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Levels of polycyclic aromatic hydrocarbons in soils situated around fuel stations in Nibo, Awka South L.G.A., Anambra state

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ABSTRACT

Studies were carried out to investigate the levels of selected polycyclic aromatic hydrocarbons in the soils situated around fuel stations in Nibo, Awka South Local Government Area of Anambra State following preparation procedures and Gas chromatographic instrumentation. The soil samples at site P1 had mean levels of 0.18±0.06, 0.11±0.02, 0.27±0.03. 0.40±0.17 and 0.20±0.06mg/kg for anthracene, phenanthrene, chrysene, pyrene and benzo(a) anthracene respectively. Soil samples at site P2 had mean levels of 0.49±0.06, 0.16±0.01, 0.22±0.04, 0.02±0.01, 0.27±0.06 and 0.39±0.05mg/kg for anthracene, acenapthene, phenanthrene, chrysene, pyrene and benzo(a)anthracene respectively. The control soil samples had mean levels of 0.04±0.02, 0.02±0.01, 0.07±0.02 and 0.06±0.01 mg/kg for phenanthrene, chrysene, pyrene and benzo(a)anthracene respectively. The mean levels of the investigated PAHs in the soil samples at sites P1, P2 and control were statistically significant and within the recommended threshold limits. The soil samples predominantly had higher mean levels of the investigated high molecular weight PAHs than the low molecular weight PAHs. The values obtained from the diagnostic ratios of the investigated PAHs suggests that the sources of contamination of the soil samples with PAHs were predominantly pyrolytic than petrogenic.

Key Words: Soil Samples, Polycyclic Aromatic Hydrocarbons (PAHs), Diagnostic ratio, Fuel Station and Nibo

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are common environmental pollutants produced mainly as a result of the partial combustion of organic materials (examples include coal, oil, petrol and wood). According to [1]. Polycyclic aromatic compounds are mainly colourless, white or pale yellow solids. Polycyclic aromatic hydrocarbons can be divided into two categories; low molecular weight PAHs, composed of less than four aromatic rings (e.g naphthalene, acenapthene, fluorene, phenanthrene and anthracene) and high

molecular weight PAHs, composed of four or more rings (e.g pyrene, chrysene, benzo(a)pyrene, benzo(a)anthracene, indeno(1, 2, 3, cd) pyrene, benzo(k) fluoranthene). The chemical stability, low solubility and high sorption capacity of high molecular weight PAHs contributes greatly to their persistence in the environment [2]. All major industries using fossil fuels in the production of goods or energy generate PAHs and higher concentrations are usually found near heavy industries. Forest fires, volcanic eruptions and decaying organic matter are all natural sources of PAHs [3, 22]. Pyrogenic, petrogenic and biological sources of exposure are the three major sources of PAHs to the environment [1]. Polycyclic aromatic hydrocarbons are produced whenever organic substances are burned at high temperatures under sparse or no oxygen conditions. Pyrogenic PAHs are formed through combustion of organic substances at temperatures ranging from 350 to 1200^{o}C [4]. Polycyclic aromatic hydrocarbons generated during crude oil progression, and including other similar processes are petrogenic while those produced by specific plants during degradation of vegetative matter are biological [5, 23]. The physicochemical factors that evaluates PAHs absorption and distribution in man, is similarly attributed to its presence in foods. Example of such factors are the relative solubility of PAHs in water and organic solvent. [6] stated that such factor as solubility governs their ability for transport and distribution between different environmental partitions and their ingestion and build up by living organisms. Polycyclic aromatic hydrocarbons are lipophilic and generally have a poor aqueous solubility [7]. In the terrestrial environment, soil are considered the primary steady sink for PAHs, since they are easily uptakened by organic matter in the soil and are difficult to degrade [8]. The soil is an important indicator that serves as a reservoir for the retention of PAHs in the environment [9]. Polycyclic aromatic hydrocarbons are persistent and hydrophobic, which makes them enrich deeply in the soil matrix adsorbed in the soil [10]. According to [8], several PAHs are perceived as environmentally problematic, based on their toxic nature and tend to accumulate in humans. According to [11], owing to PAHs documented mutagenic, carcinogenic and persistent properties, there is presently an increasing global concern about their environmental and human health effects. Embryo-toxic effects of PAHs have been described in experimental animals exposed to PAHs such as benzo(a) anthracene, benzo(a) pyrene and naphthalene [1]. [12] observed that laboratory studies conducted on mice have shown that absorption of high levels of benzo(a) pyrene during pregnancy resulted in birth defects and decreased bodyweight in the offspring. Equally [12], reported that the threat to PAH pollution during pregnancy is related to adverse birth outcomes including low birth weight, premature delivery, heart malformations, low IQ at age three, childhood asthma and DNA damage. Several studies have assessed the pollution and health risks of soil PAHs in the vicinity of petrol stations across Nigeria and other parts of the world [13, 14]. However, no such information in data form exists to the best of my knowledge on the levels of PAHs in soils around fuel stations in Nibo, a town that has emerged recently as a fast developing semi-urban area within Awka South Local Government Area of Anambra State. Such environmental data assessment is important in an agrarian community as Nibo, where the pace of development have seen an indiscriminate siting of fuel stations and therefore investigating the risk of exposure to PAHs by the people, who see these developments as beneficial to the economy of the town and the people there-in is very imperative. Such information would help enrich the baseline information on the levels of PAHs in the soils around petrol stations in Anambra State, South-Eastern Nigeria.

