Chemistry Research Journal, **2017, 2(5):242-256**

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Concentrations of Physicochemical Properties and Polycyclic aromatic hydrocarbons in Soil at Akala-olu Ahoada West Rivers State Nigeria

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Abstract The levels of Polycyclic Aromatic Hydrocarbons, Physicochemical Properties and Heavy Metals in Akala-Olu, a crude oil producing community in 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 results showed ranges of pH 6.20 - 6.78, total organic carbon 0.633% - 1.05% organic matter varied 2.14% - 2.88%, Electrical conductivity 274µS/cm - 463 µS/cm, total Nitrogen 0.053% at - 0.977%, Available phosphorus 0.15mg/kg - 0.465mg/kg, Ca 199.67mg/kg - 245.08mg/kg, Mg 51.53mg/kg - 75.53mg/kg, Na 44.09mg/kg - 74.70mg/kg, K 41.11mg/kg - 69.83mg/kg, Cd 0.055mg/kg - 0.105mg/kg, Pb 4.065mg/kg - 5.850mg/kg, Al 0.999mg/kg - 2.085mg/kg, Cr 1.978mg/kg - 3.367mg/kg, Zn, 42.065mg/kg - 50.731mg/kg, Cu 1.474mg/kg - 2.663mg/kg, Fe 4484mg/kg - 6502.50mg/kg, Mn 29.876mg/kg - 33.995mg/kg, Co, 0.001mg/kg did not show any variation in the area. The concentrations of toxic and carcinogenic PAHs ranged from 4.39×10^{-3} - 5.03×10^{-2}ppm Benzo(a)anthracene, 2.37×10^{-3} -3.68×10^{-2} ppm Indeno(1,2,3-c,d)pyrene, 3.84×10^{-3} – 7.08×10^{-2} ppm Dibenz(a,h)anthracene and 1.40×10^{-4}- 7.38×10^{-3}ppm Chrysene. The levels of pH measured indicate that the soils are moderately acidic. The concentrations of most toxic and carcinogenic PAHs such as Benzo(a)anthracene, Indeno(1,2,3-c,d)pyrene, Dibenz(a,h)anthracene and Chrysene exceeded their permissible limits and therefore pose grave environmental and health concerns in the area. There should be awareness campaign and the water in the area should be monitored regularly.

Keywords Top soil, carcinogenic PAHs, Physicochemical parameters, Akala-Olu

Introduction

Soil is a vital part of the Earth. It serves as a natural medium for plants growth [1]. Plants as an integral part of the ecosystem when grown on polluted soil contaminates fruits, food crops due to the accumulation of toxic metals and has become an inevitable problem because the entry of these heavy metals such lead, chromium, cadmium, zinc, arsenic and hydrocarbons into the food chain may lead to increased vulnerability and exposure of the populace to metal poisoning.

Heavy metals are natural components of the Earth's crust. They are not biodegradable or perishable. Heavy metals, such Cu, Co, Fe, Zn and Mo are important to plants and animals, including humans at low concentrations for enzyme activities. If these metals are removed from our nutrition, we are expected to be in the grip of a disease. They are like vitamins and if we are deficient in even one of them, we are likely to suffer from one of them, we are

likely to suffer from one or more health challenges [2], and meanwhile, high level exposure of heavy metals can cause different health problems. Ingestion is one of the major routes of intake of heavy metals into the human body.
The study by Ideriah *et al.,* [3] on "Heavy metal contamination of soils around municipal solid waste dump in Port Harcourt" showed that levels of heavy metals in the soil around waste dump are influenced by the composition and topography of the dumpsite, run-off and levels of scavenging.
Crude oil products are made up of hydrocarbons consisting of short and long-chain aliphatic and aromatic hydrocarbons. Constituents of petroleum are namely volatile organic compounds (VOCs), such as toluene, xylene and benzene and the polycyclic aromatic hydrocarbons (PAHs), have a variety of harmful effect on humans [4]. Polycyclic aromatic hydrocarbons (PAHs) are powerful environmental pollutants which are composed of fused aromatic rings. They are almost everywhere in the environment and are usually formed during incomplete combustion of organic materials such as coal, oil, wood, gasoline *e.t.c*. PAHs are present in asphalt, crude oil and coal tar [5]. As a result of human activities PAHs are found in environment. High levels of PAHs are present in cities and in places where bush burning, petroleum activities are persistently practiced [5]. PAHs have been seen as a potent environmental pollutants by the United Nations Environmental programme [6], and the U.S Environment protection Agency [7]. Health effects of PAHs have been intensively studied, probably because of their carcinogenic nature. The health effects of PAHs exposure depends on some factors such as; duration of exposure, dose taken and the individual characteristics which include nutritional status, age, life style [8]. Generally, the carcinogenic properties of PAHs increase progressively with the number of aromatic rings [9]. Several toxicological studies in animals (World Health Organization – International programme on chemical safety) [10] and occupational studies in humans [11] demonstrate a high risk of lung cancer related to PAHs inhalation. According to the World Health Organization [12] and Dionex [13] PAHs are classified as carcinogenic as well as mutagenic to higher animals.
The study is aimed to evaluate the impact of oil exploitation activities on the quality of soil in Akala-olu community in Ahoada West Local Government Area of Rivers State in other to create awareness among the inhabitants.

Materials and Methods

Study Area

Akala-Olu community in Ahoada West local Government Area of Rivers state. It lies within latitudes 5˚ 5′ 0″ N and longitude 6˚ 39′ 0″ E, with a total land area of 493km^2, altitude of 71, elevation of approximately 12m and a population of about 249,232 [14]. It is bounded by Ogba/ Egbema/Ndoni local government area, Abua/ Odua local government local area, Ahoada East local government area on the east and Biseni and Yenagoa both of Bayelsa state on the north and west respectively (Fig 1). Its vegetation is mainly a high dense rain forest. Thus, the occupations of the people are mainly farming, fishing and hunting. The stations and their geographical positions are shown in Table 2.

Table 1: Geographical Location of soil Sampling Stations

Station	Geographical Location	
	EAST (Longitude)	**NORTH** (Latitude)
1	006˚ 30′ 18.9″	05˚ 06′ 12.6″
2	006˚ 30′ 15.4″	05˚ 06′ 24.8″
3	006˚ 30′ 13.5″	05˚ 06′ 26.9″
4	006˚ 30′ 16.7″	05˚ 06′ 22.3″
5	006˚ 30′ 17.2″	05˚ 06′ 15.4″

Sample Collection and Preparation

Soil samples were collected with an auger. Soil samples from five (5) sampling points within the impacted area. A total of thirty samples comprising fifteen 0-15cm depth and fifteen 15-30cm depth were collected into polythene bags using hand auger. Ten (10) composite samples comprising of five 0-15cm and five 15-30cm were taken to the laboratory for preparation and analyses. The composite samples were air-dried, ground to pass through a 2mm mesh and stored at room temperature in well labeled polythene bags.

Analytical Methods

Physico-chemical Parameters

The samples collected were analyzed for pH, electrical conductivity, total nitrogen (TN),
Organic matter, total organic carbon(TOC), available phosphorus (Av.P), organic matter (OM), potassium (K), magnesium (Mg), sodium (Na), calcium (Ca), copper (Cu), zinc (Zn), lead (Pb), Iron (Fe), cadmium (Cd), manganese (Mn), chromium (Cr), nickel (Ni), cobalt (Co).

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 samples were weighed into a beaker. Ten mililitres (10ml) of distilled water was added, stirred and allowed to stand for 30minutes before measurement of the pH [15].

Available Phosphorus

Available phosphorus was determined spectrophotometrically using Bray no.1 method, modified by Olsen and Sommers [16].

