Research Article

Pollution (Poly Aromatic Hydrocarbons and Heavy Metals) Evaluation in Soil of Selected Area of Kaduna Towns in Kaduna State

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Abstract

The Polycyclic aromatic hydrocarbons (PAHs) and some heavy metals were analysis in the soil samples from urban areas of Kaduna state for their concentration and distribution. Naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a) pyrene, indeno(1,2,3-cd)perylene, benzo(ghi) perylene and dibenzo(a,h) anthracene were analyzed in three urban soils of Kaduna North, Alegbi and Kaduna South, at 0-15 cm and 16-30 cm depth in wet and dry seasons. After extraction using ultrasonication with hexane and dichloromethane and clean-up, PAHs concentration was measured using gas chromatography. The concentration of all the PAHs obtained ranged between 178.00 mg/g and 787.0 0 mg/g for wet season and 105.10 mg/g and 437.70 mg/g for dry season. The concentrations of PAHs were higher in the subsoil (15-30 cm depth) in the wet season than in the dry season while higher concentrations of all the PAHs were observed in topsoil than subsoil during the dry season. The concentration of PAHs followed the order Kaduna North > Kaduna South > Algabi during the wet season and Kaduna South > Algabi > Kaduna Nort during the dry season. The concentration values of all determined PAHs were below the target value of 1000 mg/g stipulated by Department of Petroleum Resources. The Cd, Cr, Cu and Pb levels in the soil from the study sites were higher than the corresponding control values. The degree of pollution of various metals using the graded standard of Nemero pollution index varied. The concentrations of the metals were found to be above the recommended limits given by USEPA/WHO. This could pose risks and hazards to human and the ecosystem through direct ingestion of contaminated soil.

Keywords: Poly aromatic hydrocarbons, Heavy metals, Pollution, Evaluation, Soil, Kaduna towns.

Introduction

Poly aromatic hydrocarbons (PAHs) are organic pollutants that are widely distributed in the environment, are toxic, and very persistent. Different types of PAHs are formed based on combustion temperature, where high temperatures form simple PAHs; low temperatures create more complex PAHs. PAHs are released into the environment through natural sources such as volcanoes and forest fires, but the most predominant sources which are also responsible for most atmospheric pollution are the anthropogenic sources. The combustion of fossil fuels, including motor vehicle emission and power generation, wood burning, municipal and industrial waste incineration, and a host of others were typical examples of anthropogenic sources. PAHs are included in the "priority pollutants" listing of the US Environmental Protecting Agency (US EPA). Although PAHs are found everywhere, they are more concentrated in places such as auto-mechanic workshops sites, gas works, coal gasification sites and sites of oil spills. Even though they are biodegradable, their sequestration and recalcitrance, complicates the process of biodegradability and availability to chemical attack. PAHs are also hydrophobic in nature with very low water solubility and high octanol-water partition coefficient, making them to adsorb strongly to organic matter in soil and less susceptible to biological and chemical degradation.

Many PAH compounds enter water, sediment, soil and biological resources through the atmosphere. The presence of PAHs in soils is an issue of concern because some of them are known to have carcinogenic, mutagenic and teratogenic effects.

A lot of research has been carried out on PAHs in soil and the results obtained show that soil contamination by PAHs is considered to be a good indicator of the level of environmental pollution by human activities. Similarly, it can provide information on regional pollution sources, the long-range transport of PAHs, the rate of pollutant retention and their ultimate destination.

Heavy metals are widespread in soil as a result of geo-climatic conditions and environmental pollution through industrial activity, automobile exhaust, heavy-duty electric power generators, municipal wastes, refuse burning and pesticides used in agriculture. Therefore, their assimilation and accumulation in plants is obvious. Together with other pollutants, heavy metals are discharged into the environment. Human beings, animals and plants take up these metals from the environment through air and water. Heavy metals have

the tendency to accumulate in both plants and human organs. The accumulation of heavy metals can have middle-term and long term health risks, and strict periodical surveillance of these contaminants is therefore advisable.

This work is aimed at determining PAHs and heavy metals pollution profiles in soils samples in the selected areas of Kaduna towns in Kaduna state to study the variation in their concentrations along the and soil and soil profile.

Study Area
Kaduna State, north central Nigeria, is politically classified as belonging to the now 'North - West' zone of the current six (6) Geo - political zones of Nigeria. It is populated by about 59 to 63 different ethnic groups if not more with the exactitude of the number requiring further verification through a genuine field work. The Hausa and Fulani are the dominant ethnic groups followed by at least 60 others. It was from the old Northern Region that in the year 1967 gave birth to six states in the north, leaving Kaduna as the capital of North-Central State, whose name was changed to Kaduna State in 1976. Most of the industries in Kaduna state are sited in Kaduna south. Kaduna south industrial areas are bounded by residential areas of Kakuri, Makera, and Nassarawa. Another important neighbouring is Unguwar Television. These areas provide residential accommodation for about 80% of the low income industrial workers. The industrial area in Kaduna south is about seven kilometres from the city centre but all the industrial effluent is discharged into the river Kaduna and river Kaduna tributaries within Kaduna Metropolis. Kudenda industrial area is located at the edge of the city but lies close to some residential areas of Nassarawa, Unguwar Muazu and Tudun Wada which are located at the opposite the industrial area, the two industrial area in Kaduna are located close to each other and they discharging the waste and effluent into environment. However the study area comprises of the three urban areas (Kaduna south, Kaduna north and Algabi) of Kaduna in Kaduna state.

Collection of Samples
After reconnaissance survey, soil samples were collected from eighteen sites i.e. six sites from each of the three areas at depth 0-15 cm and 16-30 cm representing top and sub soils respectively between the months of July and October (wet season) and November and March (dry season) 2016. Soil samples were collected with an auger stainless steel after removal of the uppermost (debris) soil layer. Preservation of samples was carried out in stainless-steel holders and immediately transferred to the laboratory. Prior to analysis, samples were air dried in the dark, twigs and stones removed and sieved over stainless steel sieves (< 2 mm). Samples were stored in sealed stainless steel containers at 4oC.

