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Effects of soil pH, Total Organic Carbon and texture on fate of Polycyclic Aromatic Hydrocarbons (PAHs) in soils

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are a group of quotidian organic compounds having between two and six condensed aromatic rings braced in angular, cluster or linear forms possessing hydrogen and carbon atoms only. This work aims to evaluate the physicochemical characteristics of soil as determinants of PAHs distribution and fate. The study area is situated on the Benin River beneath the convergence of Jamieson River and River Ethiope. The weather and climatic conditions of the area are of the Niger Delta region. Sixteen priority PAHs were determined in ten sample stations. Upon extraction, purification and quantification of PAHs was done using GC-FID. According to the methods of Walkey-Blacks, Black and Bouyoucus, soil total organic carbon, pH and texture were analyzed respectively. Four replicate samples were chosen to create a composite and used as quality control. Kruskal-Wallis test with tied rank was used to determine a causative correlation between soil physicochemical parameters and ∑PAHs. Results showed that the study area is contaminated with high concentration of PAHs ranging from 60.76 – 271.11 239 $\mu g.g^{-1}$ with higher percentages of HPAHs i.e. PAHs with LogKow>4.0. It is observed that observed alkaline pH favour significant fungal, asperigellus and microbial degradation of PAHs, and hinder photo-catalytic degradation. However, acidification with elemental sulfur, ferrous sulfate and aluminum sulfate could enhance photo-catalytic degradation. Results of TOC and soil structure do not favour significant degradation of HPAHs. Kruskal-Wallis tied rank test revealed that there was a positive significant difference between pH, TOC, percentage clay, and silt fractions with ∑PAHs concentrations since calculated K is greater than critical $K_{0.05}$, $P<0.05$ except percentage of sand fractions and ∑PAHs with $P>0.05$. A substantial percentage of these PAHs have no anthropic origin and are characterized as having high lipo-affinity, semi-volatility and resistance to biotic and/or abiotic transformations. Due to edaphic factors the observed HPAHs may partially degrade with the consequent formation of highly toxic by-products. Therefore, oral or dermal ingestion of soil in the study area may cause significant exposure of the human population to these PAHs. Risk assessment and probable toxicity effects on animal diversity should be carried out in soil samples of the study area.

Keywords: Soil TOC, pH and Texture, PAHs Availability, Degradation and Fate.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of quotidian organic substances having between two and six condensed aromatic rings fixed in angular, cluster or linear forms and bearing hydrogen and carbon atoms only, (Zeng *et al.,* 2000; WHO, 2002; Emoyan, *et.al.,* 2015c). Several research findings have established that there are various soil concentrations of PAHs from point and/or diffuse contamination, (Soleimani *et al.,* 2013; Valentin *et.al.,* 2013). They are naturally produced during forest fires and volcanic eruptions. Anthropogenically, PAHs originate mainly from partial combustion of fossil fuel, wood, industrial, domestic and commercial waste, automobile fumes, petroleum, and derivative spills, (Dabastanni and Ivanov, 1999). Polycyclic aromatic hydrocarbons are non-dipole hydrophobic compounds that are soluble in water. They decrease with increase in molecular weight and show low affinity for fine particulate matter hence sediment and soil are major sinks for PAHs, (Dabastanni and Ivanov, 1999; CCME, 2008). Henry's Constant, Octanol-Water Partition Coefficient (Kow), Organic Carbon-Water Partition Coefficient (Koc), aqueous solubility and vapour pressure are distinct chemical variables that are useful in predicting bioaccumulation, multimedia-partitioning behavior, environmental fate, resistance to bio-chemical degradation and toxicity of these persistence organic compounds (POC), (CCME, 2008; WHO, 2002; Emoyan *et al.,* 2015ab). Polycyclic aromatic hydrocarbons have carcinogenic properties, affect human reproduction as well as giving rise to respiratory toxicity. They are, therefore, grouped as 'priority pollutants' (CCME, 2008).

