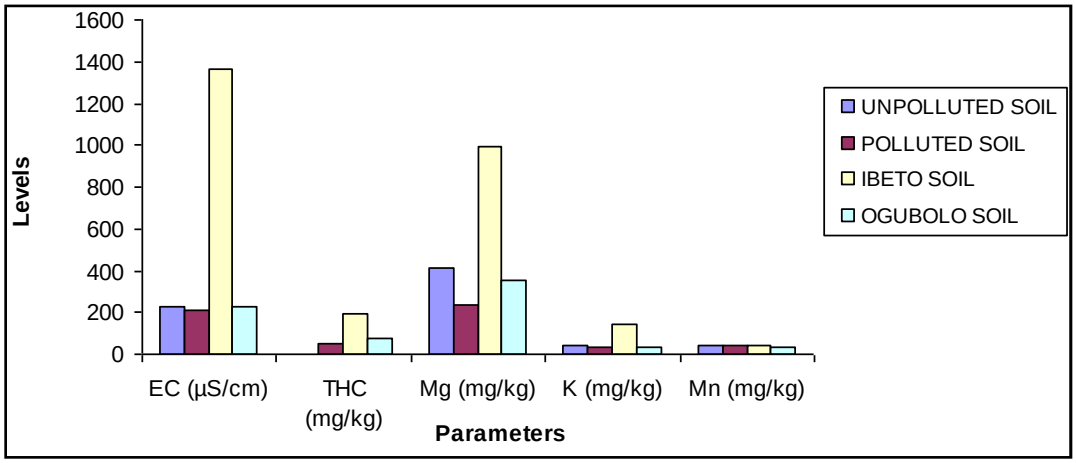

Figure 3b: Variations in Levels of some Parameters in Soils

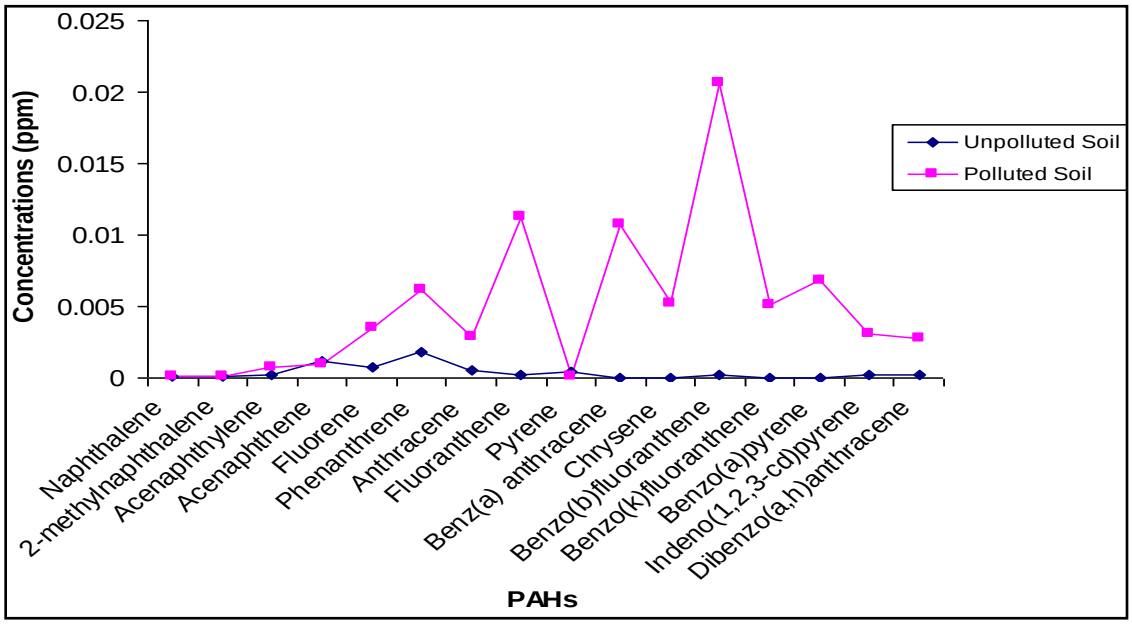

Figure 4a: Variations in Concentrations of PAHs in Unpolluted and Polluted Soils

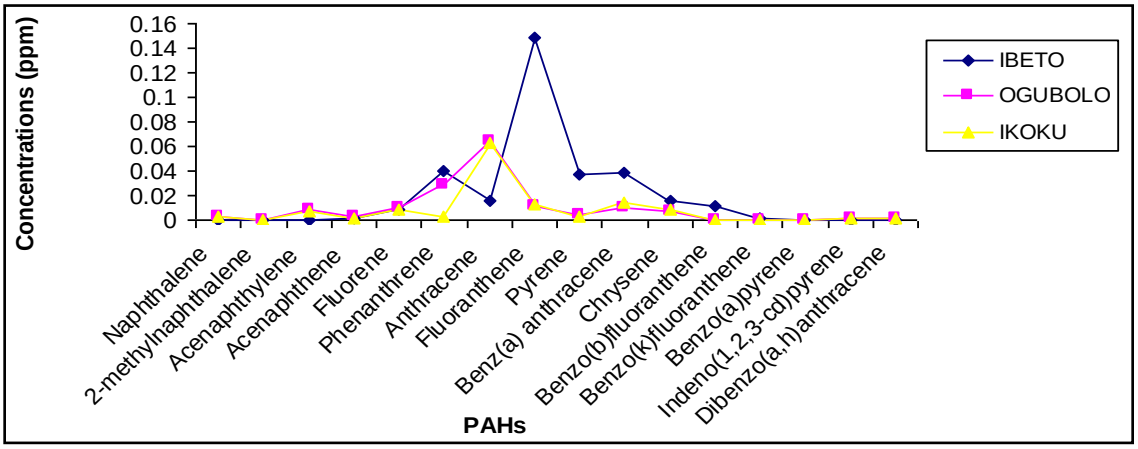

Figure 4b: Variations in Concentrations of PAHs in Soils at the Study Area

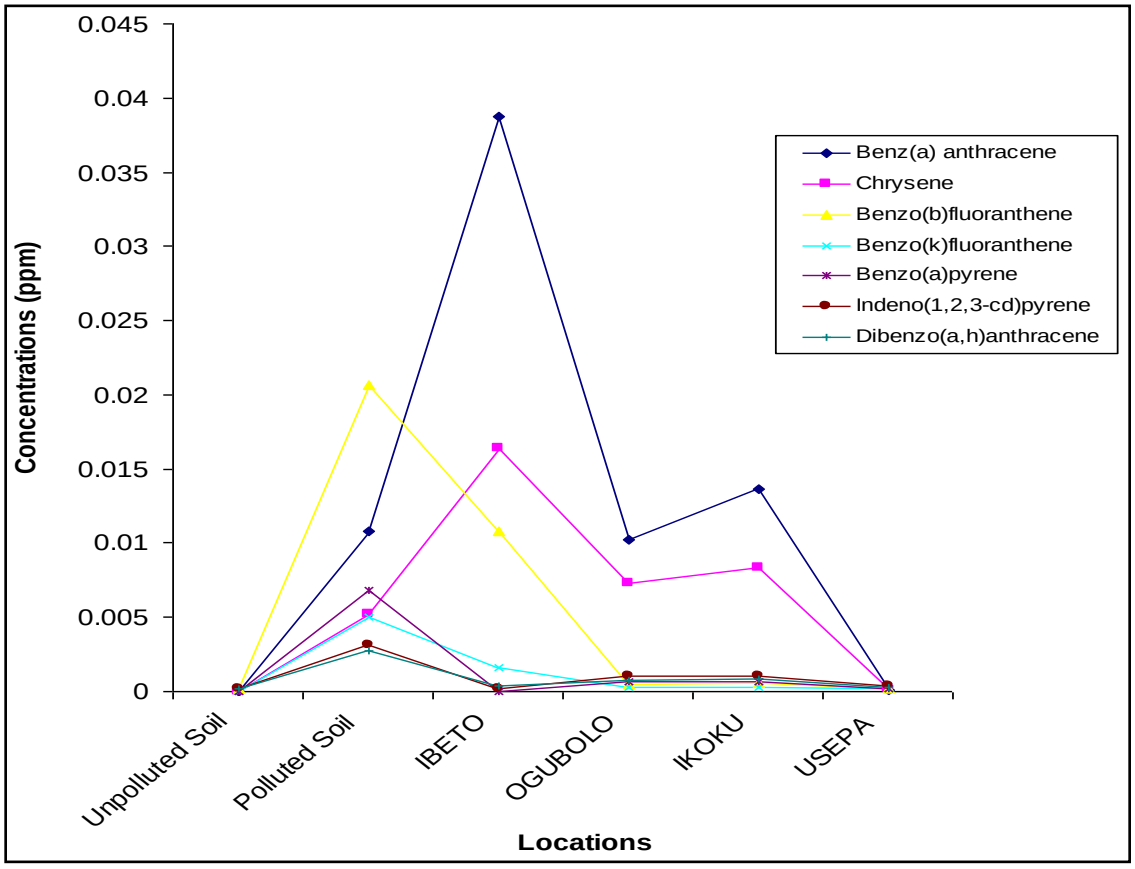

Figure 4c: Variations in Concentrations of Carcinogenic PAHs in Soils at the Study Areas

Discussion

Soil quality

pH

The levels of pH measured indicate that the soils are moderately acidic except soil at Ogubolo which was slightly alkaline. The range of pH measured is typical of Niger Delta soils [13],[14]. The observed soil pH can influence nutrient absorption and plant growth through its influence on nutrient availability and the presence of toxic ions. For instance phosphorus is readily available at pH 6.5 [15].