PAHs Extraction and Clean-up
The US EPA-3550C-Ultrasonic extraction method, was used for the preparation of soil samples for analysis, thus 10 g of the soil samples was mixed with same quantity of Na_2SO_4 [1]. The resulting mixture was extracted by ultra sonication with 50 mL of hexane/ dichloromethane (1:1 v/v) at 30°C for 30 min and filtered. The extract was evaporated to 1 mL using a rotary evaporator and subsequently purified by solid phase extraction with silica gel and alumina. PAHs were thereafter eluted using 15 mL hexane and dichloromethane (9:1). The eluted fraction was evaporated to 0.5 mL using nitrogen gas.

PAHs Determination Using Gas Chromatographic
Gas chromatograph (HP 6890 Palo Alto, C A, USA) with a flame ionization detector (FID) was used to quantify each PAH in the extracts as described by Tesi et al., and Iwegbue et al. [2,3]. Separation was carried out using HP5 (cross-linked PHME siloxane) column with dimensions of 0.25 µm × 30 m and 0.25 µm film thickness. Helium was used as a carrier gas with a linear velocity of 30 cm/s. The initial column temperature was 100°C and it was subsequently increased at 4°C/ min to 310°C as final temperature. The injector temperature and injection volume was 250°C and 2.0 µL in the split-less mode respectively. The quantification was carried out by the use of external calibrations which was obtained with PAH solutions at five concentration levels.

One gram (1.0 g) of each of the sieved soil samples were weighed into separate digestion flasks, 10cm³ of $HNO_3 – HClO_4$ acid mixture (3:1 by volume) was added and the content mixed. The flask was placed on the hot plates inside fume cupboard. The samples were digested until a clear solution was obtained (white fuming stage). Distilled water was added periodically to avoid drying up of the digest. The flask was then removed from the hot plate and 30 cm³ of distilled water was added within a few minutes. The content was filtered through a Whatman NO. 41 filter paper into a 50 cm3 volumetric flask and then made up to the mark with distilled water.

Cadmium, chromium, copper, lead and nickel were analysed in the soil samples using atomic absorption spectrometer (Model D100XB4J), with the analyses being done in triplicate.

Quality Control and Assurance
Reagents are of chromatographic grade. Equipments and apparatus were properly cleaned to check cross-contamination of samples during sampling, preservation and preparation. Four unit-samples were added to form a unit. To evaluate the PAHs extraction efficiency, a known concentration of a standard PAH mixture was added to already analyzed sample and re-analyzed. Recoveries for the PAH compounds were between 85.5 and 95.5%. The relative standard deviations for replicate analyses (6) were less than 5%.

Approach to Data Analysis
The statistical evaluations were performed using SPSS 19 version. Relationship between PAHs was established by means of Pearson correlation coefficient. Student's t-test was used to determine the significant variation between the concentrations and profiles of PAHs in depth and between seasons, with p-value less than 0.05 ($p<0.05$) considered to be statistically significant. One-way Analysis of variance (ANOVA) was applied to evaluate the significant variability of PAHs among various sites.

Results and Discussion
PAHs Concentrations and Distribution
The concentrations of the PAHs analyzed in this study areas during wet and dry seasons are presented in Table 1, the concentrations varied significantly ($p<0.05$) among the different sites. Also, there was significant variation ($p<0.05$) in the concentrations between the dry and wet season as well as between the top and sub soil. The concentration of all the PAHs obtained ranged between 178.00 mg/g and 787.0 0 mg/g for wet season and 105.10 mg/g and 437.70 mg/g for dry season. The concentrations of PAHs were higher in the subsoil (15-30 cm depth) in the wet season than in the dry season while higher concentrations of all the PAHs were observed in topsoil than

subsoil during the dry season. The relatively high concentrations of PAHs recorded in the subsoil in wet season could be attributed to leaching [4]. The concentration of PAHs followed the order Kaduna North > Kaduna South > Algabi during the wet season and Kaduna South >Algabi> Kaduna North during the dry season. The concentration values of all determined PAHs were below the target value of 1000 mg/g stipulated by Department of Petroleum Resources [5]. Comparative concentrations evaluation of all determined PAHs obtained in this study were in agreement with others in literatures [6-9] Table 2.

Table 1: PAHs Concentrations (µg/kg) in the study Soil Samples (wet and dry season)