Total Nitrogen

Total nitrogen concentration was determined using the macro Kjeldahl method [17-18]. In this method, 5g of the sample was digested and distilled. The distillate was titrated with 0.01M standard sulphuric acid. The percent total nitrogen was then determined by calculation [15].

Organic Matter (OM)

The organic matter was determined by the Walkley and Black method which involve the titration the titration of un-reacted dichromate ion with standard ferrous ions. The percent organic matter was calculated by multiplying percent organic carbon by 1.724

Organic Carbon (OC)

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

Potassium, Sodium and Magnesium

Potassium, was determined using a flame photometer [19]. Sodium and magnesium were determined by flame emission photometer

Particle Size

The particle size distribution was determined using the hydrometer method and the textual class determined from the Textural Triangular Diagram' [15].

Heavy Metals

Heavy metals (Cu, Zn, Pb, Fe, Cd, Mn, Cr, Ni,) were analyzed using atomic absorption spectrophotometer (AAS) by GBC Avanta version 2.20. (following the standard procedures as given in (APHA, 1995) [20].

Polycyclic Aromatic Hydrocarbons

Extraction: Soil sample, 10g, were transferred into a separate separation funnel; 25ml of dichloromethane was used to rinse the measuring cylinders and also transferred into the separation funnels. The separation funnel were shaken to mix the water sample as well as that of the soil sample and the organic solvent; so as to have all available organic solvent, 25ml of dichloromethane was to rinse to ensure that no trace of organic materials are left un-extracted.

Clean up/separation: The organic extract is collected into receiving container (sample vial), passing the organic extract through an extraction column packed with glass-wool, silica-gel and anhydrous sodium sulphate. The silica-gel aids the cleanup of the extract by disallowing the passage of debris and impurities of other compounds that are PAH's. The anhydrous sodium sulphate acts as a dehydrating agent to rid the organic extract of every form of moisture contained in the sample.

ANALYSIS: The concentrated aromatic extracts were transferred into labeled glass vials with Teflon for gas chromatographic analysis. Polycyclic aromatic hydrocarbons were determined using gas chromatographic analysis (HP 5890 series II)

Results and Discussion

Results

The results of levels of physicochemical properties and Polycyclic Aromatic Hydrocarbons in the top soil at the study area are presented in Tables 1 and 2 respectively and Figs. 1 - 13. Correlation matrices of the parameters are in Tables 3 and 4 respectively. The levels of pH varied between 6.20 at station 2 and 6.78 at station 5. The concentrations of total organic carbon ranged from 0.633% at station 2 to 1.05% at station 3. The concentrations of organic matter varied from 2.14% at station 2 to 2.88% at station 5. The concentrations of Electrical conductivity ranged from 274µS/cm at station 4 to 463 µS/cm at station 5. The concentrations of total Nitrogen varied between 0.053% at station 2 to 0.977% at station 4. The concentrations of Available phosphorus varied from 0.15mg/kg at station 2 to 0.465mg/kg at station 5. The concentrations of Ca varied between 199.67mg/kg at station 2 to 245.08mg/kg at station 3. The concentrations of Mg varied from 51.53mg/kg at station 5 to 75.53mg/kg at station 3. The concentrations of Na ranged from 44.09mg/kg at station 2 to 74.70mg/kg at station 3. The concentrations of K varied from 41.11mg/kg at station 2 to 69.83mg/kg at station 4. The concentrations of Cd varied from 0.055mg/kg at station 2 to 0.105mg/kg at station 5. The concentrations of Pb varied from 4.065mg/kg at station 2 to 5.850mg/kg at station 3. The concentrations of Al varied from 0.999mg/kg at station 3 to 2.085mg/kg at station 4. The concentrations of Cr varied from 1.978mg/kg at station 2 to 3.367mg/kg at station 3. The concentrations of Zn varied from 42.065mg/kg at station 5 to 50.731mg/kg at station 3. The concentrations of Cu varied from 1.474mg/kg at station 2 to 2.663mg/kg at station 3. The concentrations of Fe varied from 4484mg/kg at station 5 to 6502.50mg/kg at station 3. The concentrations of Mn varied from 29.876mg/kg at station 2 to 33.995mg/kg at station 4. The concentrations of Co, 0.001mg/kg did not show any variation in the area.

Discussion

Soil pH

The pH of the soils in the area, 6.20 – 6.78 is moderately acidic. This range is typical of Niger Delta soils [21-22]. The soils were slightly acidic based on pH ratings by Brady and Weil [23]. 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.

Itanna [24] reported that the availability of heavy metals increases with decreasing pH. The pH values obtained in this study imply high tendency of heavy metal availability. 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, as pH increase from 5.0 to 8.0, iron, manganese, zinc and copper become less available while phosphorus is readily available at pH 6.5 [25].

Organic Matter

Organic carbon levels below 2% are taken to be very low for tropical soils [26-27]. Based on this rating, all the soil samples analyzed are moderately high in organic matter. The values of organic matter in this study are below the permissible limit, 3-5% recommended for 0-15cm depth by Brady [25]. 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 [28]. 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.

According to Stocking [29], when soil organic carbon declines, plant nutrients such as nitrogen and phosphorus are mostly at risk.

Total Organic Carbon

The levels of total organic carbon in the area are low. Stegman and Heevenklage [30] reported that reduction of organic carbon in soil is as a result of the ability of microorganisms to degrade organic carbon.

Total Nitrogen

Landon [26] rated soils with total Nitrogen levels from 0.1 – 0.2% as low and <0.1% as very low for tropical soils. The soils of the area are very low in their total nitrogen content except station 4 which is low. Nitrogen is deficient in soils from the area and this can limit vegetation growth and sustained productivity.

The low levels of total N in the area except station 4 suggest low mineralization of soil organic nitrogen. This does not agree with the report by Baker and Herson [31] who observed that high levels of total nitrogen suggest active mineralization of organic nitrogen in soil. The variations observed in the levels of total N suggest that they depend on the type of plants grown in the area. 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. Enwezor *et al*. [32] further classified total nitrogen in soils as < 8µg/g (low), 8 - 20µg/g (moderate) and > 20 µg/g (High).

Available Phosphorus

According to Ilaco [33] and Landon [26], available phosphorus value below 15mg/kg is regarded as low for tropical soils. The results of this study show that the surface soils had available phosphorus values that are below the critical limit. Low phosphorus levels could hinder nitrogen accumulation since symbiotic N-fixing bacteria have a high phosphorus demand.

Exchangeable Ca

Ilaco [33] and Landon [26] rated soils with < 2.0meq/100g as very low in calcium, 2-5meq/100g as low and 5-10 meq/100g as medium. The levels of exchangeable calcium show that the soils of the study area are very low to medium in exchangeable calcium.

Exchangeable Mg

The soils were found to range from low to medium in exchangeable magnesium based on the ratings by Ilaco [33] and Landon [26]. According to these authors, exchangeable magnesium values from 1.5 – 3.0 meq/100g is medium, 0.5-1.5meq/100g low and <0.5 meq/100g very low.

Exchangeable K

According to Ilaco [33], levels of exchangeable potassium between 0.1 – 0.3 meq/100g soil are regarded as low for tropical and sub-tropical soils and below 0.1 meq/100g soil very low. Based on this rating, the soils analyzed in this study ranged between low to moderate in their exchangeable potassium content with most of the samples falling within the 'low' and 'very low' ranges. According to Jones and Wild [34], amounts of exchangeable potassium in the tropical savannah is low. The surface horizons of the cultivated spoils have the highest mean exchangeable potassium value. This could be attributed to cultivation and enrichment of the soils with fertilizers. Udechukwu [35] reported that the soils of the humid southern zone of Nigeria were deficient in potassium as a result of high leaching intensity.