The soils were slightly acidic in reaction based on pH ratings by [16]. Low pH implies increased solubility and availability of toxic metals (Fe, Al, Mn) and this could lead to reduced vegetation growth, reduced population of N-fixing bacteria and allows for leaching of essential nutrients [17].

Texture

The texture of all the soils is predominantly sandy. This indicates that ground water in the area is susceptible to contamination by surface pollutants. The texture of soil can influence the percent humus and nitrogen present. Sandy soils carry less organic matter than that of a finer texture [15]. The soils have low silt, clay and organic matter contents which may limit their permeability.

Organic Carbon

Organic carbon levels below 2% (organic matter equivalent of 3.44%) are taken to be very low for tropical soils [18]. Based on this rating, all the soil samples except those from Ogubolo are high in organic matter.

According to [19], when soil organic carbon declines, plant nutrients such as nitrogen and phosphorus are mostly at risk.

Total Organic Matter

The organic matter content of the polluted soils and Ibeto exceeded the permissible limit, 3-5% recommended for 0-15cm depth by [15]. The organic matter content of soil depends on the rate of production and decay of wastes and is a function of temperature, rainfall and nutrient status [20]. The level of biochemical activity influenced the variations in organic matter content. Increased biochemical activity depends on the level of organic matter as it is the main source of energy for microorganisms. [21] reported that reduction of organic carbon in soil is as a result of the ability of microorganisms to degrade organic carbon.

Total Organic Nitrogen

The low levels of total N in the area suggest low mineralization of soil organic nitrogen. This does not agree with the report by [22] who observed that high levels of total nitrogen suggest active mineralization of organic nitrogen in soil. The levels of nitrogen can be classified as low, medium or high depending on the organic matter content, total nitrogen and nitrate nitrogen level of the soil. They showed that when organic matter is 0 – 1.5% and total nitrogen is 0.1%; the availability of nitrogen is regarded as low. It is medium when organic matter and total nitrogen are 1.5 – 2.5% and 0.1-0.2%, respectively and high when the soil has more than 0.2% total nitrogen. [23] further classified total nitrogen in soils as < 8µg/g (low), 8 - 20µg/g (moderate) and > 20 µg/g (High). Thus the total N obtained is low in the area.

The concentrations of available phosphorus are high as a result of low organic matter. According to [24], the levels of available phosphorus in the soils at the study area were fairly high.

Potassium

The concentrations of potassium are low. [25] reported that the soils of the humid southern zone of Nigeria were deficient in potassium as a result of high leaching intensity. This may be responsible for the variation in the concentrations of potassium in soils since high leaching rates are features of sandy soils and the soils in the area are sandy soils.

Heavy metals in Soils

The highest concentration of Pb in the area was found to be within permissible limit of 2 – 20mg kg^{-1} [26].

The concentrations of Cr are low. Chromium does not descend below horizons rich in organic carbon at 0-60cm depth [27]. Clay minerals play an indirect role in the retention of Cr [28]. The concentrations of Cr were within permissible limit of 10-200 mg kg^{-1} [26].

The concentrations of Ni were low and below permissible limit of 5-500mg kg^{-1} [26],[29].

Low pH (below 5.5) makes metals such as Zn, Cu, Mn, Fe and Al more soluble for plant uptake [30],[31]. With the low pH values obtained in this study, the Mn values obtained show that the acidic condition of the soils increased its solubility and availability. This situation encourages leaching of nutrient elements.

High levels of physicochemical parameters, heavy metals and PAHs were measured in the soils of the study areas. However, the mean levels of the parameters measured between stations were statistically not significant ($p<0.05$, $F<0.05$). This implies similar sources of contribution to the parameters at the stations. The result of simulation of lube oil discharged on soil put in perspective the contribution of spent or used lube oil to the levels of pollutants in soil at the study areas. It was observed that the level of pollutant measured in the soil mixed with lube oil (Polluted soil) were generally higher than the levels in soil not mixed with lube oil (Unpolluted soil). The difference in mean levels of the parameters between the polluted and unpolluted soils in all the stations were statistically showed no significant difference. This implies similarity in the sources of the pollutants.