PAH	WET SEASON						DRY SEASON					
	AGBOR		ISSELE-UKU		ASABA		AGBOR		ISSELE-UKU		ASABA	
	0-15 cm	16-30 cm	0-15 cm	16-30 cm	0-15 cm	16-30 cm	0-15 cm	16-30 cm	0-15 cm	16-30 cm	0-15 cm	16-30 cm
Nap	BDL	BDL	30.5	57.0	BDL	59.0	BDL	BDL	BDL	BDL	BDL	16.1
Acy	BDL	29.0	30.0	20.0	29.0	BDL	BDL	BDL	BDL	14.2	BDL	32.0
Ace	BDL	33.0	54.0	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	39.0
Flu	BDL	26.0	15.5	BDL	BDL	BDL	BDL	BDL	BDL	47.0	44.0	4.0
Phe	BDL	BDL	35.0	BDL	84.0	BDL	BDL	BDL	15.0	15.7	16.0	34.0
Ant	BDL	BDL	17.0	BDL	BDL	BDL	BDL	BDL	40.0	47.0	23.0	37.0
Flt	BDL	31.3	24.0	40.0	43.0	43.0	176.0	BDL	49.0	36.0	18.0	BDL
Pyr	59.0	58.7	22.0	16.0	83.0	67.0	BDL	56.0	57.0	42.0	17.0	5.0
BaA	BDL	99.0	16.1	45.0	34.0	BDL	BDL	BDL	17.0	15.1	17.0	BDL
Chry	BDL	25.0	19.1	114.0	27.0	BDL	BDL	BDL	21.0	24.0	17.0	BDL
BbF	15.0	22.0	13.9	44.0	27.0	316.0	55.0	BDL	21.0	75.0	18.0	BDL
BkF	BDL	BDL	BDL	BDL	198.0	BDL	BDL	BDL	BDL	BDL	BDL	BDL
BaP	104.0	16.0	82.9	15.0	41.0	302.0	134.0	49.1	44.0	29.4	20.0	BDL
IBDLP	BDL	23.0	64.7	18.0	37.0	BDL	BDL	BDL	70.0	19.3	BDL	BDL
DahA	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
BghiP	BDL	20.0	17.0	17.0	BDL	BDL	BDL	BDL	40.0	73.0	24.0	BDL
TOTAL	**178.0**	**383.0**	**441.7**	**386.0**	**603.0**	**787.0**	**365.0**	**105.1**	**374.0**	**437.7**	**214.0**	**167.1**
2 RINGS	0.0	0.0	30.5	57.0	0.0	59.0	0.0	0.0	0.0	0.0	0.0	16.1
3RINGS	0.0	88.0	151.5	20.0	112.0	0.0	0.0	0.0	55.0	123.9	83.0	146.0
4RINGS	59.0	214.0	59.2	215.0	187.0	110.0	176.0	56.0	144.0	117.1	69.0	5.0
5RINGS	119.0	38.0	96.8	59.0	226.0	618.0	189.0	49.1	65.0	104.4	38.0	0.0
6RINGS	0.0	43.0	81.7	35.0	37.0	0.0	0.0	0.0	110.0	92.3	24.0	0.0

Table 2: Comparison of PAH of soil in this study with others in literatures (Adapted in part from Tesi, et. al., 2016)

Location	Studied Soil	Distribution Range (µgkg⁻¹)	Reference
Nigeria	Urban soils	105.1-787	This study
America (Miami florida)	Urban soils	251-2364	Banger e.t al. (2010)
Canada	Flood plain	0.016-12.0	Sartori et. al. (2010)
China (Beijing)	Rural and suburban soils	20-3900	Mai et. al. (2005)
China (Beijing)	Urban soil	467-5470	Li et. al. (2006)
China (Guangzhou)	Vegetable soils	42-3077	Chen et.al. (2005)
China (Hong Kong)	Rural and urban soils	30-170	Zhang et .al. (2006)
China (Huanghuai plain)	Agricultural soils	15.7-1247.6	Yang et. al. (2012)
Estonia	Rural, urban and Industrial soils	50-22,200	Trapido (1999)
Germany (Mosel & Saar River)	Floodplain	100-81500	Pies et. al. (2007)
Germany (Rhine river)	Alluvial soils	20-3600	Gocht et. al. (2001)
India (Kuruksheta)	Urban Roadside soils	16.1- 2538.0	Kumar et. al.(2012)
Korea (An-san city)	Industrial soils	109.93-178.92	Imran et. al. (2006)
Nigeria (Niger Delta)	Soil vicinity oil installation	24-120	Sojinu et. al. (2010)

Nigeria (Niger Delta)	Urban soils	182-433	Olajire et. al. (2005)
Nigeria(Lagos)	Mangrove fresh soil	65.5 188.0	Sojinu et. al.(2012)
Spain (Sevilla)	Agriculture and urban soils	89.5-4004.2	Morello et. al. (2008)
Switzerland	Pasture grassland and urban soils	50-600	Bucheli et. al. (2004)
United kingdom	Urban soil	2700 ± 500	Meharg et .al. (1998)

Ring-Wise PAHs Distribution

The ring-wise concentrations and distribution patterns of PAHs in this study are in the order; 2-ring < 6- ring < 3-ring < 4-ring < 5-ring, Table 3. The concentration of the two ringed PAH compound (Naphthalene) ranged from 0.00 to 59.0 mg/g for wet season and 0.00 to 16.10 mg/g for dry season. Naphthalene was only detected in soil sample from Kaduna North during the dry season. The low concentration of Naphthalene observed in the soil sample may be due to volatilization.

Table 3: BaPTEQ Values for PAHs (µg/kg) in the Study areas

	WET SEASON						DRY SEASON					
											SABA	
	0-15cm	16-30cm	0-15cm	16-30cm	0-15cm	16-30cm	0-15cm	16-30cm	0-15cm	16-30cm	0-15cm	16-30cm
BaA	0.00	9.90	1.61	4.50	3.40	0.00	0.00	0.00	1.70	1.51	1.70	0.00
Chry	0.00	0.03	0.02	0.11	0.03	0.00	0.00	0.00	0.02	0.02	0.02	0.00
BbF	1.50	2.20	1.39	4.40	2.70	31.60	5.50	0.00	2.10	7.50	1.80	0.00
BKF	0.00	0.00	0.00	0.00	1.98	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BaP	104.0	16.00	82.90	15.00	41.00	302.0	134.0	49.10	44.00	29.40	20.00	0.00
IndP	0.00	2.30	6.47	1.80	3.70	0.00	0.00	0.00	7.00	1.93	0.00	0.00
DahA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BaPTEQ	105.5	30.4	92.4	25.8	52.8	333.6	139.5	49.1	54.8	40.4	23.5	0.00

The 3-ringed PAH concentration ranged between 0.00 to 151.50 mg/g and 0.00 to 146 mg/g in wet and dry seasons respectively. The 3-ring PAHs are the dominant PAH compounds at 0-15cm depth in soil samples from Kaduna south during the wet season and 15-30 cm depth at Kaduna North during the dry season. Among the 3-ring PAH compounds, Acenapthylene is the dominant compound in terms of occurrence during the wet season while phenanthrene and anthracene were the dominant 3-ringed PAH compounds during the dry season.

