

Assessment of the Contamination Level of Polycyclic Aromatic Hydrocarbons in the Soil around Ekeatai River, Eket, Akwa Ibom State, Nigeria

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Abstract The presence of Polycyclic Aromatic Hydrocarbons (PAHs) in the environment has been a concern due to risk to human health and the ecosystem. This study was carried out to assess the contamination level of PAHs in the soil around Ekeatai watershed, Eket, Nigeria. Soil samples (0-30cm) were analyzed for the presence of the 16 US-EPA priority PAH and human health risk. The identification and quantification of the PAHs in the soil samples were carried out using the Aligent 7890B GC-FID. The results of the analysis revealed that amongst the 16 US-EPA priority PAHs, seven (7) were detected in the soil samples. The total concentration of PAHs detected in the study area were: fluorene (9.5870mg/kg), benzo(a)anthracene (1.2862mg/kg), pyrene (0.2782mg/kg), acenaphthene (0.1805mg/kg), anthracene (0.1545mg/kg), chrysene (0.1288mg/kg), and fluoranthene (0.0885mg/kg). PAH diagnostic ratio showed possible sources of PAHs to be pyrogenic, petrogenic and petroleum combustion. Benzo[a]anthracene and chrysene detected in the study area are known to be carcinogenic. The BaPTEQ for ΣPAH carcinogen ranged from 0.00013 - 0.13mg BaPTEQ/kg and the BaPTPE calculated in the study area was 0.13mg/kg. The values were lower than the human health-based soil quality guidelines for PAHs based on Incremental Lifetime Cancer Risk of the Canadian government.

Keywords: Polycyclic Aromatic Hydrocarbons, soil, physicochemical parameters

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1. Introduction

The soil system controls several processes in performing ecological functions [1]. It acts as a natural sink for contaminants. These contaminants are usually accumulated and concentrated in the soil from various sources, depending on environmental conditions such as soil types and the degradability of the contaminants discharged [2]. The most common contaminants in urban soils are petroleum hydrocarbons, polycyclic aromatic hydrocarbons. PAHs are a group of over 100 chemicals, the United States Environmental Protection Agency (USEPA) listed sixteen of them as priority pollutants and the International Agency for Research on Cancer (IARC) classified eight of them as possible human carcinogens. They are very common environmental pollutants and are found frequently at various sites as a result of anthropogenic contamination and natural processes [3]. The major sources of PAHs in soils are from atmospheric deposition as a result of pyrolytic processes, seepage of petroleum and oil spills. PAHs reach the soil by fallout [4]

i.e. wet or dry deposition processes etc. Other sources of PAHs in the soil are coal tars, discharge of spent oils, road runoff, industrial wastewaters, use of creosote and combustion of waste materials.

The presence of polycyclic aromatic hydrocarbons as a persistent environmental pollutant has been a problem in the past decades. In Edebuk, Eket, Akwa Ibom State, road construction and repairs are regular activities whereby bitumen are used as sealant. Ekeatai river is always busy with some commercial activities such as automobile mechanic workshops, and abattoir activities. These activities have the tendency of releasing harmful pollutants including polycyclic aromatic hydrocarbons into the environment. Polycyclic Aromatic Hydrocarbons (PAHs) are almost found anywhere i.e. they are ubiquitous and end up in the soil and aquatic environments if not inhaled (Adejoke, 2014). The indigenous people in the locality derive their livelihood from the watershed. Till date, there is no data on the extent of PAH contamination of the watershed has been documented.

This study assessed the possible sources and human health risk of Polycyclic Aromatic Hydrocarbons in the soil around Ekeatai River.

2. Materials and Methods

2.1. The Study Area

The study was carried out around Ekeatai River located at Edebuk, Eket, Akwa Ibom state Nigeria, is located in the coastal southern part of the country. It lies between latitudes 4°32'N and 5°33'N; longitudes 7°25'E and 8°25'E.

The state is located in the South-South geopolitical zone and has its borders on the East by Cross River State, on the West by Rivers State and Abia State, and on the South by the Atlantic Ocean, the Gulf of Guinea and the southernmost tip of Cross River State. The state is made up of thirty-one Local Government Areas and the capital is Uyo. The state currently covers a total land area of 7,249 square kilometers. It is the 10th largest state in Nigeria in terms of landmass. About 13.4 percent of the 960km of Nigeria's Atlantic Ocean coastline runs through the State. Towns include; Eket, Ikot Ekpene, Ikot Abasi, Oron, Abak, Itu, Etinan, Ibeno, etc. The Ekeatai river is a tributary that runs through Edebuk and empties into Qua Iboe River. The study area is the part that runs through an urban area in Eket.

2.2. Sampling Plan

The study area was divided into five sampling sites labeled A, B, C, D and E.

Site A - Mini mechanic village and cattle abattoir.
Site B - Roasting of suya meat with heavy firewood and burning of automobile tyres.

Site C - Mammy market for goats and goat abattoir where goats are burned with tyres.

Site D - The slightly vegetated area where goat market and burning of goats with tyre is at one point and no burning activity is carried out at the other part of the site.

Site E - The control site where there was no automobile or burning activity.