Soil is an unconsolidated biogeochemical material on the surface of the earth that supports evidence of life existence. Its composition includes: organic and inorganic elements/matter, air and water (Haygarth and Ritz, 2009; Robinson *et. al.,* 2012; Valentin *et al.,* 2013). It provides the

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essentials of fiber, fodder, food and fuel. Soil is also involved in ecosystem services such as reclamation of carbon, biological control of pests, screening and storage of water and regulation of the atmosphere, (Haygarth and Ritz, 2009; Robinson *et al.,* 2012; Valentin *et al.,* 2013). Therefore, its quality is important to the humans and environment. Soil physicochemical properties such as pH, TOC, sand, clay and silt are also relevant in the evaluation of PAHs behavior in terms of bioavailability, environmental fate, multi-media partitioning behavior, and resistance to biotic and abiotic degradation, (CCME 2008; Emoyan *et al.,* 2015a).

The behaviour of hydrophobic contaminants in soil is basically governed by a variety of complex processes which include; volatilization, biological and chemical degradation, sorption-desorption, runoff, leaching and uptake by plants. These processes directly or indirectly determine the rate and transport of these PPs within the soil and transport from air to food, soil or water. These processes are determined by the physicochemical properties of the contaminants, and the biochemical and hydraulic characteristics of the soil, (Okere and Semple, 2012; Robinson *et al.,* 2012)

Anthropogenic or natural soil contamination could compromise the ability of the natural ecosystem to provide its essentials of fodder, fiber, food and fuel. The evaluation of soil physicochemical characteristics is useful to evaluating the vulnerability of PAHs to abiotic and or biotic degradation, toxicity potentials and their effect on humans since research has shown that colloidal soil particles <0.002 nm have a larger surface area with high tendency to bind more to organic contaminants. Similarly, TOC usually exhibits a positive correlation with organic contaminants while biochemical degradation of organic contaminants such as PAHs depends on the pH condition of the environment. This investigation is aimed at determining soil physicochemical characteristics as determinants of PAHs degradation and fate which is of significant interest in bioremediation.

2. Materials and methods

2.1. Study Area Description

The study location is situated on the River Benin beneath the convergence of River Jamieson and Ethiope, (Emoyan, 2014; Emoyan *et al*., 2015abc, and Opafunson, 2007). It has an approximate human population density of 142,652 with geographical coordinates of Latitude 5^0 54' – 5^0 9' N and Longitude $5^0 40^{'}$ - 5^0 $66^{'}$E as shown in Figure 1. The weather and climatic conditions are of the Western Niger Delta located in the Gulf of Guinea on Latitude 3^0N and 6^0N Longitude 5^0 and 8^0E, i.e. rain forest zone, high humidity and temperature.