The four ring PAHs are the second dominant PAH compounds in samples from the study areas. The four ring PAH compounds were detected at all locations, depth and seasons. The concentrations of the 4-ringed PAHs ranged between 59.00 –215.00 mg/g in wet season and 5.00 – 176.00 mg/g in dry season. Pyrene is the predominant 4-ring PAH compound in the samples from the study areas. Pyrene was detected in all samples except 0-15 cm depth at Algabi.

The 5-ring PAHs are the most dominant in the samples from the study areas. The concentrations of the 5-ring PAHs ranged from 38.00 – 618.00 mg/g for wet season and 0.00 – 189.0 0 mg/g for dry season. The 5-ring PAH was not detected at 16-30 cm depth in the soil samples from Kaduna north. Benzo(a)pyrene is the most dominant 5-ringed PAH compound in the soil sample analyzed, also Benzo(a)pyrene was detected in all samples except 16-30 cm depth in Kaduna north. However, Dibenzo (a,h)anthracene was not detected in any of the samples.

The concentration of the 6-ring PAHs ranged between 0.00 – 110 mg/g and 0.00 – 81.70 mg/g in dry and wet seasons respectively.

Principal Component Analysis

Yunker et al. Larsen and Baker had used principal component analysis (as a tool to classify probable pollution sources of PAHs and results of PCA in this study are shown in Table 4 [10,11].

Table 4: PCA Factor Components With Varimax with Kaizer Normalization Rotation in Det and Dry Season

	Wet Season		Dry Season		
PAH Compounds	Component		Component		
	Factor 1	Factor 2	Factor 1	Factor 2	Factor 3
Nap	-.328		.922	-.330	
Acy	.898	.390	.937		
Ace	.785	-.305	.922	-.330	
Flu	.745			.783	
Phen		.907	.939		
Ant	.556		.564	.738	

	Col1	Col2	Col3	Col4	Col5
Flt		.427	-.546		-.716
Pyr	-.478	.588	-.354		.821
BaA	.638			.857	.360
Chry	.317			.937	.311
BbF	-.734		-.343	.668	-.577
BkF		.998	-.737		-.551
BaP	-.773				.539
IndP	.798			.428	
BghiP	.832	-.422		.955	
% Variance	37.69	20.34	37.65	35.24	13.92

For wet season, two factors were identified which accounts for 58.03 % of the variability. Factor 1 account for 37.69 % of the total variance is characterized with high loading of Ace, Acy, Flu, IndP and BghiP and moderate loadings of Ant and BaA. Acy, Ace and Flu are combustion products of pyrogenic processes such as wood combustion, IndP and BghiP are indicators of traffic emissions [9,12,13]. Ant is a product of wood and coke combustion, while BaA is a marker for diesel oxidation [10,14]. Thus, factor 1 indicates that combustion of coke, wood, diesel and traffic emissions are the primary sources of PAHs. Factor 2 accounts for 20.34 % of the total variance and is characterized by high components of Phen and BkF and moderate components of Pyr. Then which are by-products of wood combustion, BkF is a marker for coal and gasoline combustion, [15,16]. Pyr is a marker for coal combustion [11]. Therefore, factor 2 suggests that the sources of PAHs are attributed to wood and coal combustion Table 5.

Table 5: The values (µg/kg) of BaPMEQ obtained for PAHs in this study

	WET SEASON						DRY SEASON					
							AGBOR		ISSELE-UKU		ASABA	
	0-15cm	16-30cm	0-15cm	16-30cm	0-15cm	16-30cm	0-15cm	16-30cm	0-15cm	16-30cm	0-15cm	16-30cm
B(a)A	0	8.11	1.32	3.69	2.79	0	0	0	1.39	1.23	1.39	0
Chry	0	0.43	0.33		0.46	0	0	0	0.36	0.41	0.29	0
B(b)F	3.75	5.5	3.48	11	6.75	79	13.85	0	5.25	18.75	4.5	0
B(k)F	0	0	0	0	21.78	0	0	0	0	0	0	0
B(a)P	104	16	82.9	15	41	302	134	49.1	44	29.4	20	0
I(nd)P	0	7.13	20.05	5.58	11.47	0	0	0	21.7	5.98	0	0
D(ah)A	0	0	0	0	0	0	0	0	0	0	0	0
BaPMEQ	107.8	37.2	108.1	35.3	84.3	381.0	147.9	49.1	72.7	55.8	26.2	0.0

Three factors were identified for dry season which accounted for 86.81 % of the variability as Factor 1 is characterized by high values of NaP, Acy, Ace and Phe and moderate loading of Ant which constitute 37.65 % of the total variance. Factor 1 was NaP suggest incomplete combustion of wood related sources [16]. Acy, Ace, and Phen are products of combustion wood, while Ant is a by- product of wood and coke combustion, factor 1 is suggests that wood combustion is the source of PAHs [10,17]. Factor 2 accounted for 35.24 % of the total variance and is characterized by high components of Flu, Ant, BaA, Chry and BghiP with moderate components of BbF, Flu is a product of low temperature pyrogenic processes such as wood combustion, while Ant is a product of coke and wood oxidation, [9,10]. BaA is a marker for diesel oxidation while Chry is a marker for diesel and natural gas oxidation; BghiP is from traffic emissions, while BbF is a product of fossil fuel combustions [9,13,14,18]. Thus, from factor 2, the PAHs in this study are from combustion of wood, diesel, fossil fuels and traffic emissions. Factor 3 accounted for 13. 92 % of the total variance and was characterized by high components of Pyr and moderate component of IndP. Pyr is a marker for coal combustion () while IndP is from traffic emissions [9,11,13]. Thus, the source of PAHs is attributed to traffic emissions and coal combustion.

Heavy Metal Concentrations in the Soil

Table 6 shows the mean concentrations of the metals analysed in the soil from various sampling locations within the study areas: Kaduna North, Kaduna South and Algabi and compared with the control and standard limits given by USEPA/WHO. The results indicated that the mean concentrations of all heavy metals analysed in wet and dry season in the soil were higher than that of the control site. Using one way ANOVA followed by Turkey's HSD Test, the means sharing the same superscript are not significantly different from each other ($P > 0.05$) or means that have no superscript in common are significantly different from each other ($P < 0.05$).