2. MATERIALS AND METHODS

Five (5) samples each were collected from three locations denoted with P1, P2 and control. P1 and P2 represents soil samples from fuel stations situated very close to places of intense farming and residential activities. The control was soil samples from a place very far from economic activities such as fuel stations and also where no such activity takes place.

The soil samples were collected using stainless hand held auger and wrapped in neatly labelled aluminum foils and taken to the laboratory for analysis. The samples were collected at depth 0 - 20cm. The reagents used for the analysis were of high purity and of analar grade.

Preparation and Analysis

The soil samples were prepared for the analysis according to the procedures of [15]. The soil samples were sieved and oven-dried prior to the analysis. 10g of the soil samples each was taken and extracted for 72hr using about 100ml combination of hexane-acetone (1:1) in a soxhlet apparatus. The extract was decanted into a clean dried round bottom flask and transferred to the rotatory evaporator to be concentrated to 5ml. This was then fractionated with a fractionating column of silica gel into an aromatic portion using dichloromethane. The dichloromethane fractionates was transferred to a rotator evaporator for reconcentration to 5ml. The 5ml reconcentrate fractionates was transferred to the Gas Chromatography vials, corked and subsequently, the levels of anthracene, acenapthene, phenanthrene, chrysene, pyrene, benzo(a) anthracene and flouranthene were analyzed using Gas Chromatography(G.C 6890 Series).

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The recovery tests of the PAHs were performed in triplicates. The mean results ranged from 82 to 97% and this represents an acceptable recovery experiment according to [16].

Statistical Analysis

The data obtained were represented in mean±standard deviation and subjected to one way analysis of variance (ANOVA) at 5% confidence level using IBM SPSS version 22.0.

3. RESULTS AND DISCUSSION

Mean levels of the investigated PAHs in soils situated around fuel stations in Nibo, Awka South L.G.A., Anambra State.

Sample site	Soil Depth (cm)	Mean levels of the PAHs (mg/kg)							p - value
		Anthracene	Acenapthene	Phenanthrene	Chrysene	Pyrene	Benzo (a) anthr acene	Flouran thene	
P1	0- 20	0.18 ± 0.06	-	0.11 ± 0.02	0.27 ± 0.03	0.40 ± 0.17	0.20 ± 0.06	-	0.02
P2	0- 20	0.49 ± 0.06	0.16 ± 0.01	0.22 ± 0.04	0.02± 0.01	0.27 ± 0.06	0.39 ± 0.05	-	0.01
Control	0- 20	-	-	0.04 ± 0.02	0.02 ± 0.01	0.07 ± 0.02	0.06 ± 0.01	-	0.02

Result of Table shows that at soil depth 0-20cm of soil samples P1, the mean levels of anthracene, phenanthrene, chrysene, pyrene, benzo(a) anthracene and fluoranthene were 0.18±0.06, 0.11±0.02, 0.27±0.03, 0.40±0.17 and 0.20±0.06 mg/kg respectively. The mean levels of the investigated PAHs decreased in the soil samples P1 in the following order; pyrene> chrysene> benzo(a) anthracene > anthracene > phenanthrene as shown in Figure 1.