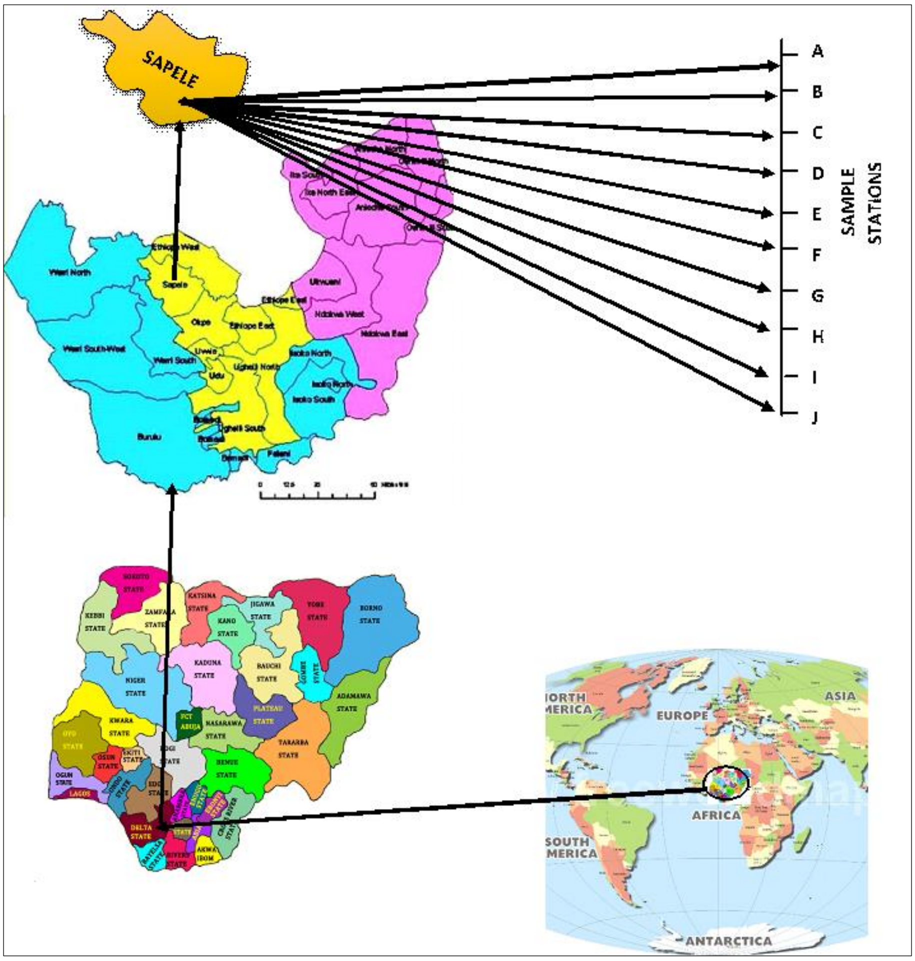

Figure 1. Map of the study area and locations of sampling stations

2.2. Sample Collection and Preparation

Soil samples were monitored in top and bottom soil for eight months in ten sample sites (160 samples) as described in Figure 1. Residual roots and stones were separated from each soil sample and stored in black polyethylene bags in the dark to prevent microbial degradation, evaporation and photo-oxidation of analytes before digestion, extraction and quantification and analyses, (OIEWG, 1999; Cavalcante *et al*., 2009; Emoyan, 2014; Emoyan *et al*., 2015abc).

2.3. Extraction and Analysis

The method of Cavalcate *et.al.,* (2009) as modified in Emoyan, (2014) and Emoyan, *et.al.,* (2015a,b,c) was used. Thus 10 g of dried sample was extracted continuously with 60 mL of CH_2Cl_2 for 8 hrs. As internal standard, 4 deuterated PAHs mixtures of d12-perylene, d10-phenanthrene, d10-acenaphthene, and d12-chrysene were added to the sample. Methylene chloride was removed using rotary evaporator at 30-35 °C thereafter, the extract was purified by solid phase extraction after retrieval with 3 portions of 1 mL n-hexane. Using 8 g of Aluminum Oxide (Al_2O_3), hydrocarbons and other hydrophobic contaminants were removed using 40 mL of n-hexane after the addition of the sample to the column. Elution of PAHs was done using 40 mL of CH_2Cl_2 and the resultant solute was re-dissolved in 1 mL of isooctane after drying. Polycyclic aromatic hydrocarbons determination was carried out using interfaced flame ionization detector gas chromatograph (*Varian model 300*). The initial oven temperature was 60 °C for 10 min, followed by a step-wise increase of 5 °C min^{-1} up to 120 °C and finally a step-wise increase of 3 °C min^{-1} up to 300 °C. The injector and detector temperatures were 200 °C and 300 °C, respectively. Concentration evaluation was based on Supelco and Merck using the internal standard. The detection limit is 0.001 µg g^{-1}. Concentration of PAHs was quantified and qualified by extrapolating from the given standards.

2.4. Total Organic Carbon

The method of Walkey-Black, (1934) was used. Thus, 1 g of soil sample was weighed into 200 mL Erlenmeyer flask. Ten milliliters of 0.5 M $K_2Cr_2O_7$ solution was added to the flask. After gentle stirring, 20 mL of Conc. H_2SO_4 was added and shaken for 30 min. After the addition of 100 mL of H_2O to the solution, 10 mL of O-phosphoric acid was added to the solution. Finally, 4 drops of phenolphthalein indicator were added, and the solution was titrated against 0.25 M of Ammonium Iron (II) Sulfate $Fe(NH_4)\ SO_4$. A control was similarly treated.