Exchangeable Na

Also, Ilaco [33] and Landon [26] rated exchangeable sodium levels below 0.1 meq/100g as very low and 0.1 – 0.3 meq/100g of soil as low. Based on this, all the soils studied are low in exchangeable sodium. Landon [26] observed that although sodium could serve as a substitute for potassium, it is not an essential plant nutrient. For this reason, he added that its absence or presence in only small quantities is not usually detrimental to plant nutrition. He observed that when sodium is present in soil in significant quantities, particularly in proportion to other cations present, it can have an adverse effect, not only on many crops, but also on physical conditions of the soil.

The generally low content of exchangeable bases in the spoil soils of the study area could be attributed to the parent material that underlies the area as well as leaching of essential plant nutrients. Increasing the pH and organic matter levels will make exchangeable bases more available in the soils.

Heavy Metals

Low pH (below 5.5) makes metals such as Zn, Cu, Cr, Mn, Co, Fe and Al more soluble for plant uptake [36-38]. With the low pH values obtained in this study, the Fe, Al, and Mn values obtained show that the acidic condition of the soils increased the solubility and availability of these metals. This situation encourages leaching of nutrient elements.

Polycyclic Aromatic Hydrocarbons in Soil

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

were not classified as carcinogenic by IARC [8]. Their concentrations in soil from the area were below the permissible limit of 0.2mg/l set by USEPA [7]. 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

Naphthalene is one of the lower molecular weight PAHs with the molecular formula of $C_{10}H_8$, it is not classified as having human carcinogenicity [8]. The concentrations of Naphthalene and 2-methylnaphthalene in soils from the area are below the permissible limit of 0.04mg.l set by USEPA [39]. The soils in the area 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 [40]. In this study the concentrations of Benz(a)anthracene in soils in all the stations exceeded the permissible limit of $1.0x10^{-4}$mg/l set by USEPA [40]. Therefore Benz(a)anthrancene poses health concern in the study area.

Benzo(a) pyrene

Benzo(a)pyrene is one of the PAHs considered to be carcinogenic, mutagenic and toxic [40]. The concentrations of Benzo(a)pyrene in soil at stations 1,2 and 4 exceeded the permissible limit of $2.0x10^{-4}$mg/l set by [40]. The concentrations of Benzo(a)pyrene therefore pose health concern in the area.

Benzo(b)fluoranthene and Chrysene

These PAHs are considered to be carcinogenic, mutagenic and toxic [40]. The concentrations of Chrysene at stations 1,2,4 and 5; Benzo(b)fluoranthene at stations 4 and 5 exceeded the permissible limit of $2.0x10^{-4}$ mg/l set by USEPA [40]. Therefore they pose health concern in the study area. The high concentrations could be due to oil pollution in that environment.

Indeno(1, 2 ,3 – c, d)pyrene and Dibenzo(a,h)anthracene

These PAHs are considered to be carcinogenic, mutagenic and toxic [40]. Their concentrations in soils in all the stations exceeded the permissible limits of $4.0x10^{-4}$mg/l and $3.0x10^{-4}$mg/l set by USEPA [40]. Therefore they pose grave health concern in the soils from the study area.

Relationship between Physicochemical Parameters

There was significant correlation between the physicochemical parameters in the soil (Table 3). The parameters that showed high significant correlation are conductivity and OM(r=0.6517); P and TOC(r=0.6468), pH(r=0.7573); Mg and TOC(r=0.6642), OM(r = -0.7625); K and TOC(r=0.8908), pH(r=0.6738), P(r=0.8231); Na and TOC(r=0.9688), Mg(r=0.6583), K(r=0.8849); Ca and TOC(r=0.8948), K(r=0.6400), Na(r=0.8043); Cd and OM(r=0.8987), pH(r=0.6852), conductivity(r=0.7908), P(r=0.6458); Pb and TOC(r=0.9225), conductivity(r=0.6243), K(r=0.7562), Na(r=0.9089), Ca(r=0.9307); Co and TON(r=0.8411), pH(0.6267); Cr and TOC(r=0.8215), conductivity(r=0.7655), P(r=0.7013), K(r=0.7376), Na(r=0.8137), Ca(r=0.8362); Zn and TOC(r=0.7255), OM(r=-0.6952), Mg(r=0.9426), Na(r=0.6486), Ca(r=0.6976); Cu and TOC(r=0.8210), Na(r=0.7742), Ca(r=0.9638); Fe and TOC(r=0.6793), OM(r= -0.7372), Mg(r=0.9217), Na(r=0.6279), Ca(r=0.7055); Mn and TOC(r=0.9016), TON(r=0.6620), P(r=0.8379), K(r=0.9048), Na(r=0.7953), Ca(r=0.7875); Cr and Pb(r=0.9583); Cu and Pb(r=0.9312), Cr(r=0.8366), Zn(r=0.6201); Zn(0.9697), Cu(r=0.6922); Mn and Pb(r=0.7474), Cr(r=0.6875), Zn(r=0.6556), Cu(r=0.6119).

Relationship between Polycyclic Aromatic Hydrocarbons

There was significant correlation between the Polycyclic Aromatic Hydrocarbons in the soil (Table 4). The parameters that showed high significant correlation are between acenaphthylene and 2-methyl naphthalene (r=0.9998); acenapthene and naphthalene (0.6837); phenanthrene and acenapthene(r=0.7669); fuoranthrene and Fluorene (r=0.7774); pyrene and Fluorene (r=0.6628), anthracene (r=0.8706); Benz(a)anthracene and anthracene (r=0.9873); chrysene and Fluorene (r=0.8565), anthracene (r=0.7581), fluoranthrene (r=0.8431); Benzo(b) fluoranthrene and acenapthalene (r=0.9981), phenanthrene (r=0.9936), fluoranthrene (r=0.9993); Benzo(a)fluoranthrene and naphthalene (r=0.8421), 2-methyl naphthalene(r=0.5195), acenahpthylene (r= -0.8031), fluorene(r= -0.6746); benzo(k)fluoranthrene and fluorene(r=0.9895), fluoranthrene(r=0.8373); benzo(a)pyrene and napthalene(r=0.7105), acenahpthylene(r=0.6625), phenanthrene(r=0.6887); indeno(1,2,3-cd)pyrene and acenahpthene(r=0.7316); dibenz(a,h)anthracene and naphthalene(r= -0.7661), 2-metyl naphthalene (r= -0.7087), acenapthylene(r= -0.7571); benz(a)anthracene and pyrene(r=0.9097); chrysene and pyrene (r=0.8332), benz(a)anthracene(r= 0.8496); benzo(b)fluoranthrene and pyrene(r= -0.8796), benz(a)anthracene(r=-0.6397), chrysene(r= -0.6322); benzo(k)fluoranthrene and chrysene(r=0.8368); dibenz(a,h)anthracene and benzo(b)fluoranthrene(r= -0.8214).