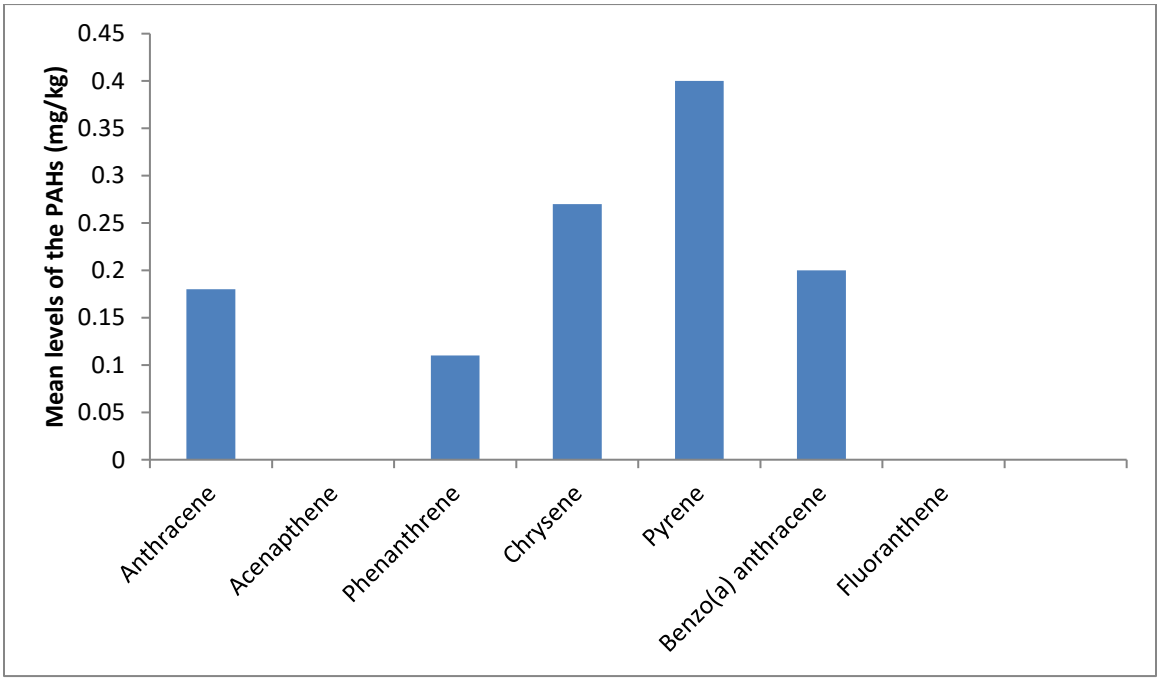

Fig 1: Bar chart representation of the mean levels of the PAHs in the soil samples at P1 situated around fuel stations in Nibo, Awka South L.G.A., Anambra State.

This result therefore indicates that there was a higher contamination of the soils at P1 with the investigated high molecular weight PAHs than the low molecular weight PAHs. This observation is therefore a worrisome development considering the toxicities associated with exposure to high molecular weight PAHs. However, the mean levels of the investigated PAHs in the soil

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samples at P1 were within the recommended permissible of 1.5mg/kg set by [17, 18]. The mean levels of the PAHs at soil samples P1 were statistically significant.

From the result of Table 1, the mean levels of anthracene, phenanthrene, chrysene, pyrene and benzo(a) anthracene in the soil samples at P2 were 0.49±0.06, 0.16±0.01, 0.22±0.04, 0.02±0.01, 0.27±0.06 and 0.39±0.05mg/kg respectively. The order of decrease of the PAHs in the samples at P2 were anthracene> benzo(a) anthracene>pyrene>phenanthrene>acenapthene>chrysene as shown in Figure 2.