2.5. pH (Soil pH in water)

The method of Black, (1965) was used, thus 20 g of 2mm sieved and air-dried sample was added into 50 mL beaker and 20 mL distilled water was added and allowed to stay for 30 min with occasional stirring with a glass rod, the electrode of a calibrated pH meter (pH 9.2 and pH 4 buffer) was inserted into the partially settled suspension and the pH was measured.

2.6. Soil Texture (Pipette method)

The method Bouyoucus, (1951), was used, thus 50 g of dry soil sample was added into 100 mL beaker and 5 mL of H_2O_2 was added to remove organic matter. Finally, 5 mL of H_2O_2 was added to the mixture until oxidation is complete. After drying the sample on a hot plate, 50 mL of 5% calgon solution was added. Using a ground shaker, the mixture was shaken for 2 hours. Using a 0.053 mm sieve, the sample was washed into a 1-liter measuring cylinder until it became clear. The final volume of the cylinder was noted. After shaking the cylinder vigorously, 20 mL of the colloidal solution was oven-dried, and the weight of the dry sample was noted, this is the weight of the clay and silt. After 2 hours, another 20 mL of the remaining sample was collected and oven-dried. The weight was noted, this is the weight of clay.

2.7. Quality Control

Reagents are of chromatographic grade. Equipments, containers and apparatus were cleaned to avoid cross contamination of analytes during sampling and preparation. Four unit-samples were added to form a unit.

2.8. Approach to Analysis of Data

To relate soil physicochemical characteristics to the concentrations of PAHs, a non-parametric analysis of variance i.e. Kruskal-Wallis test with tied rank, H=12n(n+1)∑ki=1R2ini−3(n+1) was performed on the mean data using *Zigma Plot Version 13*.

3. Results and discussion

3.1. Distribution of Physicochemical and PAHs Properties

The mean physicochemical properties and mean PAHs concentrations of 160 samples are summarized in Table 1 and Figures 2, 3, and 4. Results showed that the physicochemical properties are distributed and presented in the following order of minimum to maximum: pH I < G, TOC F < G, sand F < I, clay I < D and Silt H < F. Similarly, the PAHs are distributed in sample stations in the following order of minimum to maximum: Nap D > A, Acy F & J > G Ace H > A, Flu G > C, Phe D > B, Ant A > F Flt C > I, Pyr G > I Chr G > I, B[a]a A > I, B[a]p G > I, B[b]f H > I, B[k]f H > I, B[ghi]p E > I, I[123cd}p F > I, D[ah]a F > H and ΣPAHs G > I.

3.2. pH and PAHs Fate

The study area recorded mean alkaline pH range of 7.18 and 7.53 with mean PAHs range of 60.76 – 271.11 239 µg g^{-1} (Figure 2). The pH range in the study area has profound environmental – biodegradation – effects on the sixteen PAHs. In the environment PAHs are exposed to degradation via abiotic and or biotic routes, (Earl *et al.*, 2003). In sediments or soil, microbial degradation or metabolism is the major routes of PAHs, (WHO/IPCS, 1998), however, microbial degradation or metabolism is restricted to bio-available fractions in soil-pore water or surfaces of soil particles, (Miller and Alexander, 1991).

Table 1. Mean Concentration Range of PAHs in the Study Location.