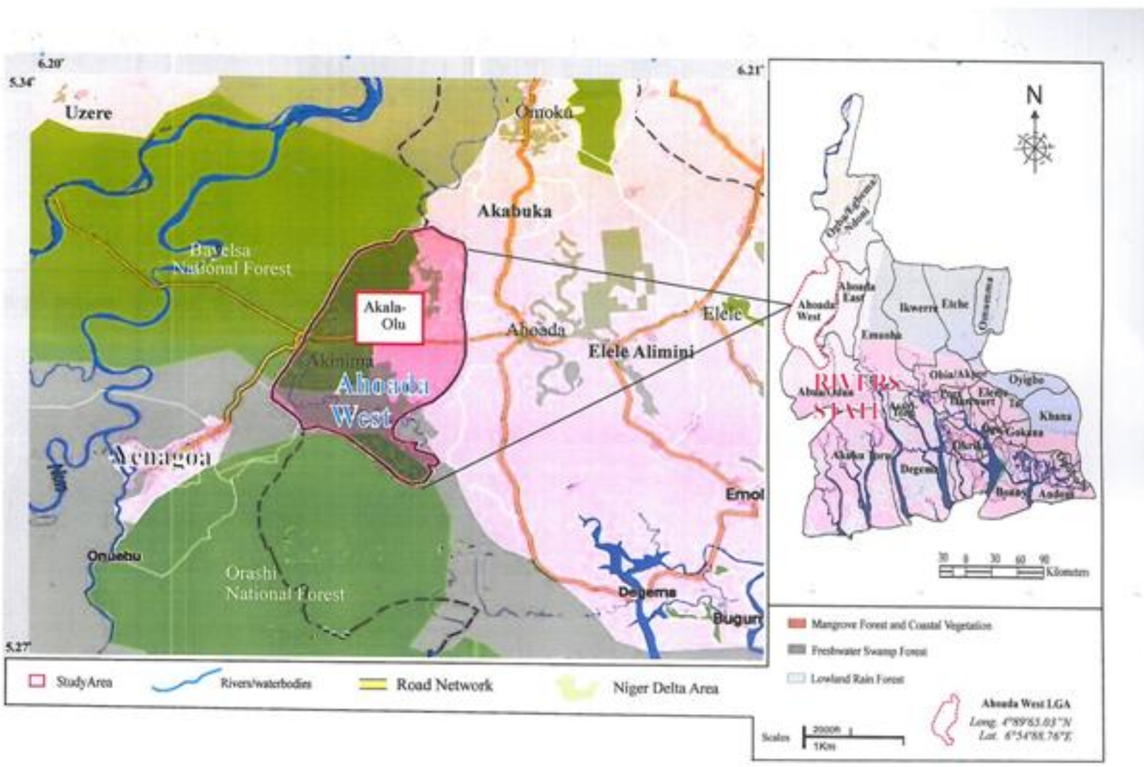

Figure 1: Map of Rivers State showing the Study Area

Table 2: Levels of Physicochemical Parameters and Heavy Metals in Top Soil at the Study Area

Parameters	Depth (cm)	Station 1	Station 2	Station 3	Station 4	Station 5
TOC (%)	0-15cm	0.859	0.633	1.05	0.953	0.891
TON (%)	0-15cm	0.074	0.053	0.099	0.977	0.086
OM (%)	15-30cm	2.14	2.35	2.25	2.30	2.88
pH	0-15cm	6.53	6.20	6.23	6.72	6.78
ECond(µS/cm)	0-15cm	343	301.50	407.5	274	463
P (mg/kg)	0-15cm	0.210	0.15	0.325	0.450	0.465
Mg (mg/kg)	0-15cm	74.885	52.705	75.53	72.286	51.53
K (mg/kg)	0-15cm	62.896	41.11	66.71	69.83	69.150

Na (mg/kg)	0-15cm	64.96	44.09	74.70	64.165	64.850
Ca (mg/kg)	0-15cm	205.253	199.67	245.03	225.285	216.885
Cd (mg/kg)	0-15cm	0.065	0.055	0.065	0.065	0.105
Pb (mg/kg)	0-15cm	4.626	4.065	5.850	4.920	5.200
Al (mg/kg)	0-15cm	1.21	1.460	0.999	2.085	1.540
Co (mg/kg)	0-15cm	0.001	0.001	0.001	0.001	0.001
Cr (mg/kg)	0-15cm	2.295	1.978	3.367	2.615	3.200
Zn (mg/kg)	0-15cm	47.400	42.984	50.731	49.820	42.065
Cu (mg/kg)	0-15cm	1.586	1.474	2.663	1.845	1.840
Fe (mg/kg)	0-15cm	5648.500	4861.000	6502.50	5811.650	4484.000
Mn (mg/kg)	0-15cm	31.55	29.876	33.150	33.995	32.482

Table 3: Mean levels (ppm) of Polycyclic Aromatic Hydrocarbons in Top Soil at the Study Area

PAH	Depth (cm)	Station 1	Station 2	Station 3	Station 4	Station 5	USEPA
Naphthalene	0-15cm	5.681×10^{-4} $\pm4.950\times10^{-7}$	4.798×10^{-4} $\pm4.879\times10^{-6}$	5.562×10^{-5} $\pm1.626\times10^{-6}$	6.227×10^{-3} $\pm7.785\times10^{-4}$	4.640×10^{-3} $\pm1.591\times10^{-4}$	4.0×10^{-2} z
2-methyl Naphthalene	0-15cm	5.196×10^{-4} $\pm1.068\times10^{-5}$	4.942×10^{-5} $\pm3.253\times10^{-6}$	5.126×10^{-5} $\pm7.071\times10^{-8}$	6.194×10^{-4} $\pm3.111\times10^{-6}$	5.176×10^{-3} $\pm7.778\times10^{-5}$	4.0×10^{-2} z
Acenaphthylene	0-15cm	3.752×10^{-4} $\pm7.071\times10^{-8}$	3.732×10^{-4} $\pm7.566\times10^{-6}$	3.672×10^{-5} $\pm1.124\times10^{-6}$	3.653×10^{-3} $\pm2.418\times10^{-4}$	3.633×10^{-3} $\pm8.697\times10^{-5}$	2.0×10^{-1} y
Acenaphthene	0-15cm	4.509×10^{-3} $\pm7.071\times10^{-7}$	2.615×10^{-3} $\pm1.499\times10^{-4}$	4.489×10^{-4} $\pm2.828\times10^{-6}$	5.566×10^{-3} $\pm2.100\times10^{-4}$	3.616×10^{-3} $\pm2.348\times10^{-4}$	2.0×10^{-1} y
Fluorene	0-15cm	1.349×10^{-2} $\pm7.071\times10^{-6}$	2.910×10^{-3} $\pm5.374\times10^{-5}$	1.316×10^{-3} $\pm4.596\times10^{-5}$	1.692×10^{-4} $\pm2.864\times10^{-5}$	1.452×10^{-4} $\pm1909\times10^{-6}$	2.0×10^{-1} y
Phenanthrene	0-15cm	1.743×10^{-2} $\pm7.071\times10^{-4}$	1.630×10^{-3} $\pm4.709\times10^{-4}$	1.718×10^{-3} $\pm1.061\times10^{-4}$	1.916×10^{-2} $\pm3.182\times10^{-4}$	1.630×10^{-4} $\pm1.435\times10^{-5}$	2.0×10^{-1}y
Anthracene	0-15cm	3.016×10^{-2} $\pm7.071\times10^{-6}$	3.726×10^{-2} $\pm1.485\times10^{-3}$	3.089×10^{-3} $\pm1.039\times10^{-4}$	4.370×10^{-3} $\pm2.991\times10^{-4}$	3.320×10^{-2} $\pm2.404\times10^{-3}$	2.0×10^{-1} y
Fluoranthene	0-15cm	3.651×10^{-2} $\pm7.071\times10^{-6}$	3.640×10^{-4} $\pm2.065\times10^{-5}$	3.710×10^{-3} $\pm8.415\times10^{-5}$	4.663×10^{-3} $\pm3.818\times10^{-4}$	2.024×10^{-2} $\pm2.173\times10^{-2}$	2.0×10^{-1} y
Pyrene	0-15cm	1.611×10^{-2} $\pm1.414\times10^{-5}$	1.708×10^{-2} $\pm6.223\times10^{-3}$	1.565×10^{-3} $\pm6.364\times10^{-5}$	6.323×10^{-4} $\pm2.128\times10^{-5}$	7.232×10^{-3} $\pm6.178\times10^{-3}$	2.0×10^{-1} y
Benz(a)anthracene	0-15cm	4.923×10^{-2} $\pm7.071\times10^{-6}$	5.025×10^{-2} ±5.176	4.608×10^{-3} $\pm4.448\times10^{-4}$	4.394×10^{-3} $\pm1.407\times10^{-4}$	4.461×10^{-2} $\pm3.281\times10^{-3}$	$1.0\text{x}10^{-4}$ x
Chrysene	0-15cm	7.380×10^{-3} $\pm8.542\times10^{-3}$	3.333×10^{-3} ±2.558	1.403×10^{-4} $\pm8.910\times10^{-6}$	2.497×10^{-4} $\pm8.542\times10^{-5}$	3.494×10^{-3} $\pm4.999\times10^{-4}$	$2.0\text{x}10^{-4}$ x
Benzo(b)fluoranthene	0-15cm	6.123×10^{-5} $\pm2.121\times10^{-8}$	4.004×10^{-5} $\pm8.160\times10^{-6}$	1.733×10^{-4} $\pm2.015\times10^{-5}$	2.765×10^{-4} $\pm1.146\times10^{-5}$	2.412×10^{-4} $\pm6.210\times10^{-5}$	$2.0\text{x}10^{-4}$ x
Benzo(k)fluoranthene	0-15cm	1.592×10^{-4} $\pm1.414\times10^{-7}$	6.273×10^{-5} $\pm8.697\times10^{-7}$	6.310×10^{-5} $\pm2.666\times10^{-6}$	5.608×10^{-5} $\pm1.916\times10^{-6}$	5.669×10^{-5} $\pm6.265\times10^{-6}$	$2.0\text{x}10^{-4}$ x
Benzo(a)pyrene	0-15cm	1.628×10^{-3} $\pm7.071\times10^{-7}$	2.434×10^{-3} $\pm1.063\times10^{-3}$	1.653×10^{-4} $\pm3.536\times10^{-6}$	1.853×10^{-2} $\pm1.485\times10^{-4}$	1.592×10^{-4} $\pm4.320\times10^{-5}$	$2.0\text{x}10^{-4}$ x
Indeno(1,2,3-Cd) pyrene	0-15cm	2.334×10^{-2} $\pm7.071\times10^{-6}$	3.677×10^{-2} $\pm6.435\times10^{-3}$	2.371×10^{-3} $\pm8.485\times10^{-5}$	3.665×10^{-2} $\pm1.471\times10^{-3}$	2.324×10^{-2} $\pm1.485\times10^{-4}$	$4.0\text{x}10^{-4}$ x
Dibenz(a,h) anthracene	0-15cm	3.797×10^{-2} $\pm1.414\times10^{-5}$	7.083×10^{-2} $\pm4.434\times10^{-3}$	3.873×10^{-2} $\pm3.677\times10^{-4}$	2.420×10^{-2} $\pm3.182\times10^{-4}$	3.836×10^{-3} $\pm1.966\times10^{-4}$	$3.0\text{x}10^{-4}$ x