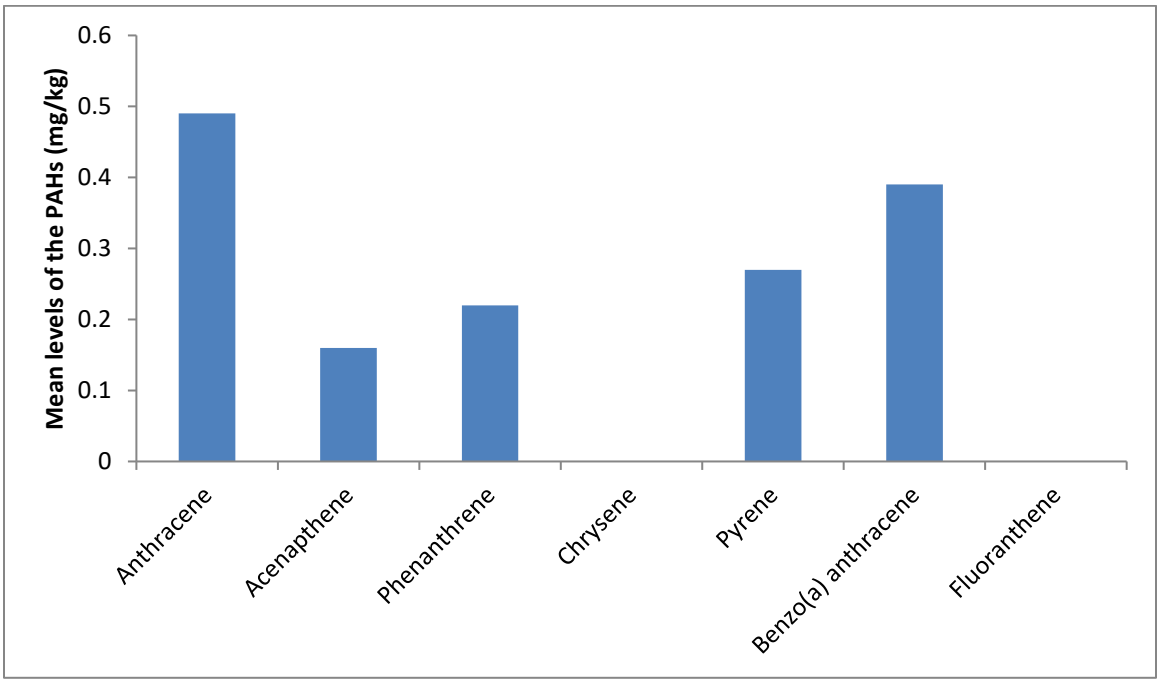

Fig. 2: Bar chart representation of the mean levels of the investigated PAHs in the soil samples at P2 situated around fuel stations in Nibo, Awka South L.G.A., Anambra State.