Soil PP					**SAMPLE STATION**	
					Min$_c$	**Max$_c$**
pH					**I** 7.18	**G** 7.53
TOC					**F** 3.39	**G** 7.74
Sand					**F** 74.44	**I** 77.40
Clay					**I** 21.61	**D** 24.13
Silt					**H** 0.80	**F** 2.19
PAHs			**Properties**			
	Ring	**t½**	**MF**	**MW**	**Min$_c$**	**Max$_c$**
Nap	2	6	$C_{10}H_8$	128.18	**A** 0.56	**D** 7.31
Acy	3	6	$C_{12}H_8$	152.20	**G** 0.67	**F & J** 2.43
Ace	3	6	$C_{12}H_{10}$	154.20	**A** 0.83	**H** 6.98
Flu	3	6	$C_{13}H_{10}$	166.23	**C** 0.70	**G** 12.91
Phe	3	6	$C_{14}H_{10}$	178.24	**B** 2.77	**D** 33.80
Ant	3	6	$C_{14}H_{10}$	178.24	**F** 0.33	**A** 40.61
Flt	4	7	$C_{16}H_{10}$	202.26	**I** 0.73	**C** 14.25
Pyr	4	7	$C_{16}H_{10}$	202.26	**I** 2.60	**G** 18.88
Chr	4	7	$C_{18}H_{12}$	228.30	**I** 1.26	**G** 24.48
B[a]a	4	7	$C_{18}H_{12}$	228.30	**I** 0.51	**A** 8.521
B[a]p	5	7	$C_{20}H_{12}$	252.32	I 0.23	G 23.97
B[k]f	5	7	$C_{20}H_{12}$	252.32	**I** 1.06	**H** 14.03
B[k]f	5	7	$C_{20}H_{12}$	252.32	**I** 3.51	**H** 16.18
B[ghi]p	6	7	$C_{22}H_{12}$	276.34	**I** 1.94	**E** 129.93
I[123cd}p	6	7	$C_{22}H_{12}$	276.34	**I** 1.37	**F** 32.87
D[ah]a	6	7	$C_{22}H_{14}$	278.35	H 8.19	F 41.57
∑PAHs					**I** 60.76	**G** 271.19

Were n= 8

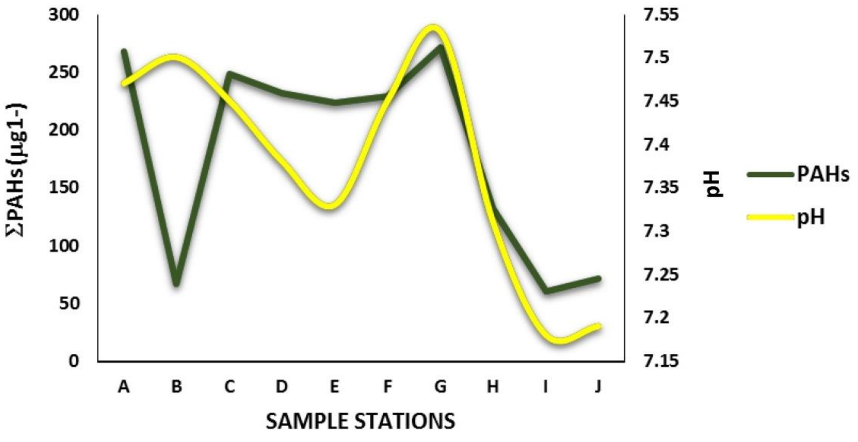

Figure 2. Distribution of pH and ∑PAHs in the study area

Pawar *et al.,* (2010) and Okere and Semple (2012), had argued that greater fungal populations are active in soil acidic pH condition. However, soil alkaline pH of 8 and 8.5 had higher population compared to neutral pH of 7.0 and 7.5 with lowest fungal population. Similarly, in acidic soil pH *Pencillium* species predominated with lower *Aspergiluss* population. While in alkaline soil pH of 8.0 and 8.5, *Asperigellus* was predominant and *Pencillium* was not detected, (Pawar *et al.,* 2010, and Okere and Semple, 2012). Research has shown that soil enzymatic actions are high at soil pH of 7.18 – 7.53, (Pawar *et al.,* 2010). This shows that soil pH in the study area could favor microbial community for the degradation of PAHs. However, observed soil pH would not favour photo-catalytic degradation since optimal photo-catalytic conditions occur in acidic pH of 6.5, (Pawar, *et al.,* 2010; Yang *et al.,* 2010). Therefore, the rate of photo-catalytic degradation of observed PAHs could be increased by modification of soil with elemental sulfur as it is oxidized by microbes to produce SO_4^{2-} and H^+ ions, causing acidic pH. Similarly, aluminum Sulfate $Al_2(SO_4)_3$ and ($FeSO_4$) could be applied to the acidic cations Al^{3+} and Fe^{2+}, (Elaton *et al.,* 2001).

Kruskal-Wallis tied rank test revealed that there was a statistically suggestive difference between pH and ∑PAHs concentrations since calculated K is greater than critical $K_{0.05}$ (i.e. 14.30 > 3.84), P < 0.05, as shown in Table 2.