2.3. Sample Collection

Samples were collected at nine locations using a hand soil auger at 0-30cm depth. Composite samples were collected at each sampling location at the depths of 0-30cm; then homogenized and further sub-sampled into three replicates making it a total of twenty-seven soil samples. Samples were collected at a control point about 3.2km away from the area of study and all sampling points were appropriately geo-referenced using a Global Positioning System (GPS). After collecting the samples, they were placed in clean polyethylene bags which were properly labeled using masking tape and marker. The labeled samples were properly preserved in a cooler under ice and were transported to the laboratory. The samples were subjected to physicochemical and PAH analyses.

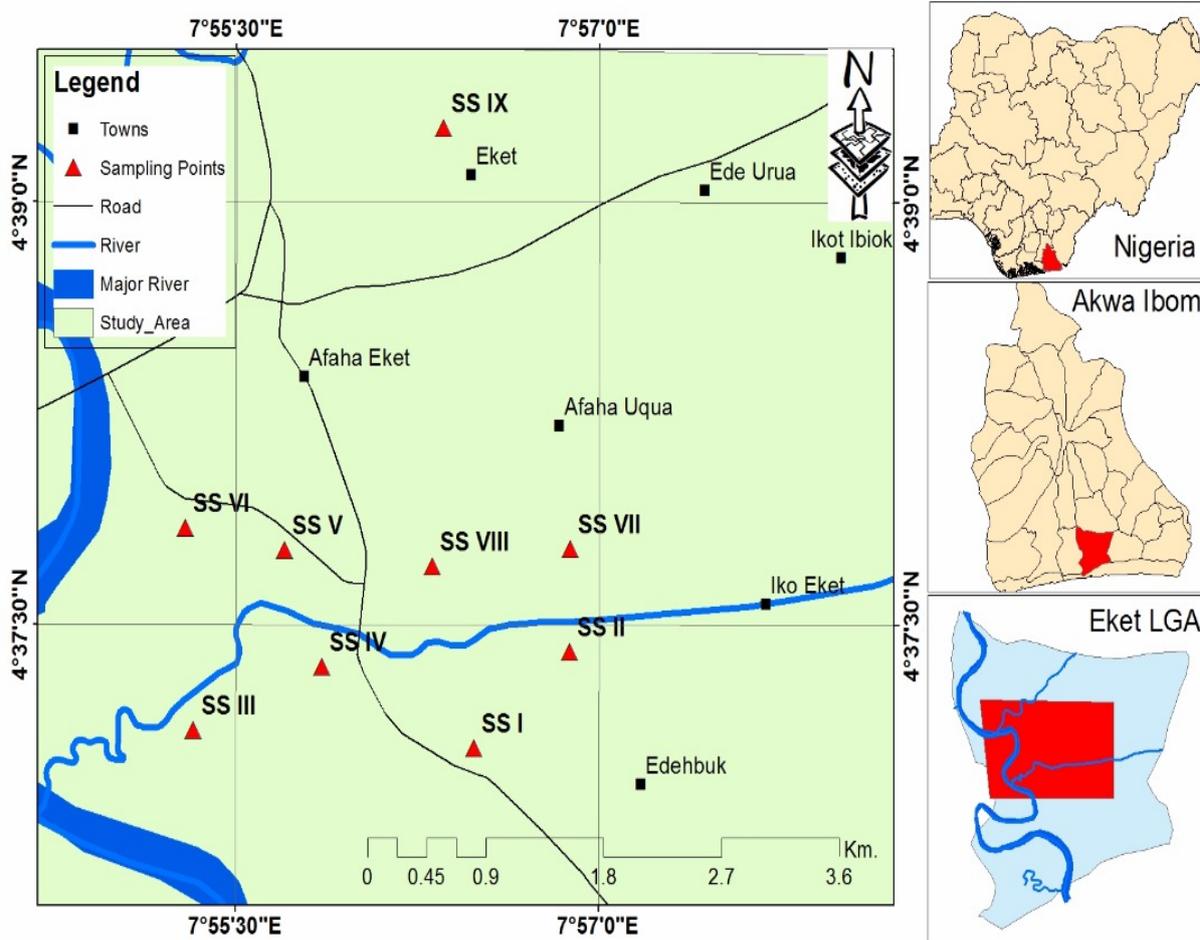


Figure 1. Map of Nigeria showing Akwa Ibom State and Eket Local Government Area, the study area and sampling points

2.4. Physicochemical Analysis of Samples

The physical parameters analysed in the samples were particle size and soil texture using the sieve analysis and soil texture triangle. Soil pH was determined using the HANNA HI9828 multi-parameter. Soil Electrical Conductivity was determined using the conductivity meter, Cation Exchange Capacity was obtained by the summation of the concentrations of exchangeable base cations and exchangeable acidity. Total nitrogen was analysed by the Micro-Kjeldahl method. Soil Organic Carbon was determined by the Walkley-Black Method and the colorimetric analysis was used for phosphate and sulphate determination.

2.5. Analysis of Polycyclic Aromatic Hydrocarbons in the Samples

The soil samples collected were analysed for Polycyclic Aromatic Hydrocarbons (PAHs) following the ASTM D7363-07 Standard Test Method for Determination of Parent and Alkyl Polycyclic Aromatics in Sediment Pore Water Using Solid-Phase Micro-extraction and Gas Chromatography/Mass Spectrometry in Selected Ion Monitoring Mode. Polycyclic Aromatic Hydrocarbons (PAHs) were analysed using the Gas Chromatography-Flame Ionization Detection (GC-FID) method. Before the instrumental analysis, the soil samples were pretreated and contaminants were extracted from the solid matrix and quantitatively transferred to another medium. Cleanup was carried out to remove co-extracted compounds that could interfere during the subsequent analysis, and to separate the different classes of analytes prior to analysis.