Single contamination index (CI) was employed to evaluate the degree of heavy metal pollution in soil. The single contamination index was obtained from the expression:

$$CI = \frac{\text{concentration of metal}}{\text{background value}}$$

Table 6: Heavy metal content of the study areas

Study Sites	Cd	Cr	Pb	Cu
Kaduna North	2.35 ± 0.05c	0.49 ± 0.07b	59.50 ±1.06c	97.73 ± 0.28de
Kaduna South	0.82 ± 0.12b	0.85 ± 0.05c	139.71 ± 0.10d	60.01 ± 0.56c
Algabi	0.11 ± 0.01a	2.64 ± 0.06e	45.60 ± 0.60b	36.15 ± 0.75b
Control	0.10 ± 0.00a	0.00 ± 0.00a	30.20 ± 1.20a	2.41 ± 0.045a

The graded Nemero Pollution Index (Table 7) reflects the degree of soil pollution caused by various heavy metals pollutants. The degree of soil polluted with Cd, Pb and Cu was very heavy (P > 3) at Kadun North, while soil from Algabi was very heavy with Cr and Pb, but Cd and Pb were very heavy at Kaduna South. The pollution status for Cr and Cu was heavy (2 < P ≤ 3) at Kaduna North and Alegabi respectively. The soils at Kaduna South and Kaduna North were slightly polluted (1< P ≤ 2) with Cr, Cu and Cd, Cu respectively. Only Cr and Cd were at warning stage (0.7 < P ≤ 1) at Kaduna North and Alegbi respectively. All of the soil samples collected from the study areas found to be clean (P ≤ 0.7) from the heavy metals analysed, due to the impact of the industrial and other commercial activities in these studied areas.

Table 7: The Graded Standard of the Nemero Pollution Index Method for Soil From Different Study Sites

	I P≤ 0.7 Clean	II 0.7< P ≤ 1 warning	III 1 < P ≤ 2 slight	IV 2 < P ≤ 3 heavy	V P > 3 very heavy
Kaduna North	-	Cr	-	-	Cd, Pb, Cu
Kaduna South	-	-	Cr, Cu	-	Cd, Pb
Algabi	-	-	-	Cr	Cd, Pb, Cu
Control	Cr, Cu	Cd	-	-	Pb

The cadmium concentration ranged from 0.10±0.00 to 2.35±0.05 mg/g in wet and dry season for the study sites and 0.10±0.00 for control site. The average value was found to be below the permissible limit. Cadmium is a toxic metal having functions neither in human body nor in animals or plants. Once accumulated in the kidney then it stays there, resulting in high blood pressure and kidney disease and difficult to remove by excretion. Cadmium directly damages nerve cells. It inhibits the release of acetylcholine and activates cholinesterase enzyme, resulting in a tendency for hyperactivity of the nervous system [19]. Critical level of cadmium in soil is 3-5 mg/kg [20]. At this level in most cases it cannot cause toxic or excessive accumulation.

The mean concentration of chromium in all samples in both seasons ranges from 0.49±0.07 to 2.64 ± 0.06 mg/g for soil samples and found to be below the detection limit for the control sites. This shows that the mean concentrations are above acceptable limit of 0.5 mg/g in the soil given by NYSDEC standards. Chromium is one of the known environmental toxic pollutants in the world. Besides these chromium plating and alloys in motor vehicles is considered to be a more probable source of chromium [21]. An elevated concentration between 5-30 mg kg^{-1} is considered critical for plants and could cause yield reduction; [20]. The presence of an excess amount of chromium beyond the tolerable limits makes the land unsuitable for crop growth. Although the majority of the researchers consider that Cr(VI) is removed by anionic adsorption onto the biomaterials, basically the removal mechanism of Cr(VI) by natural biomaterials is adsorption-coupled reduction [22,23]. The toxic effects of chromium intake is skin rash, nose irritations, bleeds, upset stomach, ulcers, weakened immune system, kidney and liver damage, nasal itch and lungs cancer.

The lead concentrations ranged from 46.19 mg/g to 140.70 mg/g which is higher than the control value (29.00 mg/g). This indicates the presence of lead in the soils polluted with wastes from different operations. This concentration of lead can lead to health risk. High concentration of lead in the body causes anemia, pale skin, decreased hand grip strength, abdominal pain severe constipation, nausea, paralysis of the wrist joint, increases chances of miscarriage or birth defects. Lead is a poisonous metal that can damage nervous connections (especially in young children's) and cause blood and brain disorders. One of the most important and serious biochemical effects of lead is its interference with haemosynthesis, which leads to haematological damage [24]. The central nervous system becomes severely damaged at blood lead concentration starting at 40 mg/dL and above 70 mg/dL causes anemia, reduction in haemoglobin levels and erythropoisis [25,26].

The mean concentration for copper in the soil in both seasons was found to be 36.1±0.75 to 105.56±8.97 for the sample site and 2.41± 0.05 for the control sites. This indicates that copper present is above acceptable limit (30 mg/g) in the soil. The concentration of copper in the polluted area is more than the unpolluted area due to Industrial and commercial activities in the study areas [20]. Copper toxicity is ascribed to the induction of reactive free oxygen species in the Fenton type reaction causing break down of DNA strands as well as damage to membranes and mitochondria [27]. Copper is an essential element for plants and animals. Critical concentration for copper in plants is in between 20-100 mg kg^{-1}. Phytotoxicity can occur if copper concentration in plants is higher than 20 mg kg^{-1} dry weight [28,29]. Copper (Cu) is a trace element essential for the healthy functioning of soil biological systems. However, at elevated concentrations Cu can be a potential toxicant. Consequently, an understanding of Cu availability and toxicity to soil biota is essential for effective ecological assessment of metal impacts in soil. High levels of copper may cause metal fumes fever with flue like symptoms, hair and skin discoloration, dermatitis, irritation of the upper respiratory tract, metallic taste in the mouth and nausea [30]. Copper accumulates in liver and brain. Copper toxicity is a fundamental cause of Wilson's disease [31]. WHO has recommended the lower limit of the acceptable range of oral intake of copper as 20 mg kg^{-1} body weight day^{-1}.