x = 2013, y = 2014, z = 1996

Table 4: Correlation Matrix of Physicochemical Parameters and Heavy Metals in Soils

Parameters	TOC	TON	OM	pH	Conductivity	P	Mg	K	Na	Ca	Cd
TOC	1										
TON	0.313438	1									

OM	-0.05574	-0.15649	1								
pH	0.272802	0.479418	0.511612	1							
Conductivity	0.369728	-0.57798	0.651678	0.164927	1						
P	0.64675	0.543152	0.574364	0.757316	0.363538	1					
Mg	0.664195	0.335831	-0.76253	-0.0786	-0.2543923	0.007118	1				
K	0.890804	0.40346	0.199601	0.67379	0.4036346	0.823119	0.473953	1			
Na	0.968843	0.120576	-0.04515	0.270134	0.4943651	0.552331	0.658338	0.884897	1		
Ca	0.894752	0.251042	-0.05108	-0.05381	0.3313317	0.540501	0.517062	0.640034	0.804266	1	
Cd	0.248162	-0.15374	0.898698	0.685175	0.7907702	0.684642	-0.45018	0.532831	0.316486	0.090217	1
Pb	0.922474	0.031238	0.150592	0.097799	0.6242703	0.598072	0.420699	0.756168	0.908985	0.930735	0.374769
Co	-0.10498	0.841082	0.232878	0.626663	-0.4979448	0.512477	-0.19252	0.15635	-0.27279	-0.16376	0.101249
Cr	0.821512	-0.03233	0.426252	0.221209	0.765498	0.701312	0.158723	0.737584	0.813657	0.836203	0.598704
Zn	0.725535	0.479632	-0.69523	-0.13812	-0.2877854	0.139715	0.942627	0.471138	0.645598	0.697594	-0.47421
Cu	0.821024	-0.00728	-0.06765	-0.24178	0.4500012	0.362787	0.467546	0.50971	0.774205	0.963756	0.066436
Fe	0.679322	0.266556	-0.73716	-0.34276	-0.1996043	-0.02114	0.921711	0.34966	0.627993	0.705474	-0.53083
Mn	0.901592	0.662006	0.054507	0.518353	0.1365665	0.837968	0.536699	0.904817	0.795252	0.787498	0.277042

	Pb	Co	Cr	Zn	Cu	Fe	Mn
Pb	1						
Co	-0.30596	1					
Cr	0.958278	-0.22726	1				
Zn	0.520866	-0.0706	0.270311	1			
Cu	0.931236	-0.40939	0.836598	0.620069	1		
Fe	0.543411	-0.29444	0.283354	0.969661	0.6921717	1	
Mn	0.747442	0.334782	0.687459	0.655614	0.6118883	0.516568	1

Table 5: Correlation Matrix of PAHs in Soils at the Study Area

PAH	Naphthalene	2-methyl Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene
Naphthalene	1							
2-methyl Naphthalene	0.53798951	1						
Acenaphthylene	0.524147025	0.99981556	1					
Acenaphthene	0.68366753	0.149398928	0.143695246	1				
Fluorene	-0.504753939	-0.389140312	-0.378087124	0.228488802	1			
Phenanthrene	0.325877733	-0.401514915	-0.409078388	0.766935851	0.4743499	1		
Anthracene	-0.225559481	0.33427374	0.35016665	0.131696391	0.3625634	-0.298596192	1	
Fluoranthene	-0.073821283	0.234119663	0.242053452	0.395740375	0.7774165	0.368714202	0.401790095	1
Pyrene	-0.532382502	-0.158964024	-0.141841348	0.07974273	0.6627506	-0.058535724	0.870632942	0.40440616
Benz(a)anthracene	-0.293863171	0.264511678	0.281159582	0.150735639	0.5029434	-0.208963826	0.987335619	0.517080432
Chrysene	-0.337777059	0.053725138	0.068399295	0.308722308	0.8564663	0.201965171	0.758065025	0.843127577
Benzo(b)fluoranthene	0.842093751	0.519498379	0.503133739	0.260648414	-0.6745939	0.103979188	-0.578896589	-0.2051103
Benzo(k)fluoranthene	-0.426480706	-0.325864604	-0.316352084	0.270220851	0.989509	0.522476708	0.292132306	0.837285991
Benzo(a)pyrene	0.710522566	-0.209276165	-0.224959555	0.662540716	-0.2833282	0.688690524	-0.517466206	-0.313718903
Indeno(1,2,3-Cd) pyrene	0.464456582	0.004513911	0.003361976	0.731606912	-0.0212076	0.368801686	0.395781143	-0.102132324
Dibenz(a,h) anthracene	-0.708663813	-0.766093868	-0.757068997	-0.33338736	0.2854596	-0.090553383	0.220054674	-0.344467021