2.6. Instrumental Analysis

This analysis was carried out to separate, identify and quantify the individual analytes in the sample. PAHs were analysed using the Aligent 7890B Gas Chromatography-Flame Ionization Detection (GC-FID). The Gas Chromatographic system had a single detector called Flame Ionization Detector, a capillary column inlet of 30m long, 1 μ m thick, internal diameter of 0.25mm and a liquid auto-sampler or injector. The carrier gases used were air, hydrogen and helium to move the samples. The flame was produced when the air and hydrogen gases were burned, this ignited the sample extract and made it elute from the column of the FID and the detector gave the response. The instrument was calibrated and its operation setup done in accordance to its method development specified in its operation manual. Individual PAHs were identified based on the internal calibration standard which contains known concentrations of the EPA 16 target PAHs. The analytes results obtained from each soil sample were recorded as electronic signal on the monitor (the chromatogram). The results were represented in milligram per kilogram concentration (mg/kg).

2.6. Statistical Analysis

The data obtained were analyzed using descriptive statistics viz mean, standard deviation and boxplots which

were used to represent variations in soil chemical characteristics and the concentration of PAHs in the study area. The data was also subjected to inferential statistics using One-way analysis of variance (ANOVA) to analyze the significant differences or variations in the physicochemical parameters and the PAH concentrations across the sampling points. The significant means were separated using the Tukey method of significant differences at 5% level of probability. Karl Pearson's correlation was used to evaluate the possible relationships that exist between the physicochemical parameters and individual PAHs analyzed in the study area.

3. Results and Discussion

3.1. Polycyclic Aromatic Hydrocarbon Concentration Level in the Soil Samples

The Polycyclic Aromatic Hydrocarbons (PAHs) detected in the soil samples from the study area and their concentrations are recorded in [Table 1](#). The result showed that seven (7) PAH components amongst the 16 EPA priority PAHs were detected in the soil samples analysed. The total concentration of PAHs detected in the study area were; fluorene (9.5870mg/kg), benzo(a)anthracene (1.2862mg/kg), acenaphthene (0.1805mg/kg), anthracene (0.1545mg/kg), chrysene (0.1288mg/kg), pyrene (0.2782mg/kg) and fluoranthene (0.0885mg/kg). Figure 2 represents the boxplot of the variations of PAHs across the soil samples. The figure shows that there were significant variations in the level of Polycyclic Aromatic Hydrocarbons across the sampling locations. In Site A, SS-I contained the highest concentration of PAHs with value 2.9378mg/kg and the highest number of individual PAHs. The individual PAHs present in SS-I were acenaphthene, fluorene, anthracene, chrysene, benzo(a)anthracene. Fluorene concentration level was highest among the individual PAHs in SS-I and also had the highest level of concentration across the sampling locations.

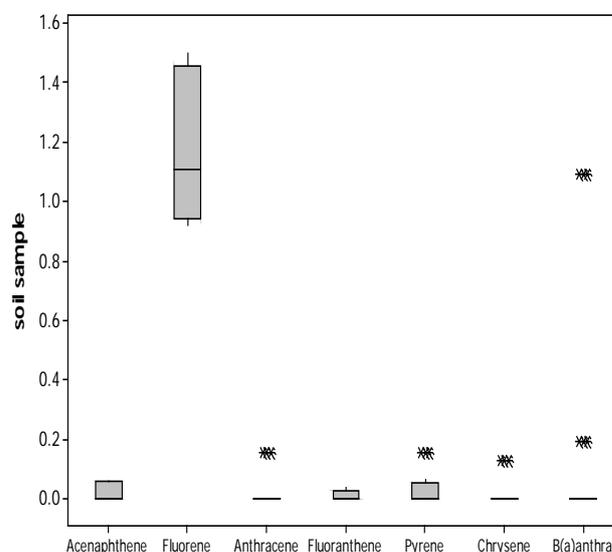


Figure 2. Boxplot of PAH concentration in the study area

Table 1. Concentration of PAHs detected in the soil samples with their mean separations across the sampling locations