High levels of heavy metals were measured in the soil (Table 2, Fig. 4.3b). The trend of the heavy metals concentrations followed: Manganese > Lead > Chromium > Nickel with the least lead concentration measured in unpolluted soil.

In general, except for manganese, the polluted soils had higher heavy metal concentrations than the unpolluted soil. This could be attributed to the presence of heavy metals in the discharged oil. t-test showed no significant difference ($p<0.05$) between the mean concentrations of heavy metals in unpolluted and polluted soils. Appreciably high levels of physicochemical parameters except for Av. P and PAHs were measured in the soil of the study areas (Fig. 4.4a). At the study areas Ibeto and the unpolluted soils were slightly acidic while Ogubolo soil was slightly alkaline. It is observed that the unpolluted soil had the least value of total PAHs (0.006mg/kg), THC (3.49mg/kg) while the soils at Ibeto and Ogubolo receiving discharges of lube oil and Artisanal Refinery diesel Oil had higher values with Ibeto having the highest values. This observation is attributed to the fact that Ibeto received discharges of lube oils from Auto activities than Ogubolo which is a swampy area. High levels of nutrients (TOM, TOC, TON, Av.P, K, Mg, EC and CEC) measured in Ibeto soils indicating that the discharged lube oils resulted in increased nutrient parameters due to degradation of organic carbon. This observation could be responsible for the luxuriant growth of plants around the auto workshop areas.

Polycyclic Aromatic Hydrocarbons in Soil

Acenaphthene, Acenaphthylene, Anthracene, Fluoranthene, Fluorene, Phenanthrene, Pyrene

These PAHs were not classified as carcinogenic by IARC [32]. Their concentrations in soil in all the areas were below the permissible limit of 0.2mg/l set by [33]. This implies that the soils are not polluted with regard to these parameters and they do not pose adverse effects to human health.

Naphthalene and 2-methylnaphthalene

These are lower molecular weight PAHs and are not classified as having human carcinogenicity [32]. The concentrations of Naphthalene and 2-methylnaphthalene in soils are below the permissible limit of 0.04mg.l set by [34]. The soils in the areas are therefore not polluted with respect to Naphthalene and 2-methylnaphthalene.

Benz(a)anthracene

Benz(a)anthracene is one of the PAHs considered to be carcinogenic, mutagenic and toxic [35]. In this study the concentrations of Benz(a)anthracene in polluted soil, soils at Ibeto, Ogubolo and Ikoku exceeded the permissible limit of $1.0x10^{-4}$mg/l set by [35]. Therefore Benz(a)anthrancene poses health concern in the study areas.

Benzo(a) pyrene

Benzo(a)pyrene is one of the PAHs considered to be carcinogenic, mutagenic and toxic [35]. In this study, the concentrations of Benzo(a)pyrene in polluted soil, soils at Ogubolo and Ikoku exceeded the permissible limit of $2.0x10^{-4}$mg/l set by [35]. The concentrations of Benzo(a)pyrene therefore pose health concern in the areas.

Benzo(b)fluoranthene and Benzo(k)fluoranthene, Chrysene and Dibenzo(a,h)anthracene

These PAHs are considered to be carcinogenic, mutagenic and toxic [35]. In this study the concentrations of these parameters in polluted soil, soils at Ibeto, Ogubolo and Ikoku exceeded the permissible limit of $2.0x10^{-4}$mg/l set by [35]. Therefore they pose health concern in the study areas. The high concentrations could be due to oil pollution in that environment.

Indeno(1, 2 ,3 – c, d)pyrene

Indeno(1,2,3–c, d)pyrene is one of the PAHs considered to be carcinogenic, mutagenic and toxic [35]. In this study the concentrations of Indeno(1,2,3 – c, d)pyrene in polluted soil, soils at Ogubolo and Ikoku exceeded the permissible limit of $2.0x10^{-4}$mg/l set by [35]. The concentrations of Indeno(1, 2 ,3 – c,d)pyrene in water were below the limit. Therefore Indeno(1, 2 ,3 – c,d)pyrene poses grave health concern in the soils from the study areas.

The mean concentrations of PAHs in polluted soils were found to be higher than those in unpolluted soils (Table 3, Fig. 4.5a and b). Statistical analysis (t-test and ANOVA) on the differences between their means showed no significant difference ($p<0.05$, $F<0.05$). The high concentrations of PAHs in the polluted soil could be attributed to the used lube oil discharged on the soil during simulation. The concentrations of the individual PAHs varied within

and between the study areas. However the differences between their mean concentrations showed no significant difference ($p<0.05$).