	Pyrene	Benz(a) anthracene	Chrysene	Benzo(b) fluoranthene	Benzo(k) fluoranthene	Benzo(a) pyrene	Indeno(1,2,3-Cd) pyrene	Dibenz(a,h) anthracene
Pyrene	1							
Benz(a)anthracene	0.90967767	1						
Chrysene	0.832225659	0.849590071	1					

Benzo(b)fluoranthene	-0.879608528	-0.639673841	-0.632150016	1				
Benzo(k)fluoranthene	0.567151831	0.438854125	0.836816654	-0.566073108	1			
Benzo(a)pyrene	-0.466917058	-0.54488871	-0.445540079	0.530003066	-0.2514247	1		
Indeno(1,2,3-Cd) pyrene	0.35559552	0.340666124	0.169135639	-0.057108626	-0.0761185	0.565373859	1	
Dibenz(a,h) anthracene	0.577513804	0.230379709	0.12478446	-0.821389003	0.154389	-0.155827334	0.188285986	1

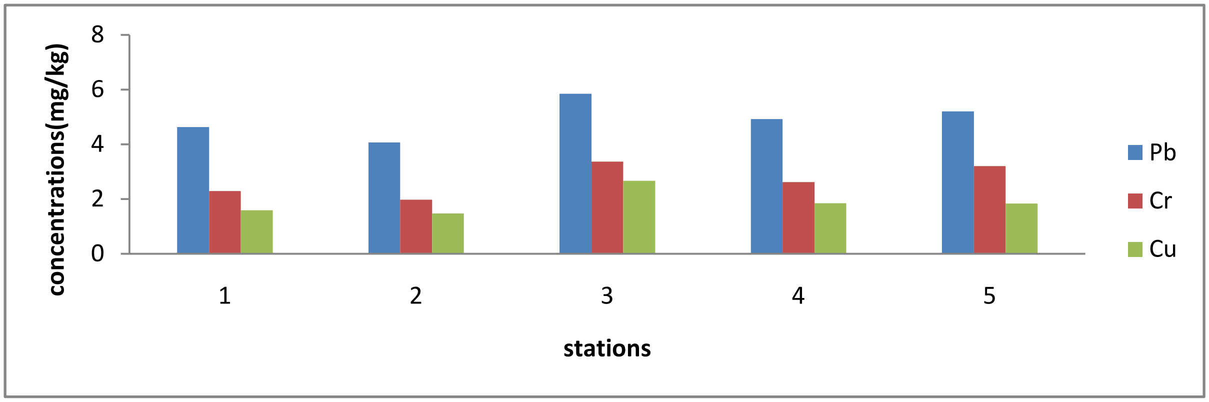

Figure 2: Variations in levels of Lead, Chromium and Copper in soil (depth 0-15)

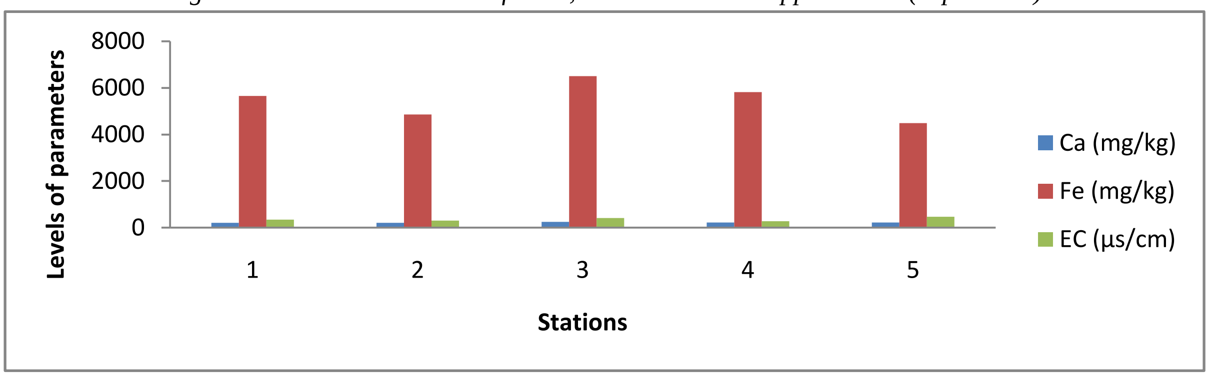

Figure 3: Variations in levels of Calcium, Iron and Electrical conductivity in soil (depth 0-15)

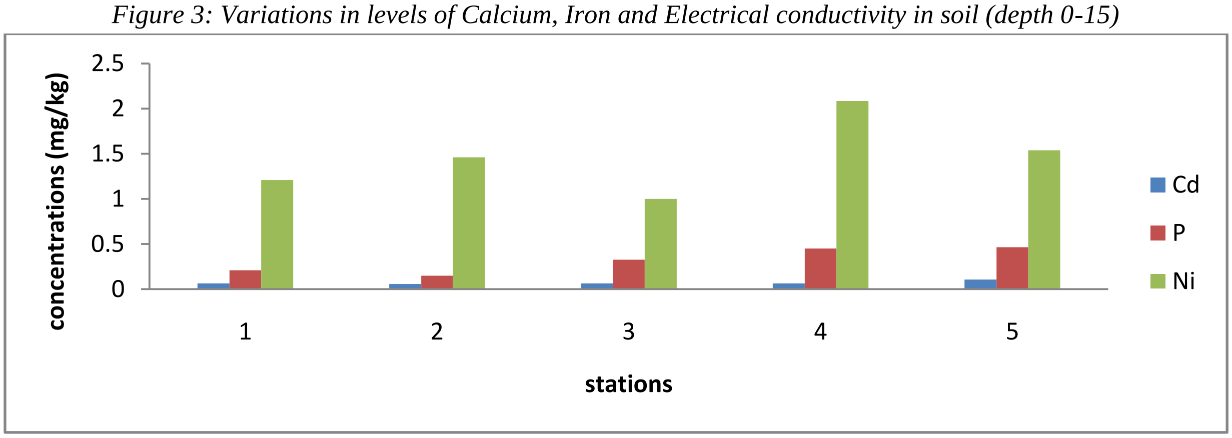

Figure 4: Variations in levels of Cadmium, Phosphate and Nickel in soil (depth 0-15)

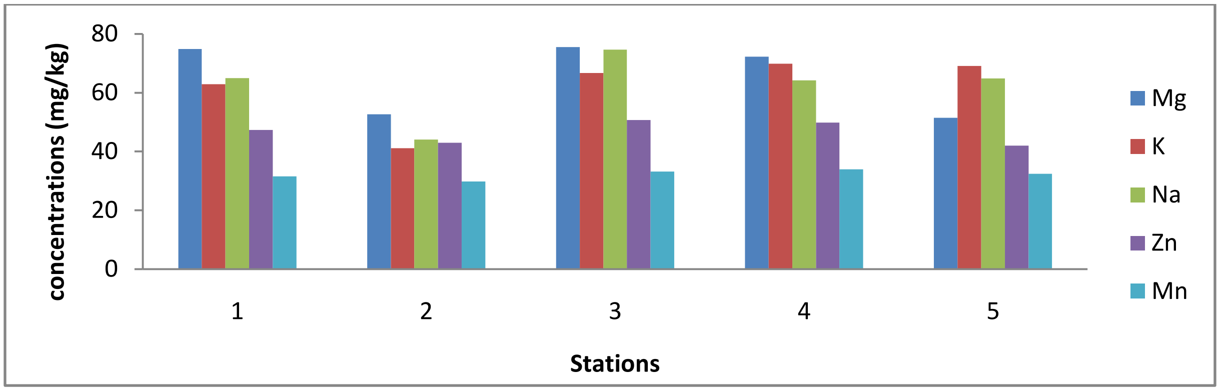

Figure 5: Variations in levels of Magnesium, Potassium, Sodium, Zinc and manganese in soil (depth 0-15)