Location	PAH Components (mg/kg)							Σ PAHs
	CAN	FLUO	ANTH	FLUA	PYR	CHRY	B(a)ANTH	
SS – I	0.0619±0.006 ^a	1.5009±0.01 ^a	0.1545±0.06 ^a	0.00 ^e	0.00 ^d	0.1288±0.006 ^a	1.0919±0.006 ^a	2.9380
SS – II	0.0573±0.006 ^b	1.4707±0.06 ^b	0.00 ^b	0.00 ^e	0.00 ^d	0.00 ^b	0.1944±0.006 ^b	1.7224
SS – III	0.00 ^c	1.2001±0.01 ^d	0.00 ^b	0.0382±0.006 ^a	0.0663±0.006 ^b	0.00 ^b	0.00 ^c	1.3046
SS – IV	0.0616±0.006 ^a	1.4593±0.05 ^c	0.00 ^b	0.0264±0.006 ^c	0.0558±0.006 ^c	0.00 ^b	0.00 ^c	1.6031
SS – V	0.00 ^c	1.1085±0.01 ^e	0.00 ^b	0.0238±0.006 ^d	0.1561±0.006 ^a	0.00 ^b	0.00 ^c	1.2884
SS – VI	0.00 ^c	0.9635±0.05 ^f	0.00 ^b	0.00 ^e	0.00 ^d	0.00 ^b	0.00 ^c	0.9635
SS – VII	0.00 ^c	0.9457±0.06 ^g	0.00 ^b	0.00 ^e	0.00 ^d	0.00 ^b	0.00 ^c	0.9457
SS – VIII	0.00 ^c	0.9371±0.02 ^h	0.0000 ^b	0.00 ^e	0.0000 ^d	0.00 ^b	0.00 ^c	0.9371
SS – IX	0.00 ^c	0.9235±0.00 ⁱ	0.00 ^b	0.0315±0.006 ^b	0.00 ^d	0.00 ^b	0.00 ^c	0.9550

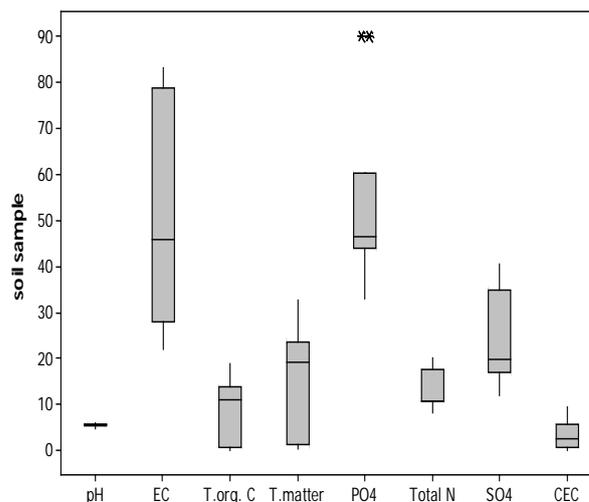
ACN = Acenaphthene, FLUO = fluorene, ANTH = anthracene, B {a} ANTH = benzo{a}anthracene, FLUA = fluoranthene, PRY = pyrene, CHRY = chrysene. Means with different alphabets as superscript for each soil sample are significantly different while those with the same alphabets are the same. SS=Soil Sample, P=Probability Value.

3.2. Physicochemical Properties of Soil Analysed

The result of the analysis is presented in Table 2. A variation plot of the physicochemical parameters is presented in Figure 3. The textural class of the study area was sandy clay which implies that the soil samples contained sand in higher proportion. The physicochemical parameters showed significant differences across the sampling locations ($P < 0.05$). The pH ranged from 4.91 ± 0.006 to 6.02 ± 0.006 showing that the soil samples all had low pH and their mean values varied slightly across the sampling locations. EC ranged from 22.00 ± 0.006 to 83.10 ± 0.1 dS/cm, TOC ranged from 0.18 ± 0.006 to $18.95 \pm 0.006\%$, TOM ranged from 0.32 ± 0.006 to $32.67 \pm 0.01\%$, TN ranged from 8.27 ± 0.06 to $20.04 \pm 0.006\%$, CEC ranged from 0.20 ± 0.006 to 9.39 ± 0.01 cmol/kg.

Karl Pearson's correlation (r) was used to evaluate the possible relationships between the chemical parameters and individual PAHs analyzed in the study area. The correlation results are presented in Table 3. The result showed that at $P \leq 0.001$, acenaphthene showed a negative correlation with pH, with correlation coefficient of -0.680 . Fluorene also showed a moderate negative correlation with pH at $P \leq 0.001$ with correlation coefficient -0.693 . Similarly, fluoranthene correlated negatively with Sulphate (SO_4) and Total Nitrogen with correlation

coefficients of -0.683 and -0.689 respectively at $P \leq 0.001$. Furthermore, the result also revealed a significant positive correlation between anthracene and Sulphate (SO_4) with a correlation coefficient of 0.926 at $P \leq 0.15$ and a confidence level of significance of 85% . Generally, the result showed weak and moderate negative and positive correlations between the PAH components and the chemical properties of the soil samples. Only the few significant and moderate correlations were described.

**Figure 3. Boxplot of PAH concentration in the study area****Table 2. The Soil Physicochemical Parameters across the Sampling Locations**