Conclusion
The PAHs as a priority pollutants were determine in the soil samples from the study areas and had been discovered that all the soil samples from the study area is contaminated with PAHs at different concentrations in top and sub soils as well as wet and dry seasons, and also the heavy metals level considered (Cd, Cr, Cu, Ni and Pb) in the study sites were higher than the corresponding control values. The main contributors of PAHs and heavy metals in the soil samples from the study areas are as a result of the industrial and commercial activities that take place in the areas. This could pose risks and hazards to human and the ecosystem through direct ingestion of contaminated soil. Therefore, it is recommended that all the activities should be check and controls to avoid humans and animals ingestion of the contaminated soil and dust [32-81].

References

1. USEPA (2007) Testing methods for evaluating solid waste, physical and chemical methods, method 3550C; ultra-sonication extraction. USEPA, Washington, DC. Retrieved from 2014
2. Tesi GO, Iwegbue CMA, Emuh FN, Nwajei GE (2016) Ladgo Dam floods disaster of 2012: An assessment of the concentrations, sources and risks of polycyclic aromatic hydrocarbons in floodplain soils of the lower reaches of River Niger, Nigeria. Journal of Environmental Quality 45: 305-314.
3. Iwegbue CMA, Obi G, Aganbi E, Ogala JE, Omo-Irabor OO et al., (2016) Concentrations and health risk assessment of polycyclic aromatic hydrocarbons in soils of an urban environment in the Niger Delta, Nigeria. Toxicology and Environmental Health Sciences 8: 221-233.
4. Emoyan OO, Akporhonor EE, Agbaire PO, Akporido SO (2015) Concentration Characteristics of Polycyclic Aromatic Hydrocarbons (PAHs) in Dept–Wise Soils, Sapele, Nigeria. International Research Journal of Public and Environmental Health 2: 70-79.
5. Department of Petroleum Resources (DPR) (2002) Environmental guidelines and standard for the petroleum industry in Nigeria (revised edition. Department of Petroleum Resources, Ministry of Petroleum and Mineral Resources, Abuja Nigeria.
6. Chen L, Ran Y, Xing B, Mai B, He J et al., (2005) Contents and sources of polycyclic aromatic hydrocarbons and organo chlorine pesticides in vegetable soils of Guangzhou, China. Chemosphere 60: 879-890.
7. Li X, Ma L, Liu X, Fu S, Cheng H et al., (2006) polycyclic aromatic hydrocarbons in urban soil from Beijing China. J Environ Sci 18: 944-950.
8. Zhang X, Cheng S, Zhu C, Sun S (2006) Microbial PAH-degradation in soil: Degradation Pathways and Contributing Factors. Pedosphere 16: 5655-5665.
9. Yang B, Xue N, Zhou L, Li F, Cong X et al., (2012) Risk assessment and sources of polycyclic aromatic hydrocarbons in agricultural soils of Huanghuai plain, China. Ecotoxicity and Environmental Safety 84: 304-310.
10. Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D et al., (2002) PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry 33: 489-515.
11. Larsen RK, Baker JE (2003) Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. Environmental Science and Technology 37: 1873-1881.
12. Fraser MP, Cass GR, Simoneit BRT, Rasmussen RA (1997) Air quality model evaluation data for organics 4. C2-C36 non aromatic hydrocarbons. Environmental Science and Technology 31: 2356-2367.
13. Simcik MF, Eisenreich SJ, Lioy PJ (1999) Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. Atmospheric Environment, 33: 5071-5078.
14. Khalili NR, Scheff PA, Holsen TM (1995) PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. Atmospheric Environment 9: 533-542.
15. Wan X, Chen J, Tian F, Sun W, Yang F et al., (2006) Source apportionment of PAHs in atmospheric particulates of Dalian: factor analysis with nonnegative constraints and emission inventory analysis. Atmospheric Environment 40: 6666-6675.
16. Dong TTT, Lee BK (2009) Characteristics, toxicity and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in road dust of Ulsan, Korea. Chemosphere 74: 1245-1253.
17. Jerkins BM, Jones AD, Turn SQ, Williams RB (1996) Emission factors of polycyclic aromatic hydrocarbons from biomass burning. Environmental Science and Technology 30: 2462-2469.
18. Kavouras IG, Koutrakis P, Tsapakis M, Lagoudaki E, Stephanou EG et al., (2001) Source apportionment of urban particulate aliphatic and poly nuclear aromatic hydrocarbons (PAHs) using multivariate methods. Environmental Science and Technology 35: 2288-2294.
19. Alloway BJ (1990) Heavy metals in soils. John Wiley & Sons 339p.
20. Kabata-Pendias A, Pendias H (1992) Trace elements in soil and plants. CRC Press.
21. Shaheen DG (1975) Contributions of Urban Roadway Usage to Water Pollution. U.S. Environmental Protection Agency. Washington, D.C.
22. Dhal B, Thatoi HN, Das NN, Pandey BD (2013) Chemical and microbial remediation of hexavalent chromium from contaminated soil and mining/metallurgical solid waste. A review. Journal of Hazardous Materials 250-251: 272-291.
23. Badel KM, Raviraj V, Kumar LU (2011) Speciation of chromium in soil and sludge in the surrounding. Tannary region, Ranipest, Tamil Nadu. International Scholarly Biology and Biochemistry 43: 1162-1168.
24. Chaitali VM, Jayashree D (2013) Review of heavy metals in drinking water and their effect on human health. International Journal of Innovative Research in Science, Engineering and Technology 2: 2992-2996.
25. Costa G (2015) Gardening Australia. Fact sheet on safe soil. ABC
26. ATSDR (2012) Toxicology profiles for metals. Blv, Atlanta USA.
27. Maderova L, Watson M, Paton GD (2011) Bioavailability and toxicity of copper in soils: integrating chemical approaches with responses of microbial biosensors. Soil
28. Nikki P (2015) Copper and soil: How copper affects plants. Gardening know how.
29. Gupta SK (1975) Partitioning of trace metals in selective chemical fraction of near shore sediments Environ Lett 10: 129-158.
30. Lenntech BV (2016) Health effects of copper. Rotterdameweg 402 M. Delff, USA.
31. Gebrekidan M, Samuel Z (2011) Concentration of Heavy Metals in Drinking Water from Urban Areas of the Tigray Region, Northern Ethiopia. MEJS 3:105-121.
32. Abrahams PW (2002) Soils: Their implications to human health. Sci. Total Environ 291: 1-32.
33. Banger K, Toor GS, Chirenje T, Ma L (2010) polycyclic aromatic hydrocarbons in urban soils of different land uses in Miami, Florida. Soil and Sediment Contamination 9: 231-243.
34. Benhaddya ML, Hadjel M (2014) Spatial distribution and contamination assessment of heavy metals in surface soils of Hassi Messaoud, Algeria. Environmental Earth Sciences, 71: 1473-1486.
35. Bucheli TD, Blum F, Desaules A, Gustafsson O (2004) Polycyclic aromatic hydrocarbon, black carbon, and molecular markers in soils of Switzerland. Chemosphere 56: 1061-1076.