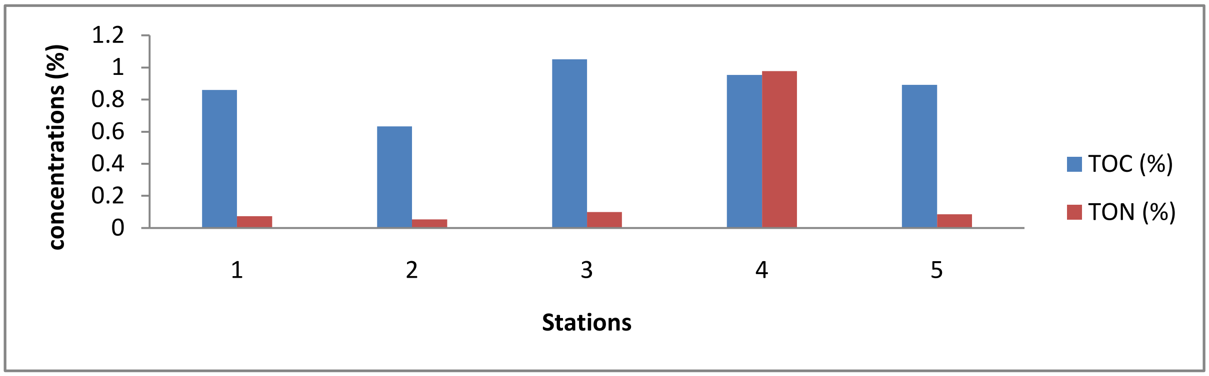

Figure 6: Variations in levels of TOC and TON in soil (depth 0-15)

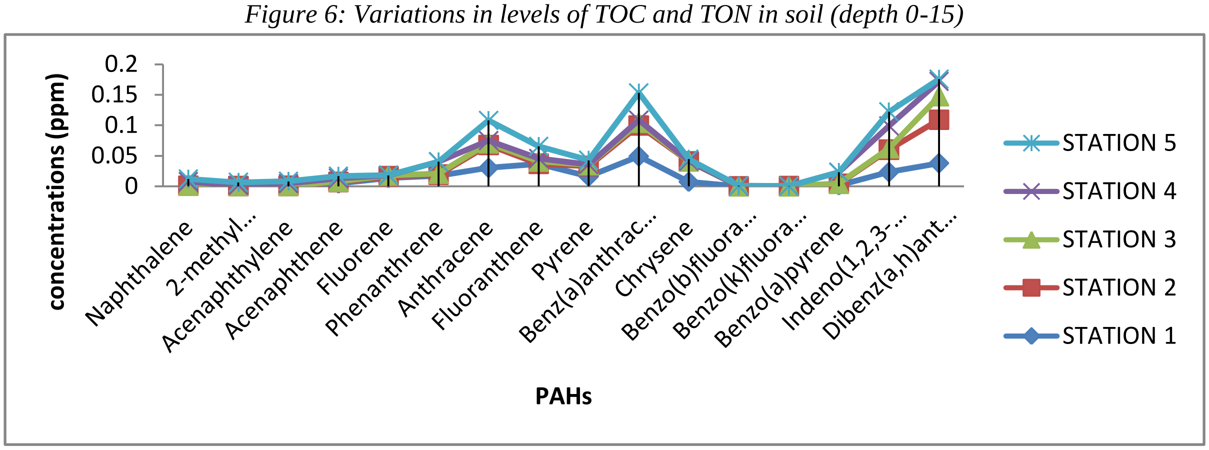

Figure 7: Variations in levels of polycyclic aromatic hydrocarbons in soil (depth 0-15)

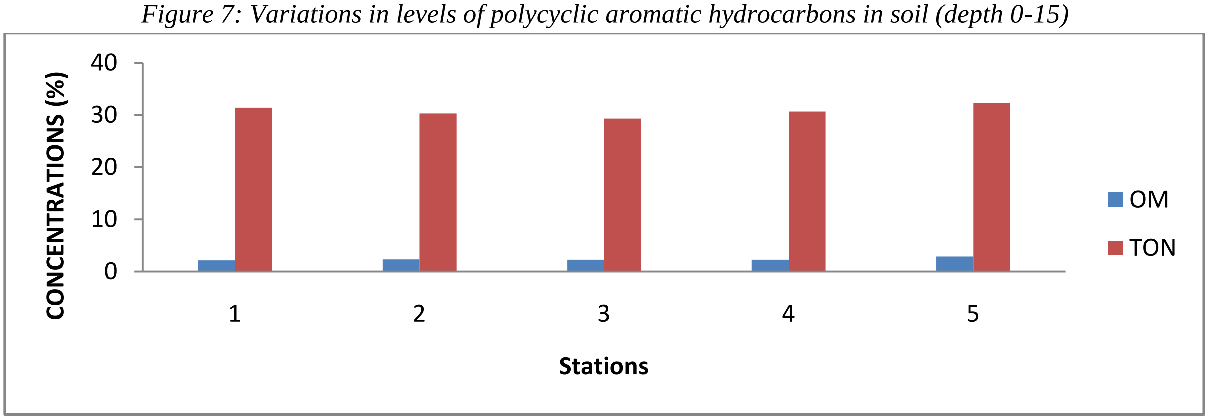

Figure 8: Variations in levels of OM and TON in soil (depth 15-30)

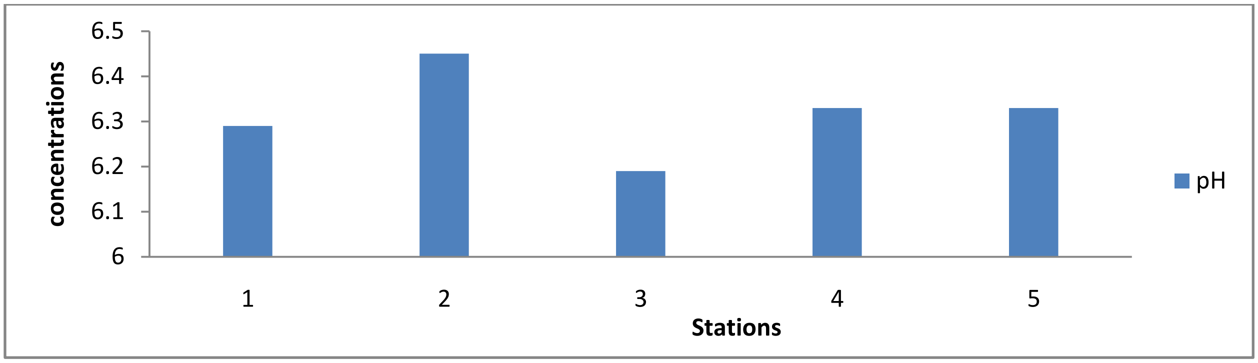

Figure 9: Variations in levels of pH in soil (depth 15-30)