Parameters	Sampling Locations								
	SS – I	SS – II	SS – III	SS – IV	SS – V	SS – VI	SS – VII	SS – VIII	SS – IX
pH	5.15±0.006 ^g	4.91±0.006 ^h	5.54±0.006 ^e	5.72±0.006 ^d	6.02±0.006 ^a	5.87±0.01 ^c	5.91±0.01 ^{bc}	5.47±0.03 ^f	5.94±0.06 ^b
EC	46.04±0.06 ^c	28.00±0.006 ^g	81.04±0.05 ^b	58.00±0.006 ^d	22.00±0.006 ^h	34.01±0.01 ^f	83.10±0.1 ^a	79.00±0.006 ^c	22.04±0.06 ^b
TOC	0.88±0.01 ^g	11.21±0.006 ^e	2.91±0.006 ^f	0.18±0.006 ⁱ	17.83±0.06 ^b	13.78±0.006 ^c	18.95±0.006 ^a	13.68±0.006 ^d	0.68±0.006 ^b
TOM	1.52±0.006 ^g	19.33±0.006 ^e	5.02±0.01 ^f	0.32±0.006 ⁱ	30.69±0.006 ^b	23.76±0.006 ^c	32.67±0.01 ^a	23.59±0.01 ^d	1.17±0.006 ⁱ
TN	17.55±0.006 ^b	20.04±0.006 ^a	10.77±0.06 ^c	10.74±0.06 ^c	8.27±0.06 ^e	9.13±0.06 ^d	17.55±0.006 ^b	20.01±0.01 ^a	10.77±0.06 ^c
PO ₄	60.27±0.006 ^b	90.04±0.05 ^a	44.04±0.05 ^e	45.00±0.006 ^d	46.34±0.3 ^c	33.08±0.04 ^f	60.23±0.06 ^b	90.04±0.05 ^a	44.00±0.006 ^e
SO ₄	35.01±0.01 ^b	40.55±0.006 ^a	17.01±0.01 ^d	12.07±0.006 ^c	20.00±0.006 ^c	12.07±0.06 ^f	35.01±0.006 ^b	40.55±0.006 ^a	17.00±0.006 ^d
Ca	13.30±0.006 ^d	1.35±0.0006 ^h	40.95±0.04 ^c	54.94±0.04 ^a	10.25±0.005 ^e	6.96±0.05 ^f	49.11±0.02 ^b	2.71±0.01 ^g	0.36±0.0006 ⁱ
Na	5.13±0.02 ^d	6.39±0.01 ^a	5.53±0.02 ^b	5.29±0.01 ^c	2.26±0.005 ^f	2.26±0.0006 ^f	0.48±0.005 ^b	2.06±0.00 ^g	4.96±0.004 ^e
K	1.76±0.005 ^f	2.13±0.01 ^d	2.75±0.007 ^c	1.07±0.001 ^h	1.83±0.006 ^e	1.65±0.002 ^g	0.28±0.001 ⁱ	7.20±0.001 ^a	2.96±0.0006 ^b
Mg	1.76±0.005 ^e	0.68±0.005 ^h	1.74±0.001 ^f	1.81±0.006 ^c	1.92±0.002 ^b	1.79±0.006 ^d	1.94±0.006 ^a	1.26±0.001 ^g	0.26±0.002 ⁱ
CEC	0.84±0.01 ^g	0.63±0.0006 ^h	2.05±0.003 ^f	2.62±0.001 ^e	9.39±0.01 ^a	8.94±0.006 ^b	3.91±0.01 ^d	5.71±0.006 ^c	0.20±0.006 ⁱ

Means with different alphabets as superscript for each soil sample are significantly different while those with the same alphabets are the same, SS=Soil Sample, P=Probability Value, EC=Electrical Conductivity, TOC=Total Organic Carbon, TOM=Total Organic Matter, TN=Total Nitrogen, PO₄=Phosphate, SO₄=Sulphate, Ca = Calcium, Na = Sodium, K = Potassium, Mg = Magnesium, CEC = Cation Exchange Capacity.

Table 3. Correlation between PAH Components and chemical parameters measured in the study area

Parameters	PAH Components (mg/kg)						
	Acn	Fluo	Anth	Flua	Pyr	Chry	B(a)anth
pH	-0.680	-0.693	-0.458	0.398	0.388	-0.458	-0.585
	0.000*	0.000*	0.016	0.040	0.045	0.016	0.001
EC	-0.174	-0.135	-0.063	-0.058	-0.177	-0.063	-0.122
	0.386	0.501	0.755	0.774	0.376	0.755	0.545
TOC	-0.484	-0.492	-0.390	-0.504	0.153	-0.390	-0.372
	0.011	0.009	0.044	0.007	0.445	0.044	0.056
TOM	-0.484	-0.492	-0.390	-0.505	0.152	-0.390	-0.372
	0.011	0.009	0.045	0.007	0.448	0.045	0.056
TN	0.334	0.198	0.287	-0.689	-0.603	0.287	0.375
	0.089	0.321	0.147	0.000*	0.001	0.147	0.054
PO4	0.274	0.184	0.060	-0.552	-0.361	0.060	0.168
	0.167	0.358	0.768	0.003	0.065	0.768	0.402
SO4	0.226	0.137	0.926	-0.683	-0.415	0.296	0.382
	0.257	0.495	0.134***	0.000*	0.032	0.134	0.050
CEC	-0.522	-0.477	-0.319	-0.175	0.456	-0.319	-0.383
	0.005	0.012	0.105	0.381	0.017	0.105	0.049
pH	-0.680	-0.693	-0.458	0.398	0.388	-0.458	-0.585
	0.000*	0.000*	0.016	0.040	0.045	0.016	0.001
EC	-0.174	-0.135	-0.063	-0.058	-0.177	-0.063	-0.122
	0.386	0.501	0.755	0.774	0.376	0.755	0.545

Cell Contents: Pearson correlation; P-Value. * = Significant at $P \leq 0.001$. ** = Significant at $P \leq 0.05$.