3.4. TOC and PAHs Fate

Results show that there are high concentrations of PAHs, with greater percentages of HPAHs as shown in Table 1 and Figure 3. This could be related to the distribution coefficient - Octanol Water (KO_W), Solubility, half-life ($t^1/_2$), Henrys' constant and Bio-concentration Factor (BCF) of PAHs. The characteristic distribution of LPAHs and HPAHs in the study area showed that soil TOC favor HPAHs adsorption on active surfaces of the soil which in turn delayed mobilization and leaching of HPAHs. Several studies have shown that organic compounds – PAHs, PCB, dioxine etc – have high level of Kow and low solubility would most likely be retained by soil surface and less susceptible to environmental processes (Valentin *et al.,* 2013; Petruzzelli *et al.*, 2010). Also, biodegradation and volatilization are slow for HPAHS over LPAHs as observed in Table 1. Several characteristics were correlated with the degradation period, i.e. $t^1/_2$ of HPAHs are related to the leaching pathway and persistence of HPAHs in the study area. Also, PAHs with LogKow>4.0 are rarely mobilized, hence Table 1 shows high percentage of HPAHs. The high percentage of HPAHs in all simple stations could be ascribed to near zero response of HPAHs to photolysis, hydrolysis, volatilization and oxidation. Several researches has shown that these reactions mostly affect molecules having simple molecular structure with reduced complexity such as PAHs<four ring and phenols, (Petruzzelli *et al.,* 2010). Kruskal-Wallis tied rank test revealed that there was a statistically positive correlation between the amount of TOC and ∑PAHs concentration since calculated K is greater than critical $K_{0.05}$ (ie. 14.29 > 3.84), P<0.05, as shown in Table 2.

Table 2. Comparison of Tied-Kruskall Wallis Test

Comparison	Observed value	Critical value	DF	P-value	alpha
pH- ∑PAHs	14.30	3.84	1	<0.05	0.05
TOC-∑PAHs	14.29	3.84	1	<0.05	0.05
Sand-∑PAHs	2.30	3.84	1	>0.05	0.05
Clay-∑PAHs	14.29	3.84	1	<0.05	0.05
Silt-∑PAHs	14.29	3.84	1	<0.05	0.05

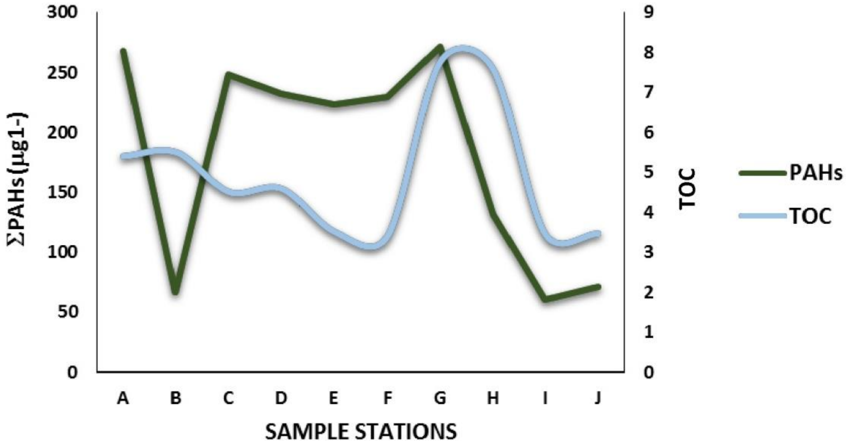

Figure 3. Distribution of TOC and∑PAHs in the Study area

3.5. Particle size and PAHs Fate

The particle size distribution obtained (Table 1 and Figure 4) indicates that the soil consists of about 77%, sand fractions with clay and silt having about 24% and 2% respectively. Results of sand fractions in Figure 4 show that there is high concentration of PAHs in all sample stations except stations B, I and J, there is similar occurrence in clay and silt fractions. Generally, fine soil particles (<0.002 nm) have a larger surface area, hence fine soil distribution is a measure of binding or adsorption of contaminants than large particles, (Lewis, 2012).