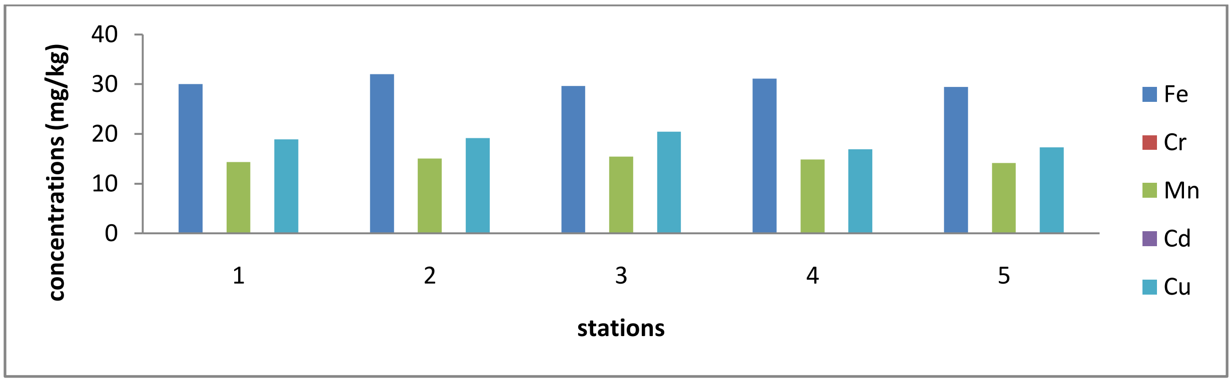

Figure 10: Variations in levels of Iron, Chromium, Manganese, Cadmium and Copper in soil (depth 15-30)

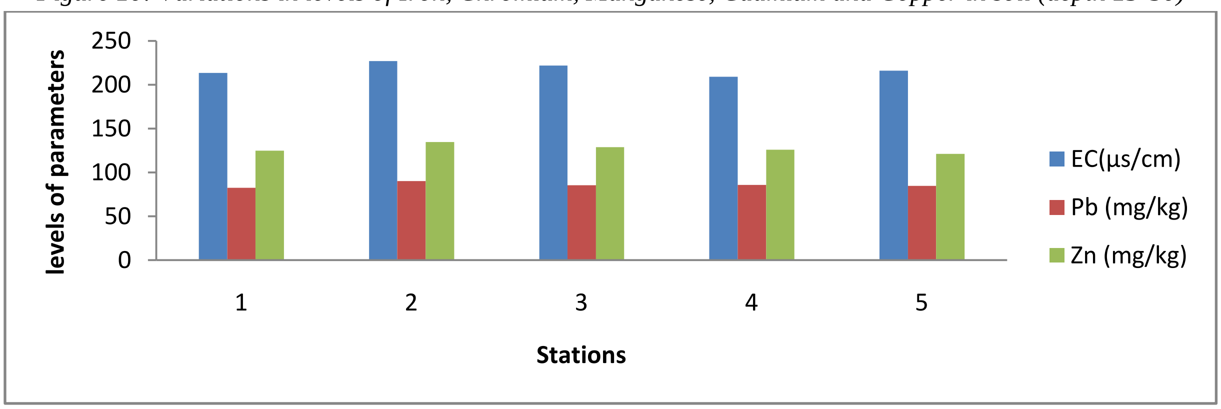

Figure 11: Variations in levels of Electrical conductivity, Lead and Zinc in soil (depth 15-30)

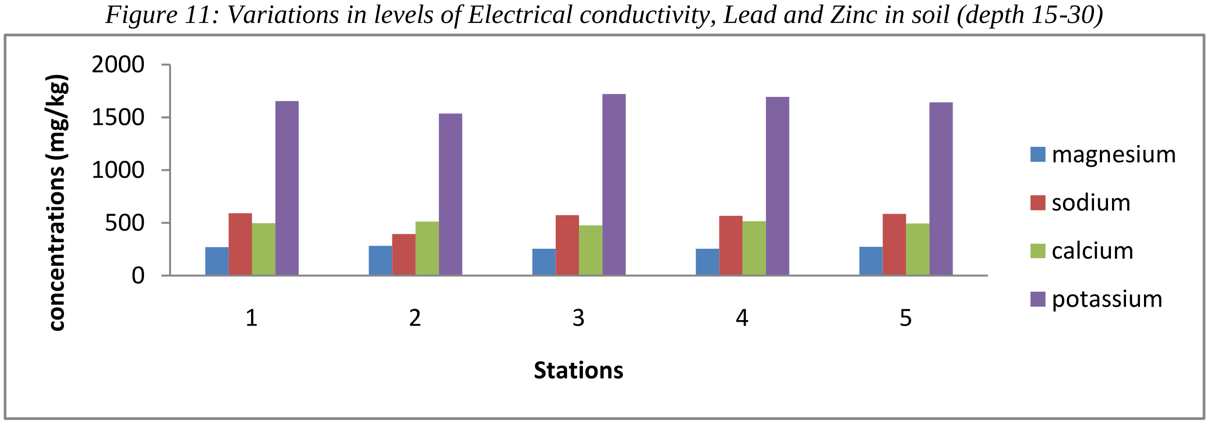

Figure 12: Variations in levels of Magnesium, Sodium, Calcium and potassium in soil (depth 15-30)

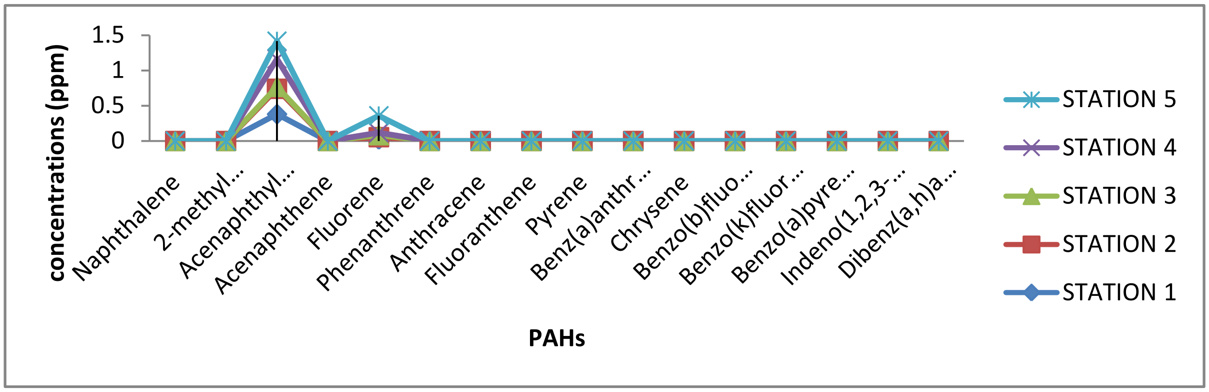

Figure 13: Variations in levels of polycyclic aromatic hydrocarbons in soil (depth 15-30)

Conclusion

The findings from this study have shown that the soils of the area are acidic and nutrient-deficient as most of the values were below permissible limits. The observed soil pH can influence nutrient absorption and plant growth through its influence on nutrient availability and the presence of toxic ions.

The soils need application of land amendment materials such as organic wastes (from plants and animals) and town refuse ash as the soil physico-chemical properties show that all the soils of the area are acidic and deficient in Organic Matter, Total Nitrogen, Available Phosphorus and Exchangeable Bases.

The concentrations heavy metals especially the high Fe, Al, and Mn values obtained show that the acidic condition of the soils increased the solubility and availability of these metals. This situation encourages leaching of nutrient elements.

The concentrations of most toxic and carcinogenic PAHs such as Benzo(a)anthracene, Indeno(1,2,3-c,d)pyrene, Dibenz(a,h)anthracene and Chrysene exceeded their permissible limits and therefore pose grave environmental and health concerns in the areas; and are attributed to the oil exploitation activities in the area.

There should be awareness campaign and the water in the area should be monitored regularly.

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