3.3. Discussion

Amongst the sixteen USEPA priority PAHs investigated in the study area, seven of them were detected. The highest total concentration for individual PAHs in the study area was fluorene at 9.5870mg/kg. The decreasing order for individual PAHs concentration in the soil within the study area was fluorene>benzo(a)anthracene>pyrene>acenaphthene> anthracene>chrysene>fluoranthene. The least individual PAH was fluoranthene at 0.1200mg/kg. Site A had the highest concentration levels of PAHs in the study area and it encompasses the location carrying out abattoir and automobile activities. This indicates that PAH contamination in the study area may have greatly risen from these activities. These PAH contamination in the study area can be attributed to the high level combustion of woods, tyres and organic materials (such as cattle horns and bones) and spent/waste oil spills during repairs of vehicles and other heavy automobiles. This may lead to PAH pollution in the Ekeatai river therefore contaminating the water body itself and accumulating in the sediments. This may occur as a result of atmospheric deposition and runoff of PAH compounds into the water body. In Site D, SS-VIII was in close proximity to SS-VII and there was no burning or automobile activity carried out there. The fluorene contamination in SS-VIII location suggested atmospheric deposition of the compound in the soil during the combustion of tyres and goats from SS-VII location. PAH compounds were also detected in the control site which is a cultivated land. This explains the ubiquitous nature of these compounds.

3.4. Characteristics of Polycyclic Aromatic Hydrocarbon Compounds in the Study Area

PAH physical and chemical characteristics vary with their molecular structure (number of rings) and molecular weight. That is, as the number of rings increases, the molecular weight also increases. They vary with high melting and boiling points, low vapour pressure, very low

aqueous solubility and tend to decrease with increasing molecular weight. They are usually classified as Low Molecular Weight (LMW) and High Molecular Weight (HMW) PAHs. PAHs with low molecular weight are those with two or three fused benzene rings while high molecular weight PAHs are those with four or more fused benzene rings [5]. [6] stated that PAHs with LMW easily degrade and volatilize faster than the HMW PAHs. The higher the molecular weight of PAHs, the higher its hydrophobicity (that is, they cannot absorb water), toxicity, lipophilic property, the lower its solubility in water, vapour pressure, and degradability [5]. The ability of HMW PAHs to persist in the environment is due to their low volatility, resistance to leaching, and difficulty in undergoing degradation easily [7] [8]. In this study, LMW PAHs with 3-rings and HMW PAHs with 4-rings were detected; but the HMW (4-ringed) PAHs dominated the study area.

3.5. Source Identification of PAH Compounds in the Study Area

The major sources of PAHs amongst others are petrogenic (petroleum sources) and pyrogenic (combustion sources). [9] stated in his work that petrogenic sources give off organic particulates which are characterized by a high mole fraction of LMW PAHs. According to [6], LMW PAHs usually originate from petrogenic sources and [10] suggested HMW PAHs to originate from pyrogenic sources. LMW PAHs dominate petrogenic sources while pyrogenic sources are dominated by HMW PAHs [11]. It is detriment to identify PAH sources for effective pollution control, environment risk management and health risk assessment. PAH sources were predicted using PAH molecular weights and diagnostic ratios. Pyrolytic (pyrogenic) sources (combustion of coal, biomass or petroleum) indicate the ratio of < 1 while the petrogenic sources (petroleum spills) usually indicate the ratio of > 1 [12] [13]. In this study, the concentration ratios of Fluo/Fluo+Pyr, Flua/Pyr, Flua/Flua+Pyr, \sum LMW/ \sum HMW and BaA/BaA+Chry were used to identify the origin of PAHs in the study area.

The result revealed that the sources of PAHs in the study area were pyrogenic, petrogenic, and from petroleum combustion origin. The major sources of pyrogenic PAHs in the study area were likely incomplete combustion of the organic matter/waste from cattle bones/horns, combustion of firewood used as fuel for suya meat, vehicular emissions. Coal burning may have originated from the burning of tyres used as fuel for goat meat production. Petrogenic sources were likely from petroleum spills, runoff and wastewater from the washing of burned goats, runoff of coal tar from roads, lubricating and spent oil drippings. Petroleum combustion sources were likely from diesel and gasoline combustion used with tyres for fuel.

3.6. Contamination Level of PAHs in the Study Area

PAH levels detected in this study were compared with the Federal Ministry of Environment and the Department of Petroleum Resources who stipulated 1mg/kg for total PAHs to be present in the soil. The DPR and Dutch soil intervention value for PAHs in soils is 40mg/kg [14]. The total concentrations of benzo(a)anthracene (1.2862mg/kg) and fluorene (9.5870mg/kg) in the study area exceeded target limits set by FME and DPR but did not exceed the intervention limit. Acenaphthene (0.1805mg/kg), anthracene (0.1545mg/kg), chrysene (0.1288mg/kg), pyrene (0.2782mg/kg) and fluoranthene (0.0885mg/kg) in the study area were within the maximum permissible limits. Comparing the total PAHs across the sampling points, SS-I (2.9380mg/kg), SS-II (1.7224mg/kg), SS-III (1.3046mg/kg), SS-IV (1.6031mg/kg) and SS-V (1.2884mg/kg) exceeded FEPA and DPR allowable limits. SS-VI (0.9635mg/kg), SS-VII (0.9457mg/kg) and SS-VIII (0.9371mg/kg) were within allowable limits of FME and DPR. Site E (SS-IX), the control point with mean concentration of 0.9550mg/kg was within allowable limits of FME, DPR and Swedish EPA. [15] determined the contamination levels of PAHs in his study by classifying soils on the basis of contamination with PAHs. The concentration of total PAHs in soils were divided into four categories; not contaminated with PAHs (< 0.2 mg/kg), weakly contaminated with PAHs (0.2 – 0.6 mg/kg), contaminated with PAHs (0.6 – 10 mg/kg) and heavily contaminated with PAHs (>10 mg/kg). Therefore, soil around Ekeatai River including the control point were categorized as contaminated with PAHs. The study area was contaminated with high molecular weight PAHs (4-ring PAHs) than low molecular weight PAHs (3-ring PAHs).