PAHs are classified into carcinogenic and non-carcinogenic types [32]. The concentrations of all the PAHs in the unpolluted soil were below permissible limits while all the carcinogenic PAHs except Benzo(a)pyrene and Indeno(1,2,3-cd) pyrene at Ibeto exceeded their permissible limits (Table 3, Fig. 4.5c). The trend of PAHs concentrations in soils followed: Ibeto> Ogubolo> Ikoku. This observation could be attributed to the auto mechanic activities at Ibeto which received more spent lube oil than diesel oil. The mean concentrations in PAHs between the soils in the areas showed no significant difference ($p<0.05$).

Relationships between Physicochemical Parameters

High significant correlation exit between TOC and TON (0.9642), phosphorus (-0.6922),sand (-0.9894). TON showed high significance correlation with phosphorus (-0.5688), sand (-0.9124), pH showed high significance correlation with electrical conductivity (-0.8581), Total hydrocarbon (-0.6318), magnesium (-0.8317), potassium (-0.8946), silt (-0.7355), PAH (0.8596), total hydrocarbon (0.9204), magnesium (0.9790), electrical conductivity showed high significance correlation with potassium (0.9969). Phosphorus showed high significance correlation with PAH (0.7802), total hydrocarbon (0.6830), Mn (-0.7493), sand (0.8074), silt (-0.6561). PAH showed high significance correlation with total hydrocarbon (0.9866), magnesium (0.8033), and potassium (0.8175). Total hydrocarbon showed high significance correlation with magnesium (0.8572), potassium (0.8894), clay (-0.6955), silt (0.9404). Sand showed high correlation with clay (-0.6661).

Relationships between Concentrations of Polycyclic Aromatic Hydrocarbons

Ogubolo PAHs showed high significant correlation with PAHs at Ikoku (0.9159). Naphthalene showed high significant correlation with acenaphthylene (0.9981), acenaphthene (0.8192), fluorene (0.6906), anthracene (0.9739), benzo(b)fluoranthene (-0.6137), benzo(k)fluoranthene (-0.51112), 2-methylnaphthalene showed high significant correlation with acenaphthylene (0.9988), acenapthene (0.8000), fluorine (0.7041), anthracene (0.9741), benzo(b)fluoranthene (-0.5560). acenaphthylene showed high significance correlation with acenaphthene (0.8264), fluorine (0.7115), anthracene (0.9752), benzo(b)fluoranthene (-0.5536). Fluorene showed high significant correlation with phenanthrene (0.6102), anthracene (0.8278), benz(a)anthracene (0.5448), chrysene (0.7247). Phenanthrene showed high significant correlation with fluoranthene (0.7958), pyrene (0.8263), benz(a)anthracene (0.7841), chrysene (0.8002). Anthracene showed high significant correlation with benzo(b)fluoranthene (-0.5703), benzo(k)fluoranthene (-0.5126). Fluoranthene showed high significant correlation with pyrene (0.9946), benz(a)anthracene (0.9600), chrysene (0.8819). Pyrene showed high significant correlation with benz(a)anthracene (0.9497), chrysene(0.8835). Benz(a)anthracene showed high significant correlation with chrysene (0.9721). Benzo(b)fluoranthene showed high significant correlation with benzo(k)fluoranthene (0.9735), benzo(a)pyrene (0.8349), indeno(1,2,3-cd)pyrene (0.8514), Dibenzo(a,h)anthracene (0.9195). Benzo(a)pyrene showed high significant correlation with indeno(1,2,3-cd)pyrene (0.9660), dibenzo(a,h)anthracene (0.9888). Indeno(1,2,3-cd)pyrene showed high significant correlation with dibenzo(a,h)anthracene (0.9880).

Conclusion

The concentrations of toxic and carcinogenic PAHs such as Benzo(b)fluoranthene, Benzo(k)fluoranthene and Indeno(1,2,3-c,d)pyrene exceeded their permissible limits. The simulation with lube oil discharged on soil showed the contribution of used or spent lube oil to the levels of pollutants measured in soils at the study areas. Lube oils discharged in soils increased nutrient parameters.

The concentrations of all the toxic and carcinogenic PAHs in soils at the study areas except Benzo(a)pyrene and Indeno(1,2,3-cd) pyrene at Ibeto exceeded their permissible limits and therefore pose grave environmental and health concerns in the areas; and are attributed to the Auto mechanic activities at Ibeto which received more spent lube oil than diesel oil.

There should be awareness campaign and local crude oil refining (Artisanal Refinery) activities and indiscriminate location of auto mechanic shops close to residential and farm lands should be discouraged.

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