36. Chahal MK, Toor GS, Brown P (2010) Trace metals and polycyclic aromatic hydrocarbons in an urbanized area of Florida. Soil Sediment Contam 19: 1-16.

37. Durant JL (1996) Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. Mutat Res 371: 123- 157.

38. Emoyan OO, Akporhonor EE, Otobrise C (2015) Comparative Correlation Investigation of Polynuclear Aromatic Hydrocarbons (PAHs) in Soils of Different Land Use: Sources Evaluation Perspective. World Academy of Science, Engineering and Technology. International Journal of Environmental, Chemical, Ecological, Geological and Geophysical Engineering 9: 1126-1131

39. Fang GC, Chang CN, Wu YS, Fu PPC, Yang IL et al., (2004) Characterization, identification of ambient air and road dust polycyclic aromatic hydrocarbons in central Taiwan, Taichung. Science of the Total Environment 327: 135-146.

40. Gocht T, Moldenhauer KM, Püttmann W (2001) Historical record of polycyclic aromatic hydrocarbons (PAH) and heavy metals in floodplain sediments from the Rhine River (Hessisches Ried, Germany). Applied Geochemistry 16: 1707-1721.

41. Heywood E, Wright J, Wienburg CL, Black HIJ, Long SM et al., (2006) Factors influencing the national distribution of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in British soils. Environ Sci Technol 40: 7629-7635.

42. Imran H, Kim JG, Kim KS, Park JS (2005) Polyaromatic hydrocarbons (PAHs) levels from two industrial zones (Sihwa and Banwal) located in An-san City of the Korea Peninsula and their influence on lake. Journal of Applied Science and Environmental Management 9: 63-69.

43. Johnsen AR, Wick LY, Harms H (2005) Principles of microbial PAH-degradation in soil. Environmental Pollution 133: 71-84.

44. Kumar B, Tyagi J, Verma VK, Gaur R, Sharma CS (2014) Concentrations, source identification and health risk of selected priority polycyclic aromatic hydrocarbons in residential street soils. Advances in Applied Science Research 5:130-139.

45. Larsen JC, Larsen PB (1998) Chemical carcinogens. In: E. E. Hester & R.R. Harrison (Eds) Air pollution and Health. Cambridge UK: The Royal Society of Chemistry 33-56.

46. Li A, Jang JK, Scheff PA (2003) Application of EPA CMB8.2 model for source apportionment of sediment PAHs in Lake Calcumet, Chicago. Environmental Science and Technology 37: 2958-2965.

47. Mai BX, Qi SH, Zeng EY, Yang QS, Zhang G et al., (2003) Distribution of polycyclic aromatic hydrocarbons in the coastal region off Macao, China: assessment of input sources and transport pathways using compositional analysis. Environmental Science and Technology 37: 4855-4863.

48. Man YB, Kang Y, Wang HS, Lau W, Li H et al., (2013) Cancer risk assessments of Hong Kong soils contaminated by polycyclic aromatic hydrocarbons. Journal Hazardous Material.

49. Meharg AA, Wright J, Dyke H, Osborn D (1998) Polycyclic aromatic hydrocarbons (PAHs) dispersion and deposition to vegetation and soil following a large scale chemical fire. Environmental Pollution 99: 29-36.

50. Morello E, Romero AS, Madrid L, Villaverde J, Maquedo C (2008) Characterization and sources of PAHs and potentially toxic metals in urban environments of Sevilla (Southern Spain). Water, Air and Soil Pollution 187: 41-51.

51. Morillo E, Romero AS, Madrid L, Villaverde J, Maqueda C (2008) Characterization and sources of PAHs and potentially toxic metals in urban environments of Sevilla (Southern Spain). Water Air Soil Pollution 187: 41-51.

52. New York States Department of Health (NYS DOH) (2007) Hopewell precision area contamination: Appendix C-NYS DOH, In: Procedure for evaluating potential health risks for contaminants of concern.

53. Okoro D, Ikolo OA (2007) Spatial variation and distribution of polycyclic aromatic hydrocarbons in soil. Bulletin of Chemical Society of Ethiopia 21: 331-340.

54. Olajire AA, Alade AO, Adeniyi AA, Olabemiwo OM (2007) Distribution of polycyclic aromatic hydrocarbons in surface soils and water from the vicinity of Agbabu bitumen field of South western, Nigeria. J Environ Sci Health A Tox Hazard Subst. Environ Eng 42: 1043-1049.