Research has shown that the characteristics of soil on the biological, chemical and physical, characteristics of each profile, and colloidal-size fractions (particles<0.002 nm) are major sites of chemical reactions in soil due to the larger specific surface area compared to sand fractions. Hence the adsorption of organic contaminants such as PAHs in soil mostly occur in the clay and silt fractions, (Lewis, 2012). Therefore, the clay and silt components are responsible for the sorption of PAHs and restrict their availability for biological and chemical degradation leading to high concentrations of PAHs in sample station A, C, D, E, F, G and H. However, the relatively low concentrations of PAHs in stations B, I and J could be as result of favorable environmental factors since the characteristics/behavior (rate and direction) of PAHs in soils are governed by a variety of complex dynamics such as; biological, chemical, degradation, run-off and leaching, sorption-desorption, volatilization and uptake by plants, (Petruzzelli *et al.,* 2010). Kruskal-Wallis test showed a positive significant difference between the percentage of clay fractions and ∑PAHs concentrations, and percentage of silt fractions and ∑PAHs concentrations since calculated K is greater than critical $K_{0.05}$ (ie. 14.29>3.84 and 14.29>3.84) respectively, P<0.05 as shown in Table 2. However, Kruskal-Wallis test revealed that there is no significant correlation between the percentage sand fractions and ∑PAHs concentration since calculated K is less than critical $K_{0.05}$ (ie. 2.28>3.84), P>0.05 (Table 2).

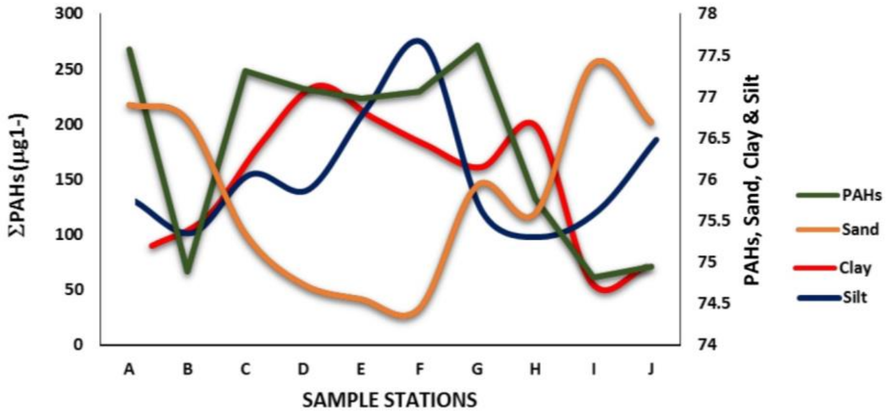

Figure 4. Distribution of Sand, Clay, Silt and ∑PAHs in the study area

4. Conclusion and Recommendations

This study shows that the study area is contaminated with varied degrees of PAHs with LogKow>4.0 and low solubility and high concentration of HPAHs over LPAHs. Though observed soil pH would favour microbial degradation of PAHs, combined results of pH TOC and soil structure could render PAHs inaccessible for microbial population and significantly limit photo and biochemical degradation. The bioavailability of these contaminants decrease with increase in concentration of TOC, neutral pH and high percentage of silt. Hence persistence in soil would increase the potential for human and environmental risk of these PPs in the study area. Kruskal-Wallis test also showed that there was a positive significant difference between pH, amount of TOC, percentage clay and silt fractions, and ∑PAHs concentration since calculated K is greater than critical $K_{0.05}$ P<0.05 except percentages of sand fractions and ∑PAHs, with P>0.05. Substantial percentages of these POP have anthropic origin and are characterized as having high lipo-affinity, semi-volatility and resistance to biotic and/or abiotic transformation. Due to edaphic factors, the observed HPAHs may not absorb but can partially degrade with the consequent formation of highly toxic by-products. Therefore, dermal or oral ingestion of soil in the study could cause significant exposure of human population to these PPs. Three-ways bioavailability index evaluation utilized in this study showed PAHs bioavailability and mobility which is of significant interest in bioremediation. Due to transport potentials, the observed PAHs under saturated order, could pose human and environmental risk. Results from this research could be used for hazard identification and risk assessment of probable toxicity effects on animal diversity.

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