3.7. Physicochemical Characteristics of Soil

According to [16], the quality of environmental media is usually influenced by its physicochemical properties. It is very important to monitor these parameters for effective environmental management. Soil parameters such as pH and redox conditions largely affect adsorption and desorption of chemical contaminants in the soil [1]. However, these sorption processes are dependent on the soil parameters aforementioned and others. The occurrence, fate, and transport of chemical pollutants in

soils are largely dependent on the properties of the soil and pollutants as well.

Soil pH affects the mobility of contaminants in the soil. The pH values measured in the study area ranged from 4.91 strongly acidic to 6.02 moderately acidic. The pH value for the control point was 5.90 indicating moderate acidity. [17] stated in their work that rise in pH level favours the biodegradation of oil. Studies have shown that higher pH range of 6-9 provides favourable conditions for hydrocarbon mineralization as some microorganisms that degrade hydrocarbons develop best at neutral pH level [18]. Also, the distribution and productivity levels of organisms in the soil are largely determined by physicochemical factors of soil. Therefore, high pH provides a good atmosphere for microorganisms to live and degrade soil contaminants. With this, the level of pollutants will decrease in the soil. Moderately low pH was measured in the study area of which is partly conducive for microorganisms to live and degrade PAHs. This may be the reason for PAH degradation in the study area.

Soil Electrical conductivity (EC) measures the ability of the soil to transmit electrical current. This is aided by the ion contents (soluble salt) of the solution which determines the current carrying capacity of the soil. The electrical conductivity of a soil solution increases as the concentration of ions increase [19]. Soil EC also indicates the availability of nutrients in the soil; therefore, the higher the soil EC, the more negatively charged sites (clay and organic particles) in the soil. Low EC levels (1-10 μ S/m) are usually found in sandy soils with low organic matter levels while high EC levels (20-800 μ S/m) are often found in high clay content soils. EC also influences the mobility and distribution of contaminants in the soil [20]. As EC increases, soil micro-organism activity decreases affecting respiration and degradation of residues. In the study area, the EC levels were higher than the control point which may be attributed to the contribution of PAH retention in the study area.

Soil organic carbon (SOC) serves as the major source of energy for soil microorganisms. It is the measure of the carbon contained in soil organic matter. Soil organic constituents such as soil organic matter (SOM) and soil organic carbon (SOC) play important role in the sorption of soil pollutants [21]. They have high affinity for pollutants. The soil organic matter (SOM) fraction in the soil influences the availability of SOC [18]. Soil that contain 12-18% OC are usually classified as organic soils because of the high percentage organic carbon. The carbon percentage in the soil also determines the percentage of organic matter. A typical soil should contain 4-6% organic matter for normal functioning. Organic matter can also influence the fate and transport of PAHs [22] depending on the type of organic matter in the soil. When organic matter is dissolved, it can alter the mobility of pollutants by forming an association and causing an increase in the solubility of the pollutants. PAH mobility in the soil may be enhanced or diminished depending on the affinity of the dissolved organic matter towards the solid phase [23,24]. Organic matter can also affect the rates of biodegradation and sorption of mobile organic pollutants. In the study area, soil samples II, V, VI, VII and VIII contained high percentage of OC and OM which

may have contributed to lower level of PAHs unlike SS-I which had elevated levels of PAHs contained low percentage of organic carbon and organic matter. Increased nitrogen content in the soil also causes an increase in organic carbon content and this favours soil microorganisms that degrade PAHs in soils.

Soil Cation Exchange Capacity (CEC) measures the soil's ability to attract, retain and exchange cations in the soil. The variability of soil CEC is usually influenced by the percentage and type of clay in the soil, content of organic matter and soil pH. High CEC soils tend to have high organic matter content and high pH levels.

3.8. Correlation between PAH Compounds and the Chemical Properties of Soil Samples in the Study Area

Karl Pearson's between the PAH compounds detected in the study area and the chemical properties of the soil samples indicates that possible relationship existed between them. It showed that the availability and distribution of the PAH compounds were influenced by the soil chemical properties. The result revealed that acenaphthene showed a moderate negative correlation with pH which indicates that an increase in pH decreases the concentration and distribution of acenaphthene in the study area. It was also observed that fluorene showed a moderate negative correlation with pH as well as indicating that an increase in pH decreases the concentration of fluorene in the soil samples. Similarly, fluoranthene correlated negatively with Sulphate (SO₄) and Total Nitrogen. This indicated that the increase in Sulphate (SO₄) and Total Nitrogen percentage reduced the concentration of fluoranthene. Furthermore, the result also revealed a significant positive relationship between anthracene and Sulphate (SO₄) showing that high concentration of sulphate increased the concentration and possible distribution of anthracene.