55. Olajire AA, Altenburger R, Küster E, Brack W (2005) Chemical and eco toxicological assessment of polycyclic aromatic hydrocarbon contaminated sediments of the Niger Delta, Southern Nigeria. The Science of the Total Environment 340: 123-136

56. Olawoyin R, Grayson RL, Okareh OT (2012) Eco-toxicological and epidemiological assessment of human exposure to polycyclic aromatic hydrocarbons in the Niger Delta, Nigeria. Toxicol. Enivironmental Health Science 4: 173-185.

57. Parrish ZD, Banks MK, Schwab AP (2004) Effectiveness of phyto remediation as a secondary treatment for polycyclic aromatic hydrocarbons (PAHs) in composted soil. International Journal of Phytoremediation 6: 119-137.

58. Peng C, Chen W, Liao X, Wang M, Ouyang Z et al., (2011) Polycyclic aromatic hydrocarbons in urban soils of Beijing: status sources distribution and potential risk. Environ Pollut 159: 802-808.

59. Peng C, Chen WP, Liao XL, Wang M, Ouyang Z et al., (2011) Polycyclic aromatic hydrocarbons in urban soils of Beijing: Status, sources, distribution and potential risk. Environmental Pollution 159: 802-808.

60. Pies C, Yang Y, Hofmann T (2007) Distribution of polycyclic aromatic hydrocarbons (PAHs) in floodplain soils of the Mosel and Saar River. Journal of Soil Sediments, Research Notice Toxicology, volume 2011.

61. Sartori F, Wade TL, Sericano JL, Mohanty BP (2010) Polycyclic aromatic hydrocarbons in soil of the Canadian River floodplain in Oklahoma. J Environ Qual 39: 568-579.

62. Sojinu OS, Wang JZ, Sonibare OO, Zeng EY (2010) Polycyclic aromatic hydrocarbons in sediments and soils from oil exploration areas of the Niger Delta, Nigeria. Journal of Hazardous Materials 174: 641-647.

63. Sojinu OS, Sonibare OO, Zeng EY (2012) Concentrations of Polycyclic aromatic hydrocarbons in soils of a mangrove forest affected by forest fire. Toxicological and Environmental Chemistry 93: 450-461.

64. Trapido M (1999) Polycyclic aromatic hydrocarbons in Estonia soil: contamination and profiles. Environmental Pollution 105: 67-74.

65. Uko ED, Tamunobereton-Art I (2013) Variability of Climatic Parameters in Port Harcourt, Nigeria. Journal of Emerging Trends in Engineering and Applied Sciences 4 727-730.

66. USDOE (United States Department of Energy) (2011) The Risk Assessment Information System (RAIS); U.S. Department of Energy's Oak Ridge Operations Office (ORO): Oak Ridge, TN, USA.

67. USEPA (1993) Risk–based concentration Table. U.S.

Environmental Protection Agency, Region 111 (Third Quarter).

68. USEPA (United States Environmental Protection Agency) (2009) Risk assessment guidance for superfund. Volume 1: Human Health Evaluation Manual (F, supplemental guidance for Inhalation Risk Assessment) EPA/540/R/070/002, Office of Superfund Remediation and Technology Innovation, Washington, DC.

69. USEPA (United States Environmental Protection Agency) (1989) Risk Assessment guidance for superfund, Vol. 1: Human health Evaluation Manual EPA/se0/1-89/002, office of solid waste and emergency Response, Washington, DC.

70. USEPA (United States Environmental Protection Agency) (2001) Risk assessment guidance for superfund. Volume 1: Human evaluation Manual (Part E, Supplemental guidance for defined risk assessment). EPA/540/R/99/005.7. Washington, DC, USA: Office of Emergency and Remedial response, United states Environmental Protection Agency.

71. USEPA (United States Environmental Protection Agency) (2011) Regional Screening Level Table (RSL) for Chemical Contaminants at Superfund Sites. U.S. Environmental Protection Agency: Washington, DC, USA.

72. USEPA (2010) Regional screening levels (RSL) summary tables. http://www.epa.gov/risk/risk-based-screening-table-generic-tables.

73. USEPA (2010) Regional screening levels (RSL) summary tables. http://www.epa.gov/risk/risk-based-screening-table-generic-tables.

74. Vane CH, Kim AW, Beriro DJ, Cave MR, Knights K et al., (2014) Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in urban soils of Greater London, UK. Appl Geochem 51: 300-314.

75. Wang XT, Miao Y, Zhang Y, Li YC, Wu MH et al., (2013) Polycyclic aromatic hydrocarbons (PAHs) in urban soils of the megacity Shanghai: Occurrence source apportionment and potential human health risk. Sci Tot Environ 447: 80-89.

76. Wenzl T, Simon R, Kleiner J, Anklam E (2006) Analytical methods for polycyclic aromatic hydrocarbons (PAHs) in food and the environment needed for new food legislation in the European Union. Trends in Analytical Chemistry 25: 716-725.

77. www.lenntech.com/periodic/element/Cu.htm.

78. Yang T, Ligouis B, Pies C, Achten C, Hofmann T (2006) Slow and very slow desorption of PAHs from river floodplain soils: Coal and coal-derived particles. Geophysical Research Abstracts 8: 03626.

79. Yang Y, Woodward LA, Li QX, Wang J (2014) Concentrations, sources and risk assessment of polycyclic aromatic hydrocarbons in soils from Midway Atoll, North Pacific Ocean. PLoS ONE 9 : e86441.

80. Yu G, Zhang Z, Yang G, Zheng W, Xu L et al., (2014) Polycyclic aromatic hydrocarbons in urban soil of Hangzhou, status, distribution, sources and potential risk. Environ Monit Assess 186: 2775-2784.

81. Zhang HB, Luo YM, Wong MH, Zhao QG, Zhang GL (2006) Distribution and concentrations of PAHs in Hong Kong soil. Environmental Pollution 141: 107-114.