3.9. Health Risk Assessment of PAH Contamination

PAHs in the environment pose direct threat to living organisms including humans. The major exposure routes of PAHs to humans and other living organisms are through ingestion, dermal contact and inhalation. PAHs are majorly known to be carcinogenic, teratogenic, genotoxic, cytotoxic and immune-suppressants [25] and cause both acute and chronic health effects in humans. The river may likely be contaminated due to runoff from the soils into the water body. This water body is often used by the dwellers in the study area for different purposes including domestic purposes and may pose health risk to them and the aquatic ecosystem. Consumption of crops grown on PAH contaminated soils and eating meat roasted with tyre may cause health risk.

In this study, ingestion of soil was considered as the pathway of exposure of PAHs for human health risk assessment. The benzo(a)pyrene (BaP) toxicity equivalent (TEQ) concentration was calculated using the BaP toxic equivalent factors (TEFs) of individual PAHs detected in the study area. BaP is considered by World Health

Organization (WHO) as the potential reference for other PAH toxicity and is often used as a general indicator for PAHs contamination [11]. It is calculated as

$$BaP_{TEQ} = \sum [C \times TEF]$$

Where, C = the concentration of individual PAH (mg/kg), TEF = the toxic equivalency factor of the individual PAH. The BaP_{TEQ} for ΣPAH_{carcinogen} (carcinogenic PAHs) ranged from 0.00013 – 0.13 mg BaP_{TEQ}/kg with the mean of 0.07 mg BaP_{TEQ}/kg.

Similarly, direct contact with PAHs contaminated soil was also considered as a pathway for exposure of PAHs for human health risk assessment. The Benzo(a)pyrene total potency equivalents (BaP_{TPE}) was used to assess the human health risk of PAHs from direct contact with contaminated soil. The BaP_{TPE} is known as the sum of estimated cancer potency relative to BaP for all potential carcinogenic PAHs. It is calculated as

$$C \times PEF,$$

Where, C = Concentration of individual PAH in the sample, PEF = BaP Potency Equivalent Factor.

The Canadian government stipulated that the human health-based soil quality guidelines for PAHs based on Incremental Lifetime Cancer Risk (ILCR) through direct soil exposure as 1 in 1,000,000 (10⁻⁶) and 1 in 100,000 (10⁻⁵) as 0.6 mg/kg and 5.3 mg/kg [26]. The BaP_{TPE} calculated in the study area was 0.13mg/kg and was lower than the soil quality guideline of the Canadian government.

The Index of Additive Cancer Risk (IACR) which assesses the potential threat to potable groundwater [26,27] from leaching of carcinogenic PAHs was equally evaluated and the value was 3.96mg/kg. The IACR is usually assessed following the Canadian soil quality guidelines for the protection of the environmental and human health. The IACR recommended safe guideline level for the protection of potable water is ≤ 1 and the IACR of the study area was above the recommended safe guideline level. This indicates possible threats to the potable groundwater of the study area.

Furthermore, the PAH concentrations in the study area were compared with standards of 1mg/kg, 1.5mg/kg and 5mg/kg stipulated by Denmark, the Netherlands and Australia [28,29,30] soil quality guidelines for the protection of environment and human health to determine the level of toxicity of PAHs in the study area. The total PAH concentration in SS-I to V exceeded 1mg/kg acceptable limit but SS-VI to IX was within acceptable limits. The total concentration of fluorene (9.5870mg/kg) around Ekeatai River exceeded the Denmark, Netherlands and Australia soil quality guidelines while other PAHs were within permissible limits.

However, environmental health risk was also assessed without considering the carcinogenic effects of PAHs in humans and the ecosystem; thus, the non-carcinogenic PAHs effects were considered. The ecotoxicological health risk of PAHs was assessed by comparing PAH concentration levels with the soil quality guidelines from National Oceanography and Atmospheric Administration (NOAA) of USA and Canadian government. NOAA and Canada recommended environmental soil quality guidelines for individual PAHs is 0.7mg/kg – 10mg/kg.

The mean levels of individual PAHs observed in the study were lower than the recommended guidelines except fluorene whose total concentration of 9.5870mg/kg was within acceptable limit. They indicated no environmental health risk and adverse effects on the soil biota.

4. Conclusion

Soil serves as one of the major repository for contaminants and this is done by concentration and accumulation of the contaminants from various sources. Environmental conditions (including soil types) and the degradability of the pollutants released contribute to high levels of soil pollution which pose a variety of threats to human health, animals and the ecosystem. Researches are being carried out on soil pollution because it has gradually become a major challenge and great concern considering its devastating effects. Contamination is greatly attributed to urbanization and industrialization. This study has revealed that the soils around Ekeatai River contain PAHs and some locations are contaminated with PAHs in varying concentrations. Therefore, the continuous release of PAH compounds in the study area from various sources will cause greater levels of PAHs in the future. It is important to monitor the levels of these chemical compounds in order to identify areas of high pollution for effective environmental management.

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