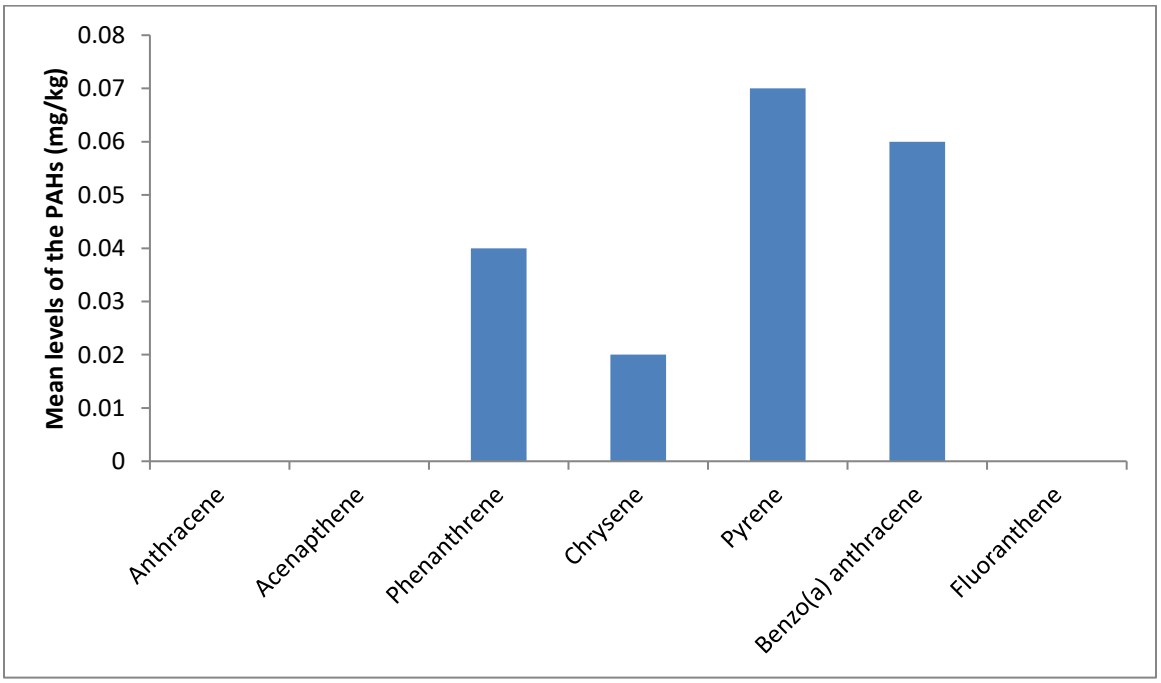

Fig. 3: Bar chart representation of the mean levels of the PAHs in the control soil samples in Nibo, Awka South L.G.A., Anambra State.

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This result indicates that a comparable levels of contamination of the soil samples with the investigated high molecular weight and low molecular weight PAHs. Both sites P1 and P2 had economic crops grown on them and therefore the possibility of the uptake of these PAHs by the plants through their roots remains very high. The mean levels of the PAHs in soil samples at P2 were within the recommended threshold limits and equally differed significantly at $p < 0.05$. Result of Table 1 shows that the mean levels of phenanthrene, chrysene, pyrene and benzo(a) anthracene in the control soil samples were 0.04±0.02, 0.02± 0.01, 0.07±0.02 and 0.06±0.01mg/kg respectively. The investigated PAHs decreased in the control soil samples in the following order; pyrene> benzo(a) anthracene> phenanthrene> chrysene as shown in Figure 3.

The result indicated a higher contamination of the control soil samples with the investigated high molecular weight PAHs compared to the low molecular weight PAHs. The control soil samples contained the determined PAHs within the recommended permissible limits and the mean levels of the PAHs in the soil samples were statistically significant.

The mean levels of 0.98±0.25 and 0.62±0.11mg/kg reported for acenapthene and benzo(a)anthracene respectively by [19] in soil samples from auto-mechanic workshops at Alaoji Aba and Elekhia, Port Harcourt, was higher than what was obtained for the PAHs in the soils at the investigated sites P1, P2 and control in Nibo. [20] reported a lower mean values of 0.06±0.02 and 0.02±0.01 mg/kg for benzo(a) anthracene and pyrene respectively in soils around the vicinity of petrol stations in Kogi State, than what was gotten for the PAHs in the soil samples of this study.

According to [6], when LMW/HMW is greater than 1, phenanthrene/anthracene is greater than 15, anthracene/228 is less than 0.2, chrysene/benzo(a)anthracene is less than 0.4, anthracene/ anthracene+phenanthrene is less than 0.1 and benzo(a) anthracene/ benzo(a) anthracene+chrysene is less than 0.2, then the sources of the contamination within such an environment would be petrogenic, otherwise pyrolytic source of contamination would be confirmed.

Table 2: The investigated PAHs diagnostic ratio for the soil samples at P1, P2 and control in Nibo, Awka South L.G.A., Anambra State.

PAH / Site	Ant/Ant+phen	LMW/HMW	Phen/Ant	B(a)A/ 288	Chry/B(a)A	Ant/ 178	B(a)A/B(a)+Chry
P1	062	0.33	0.62	0.00	1.35	0.00	0.43
P2	0.56	1.14	-	0.00	0.26	0.00	0.80
Control	-	0.26	-	0.00	0.29	-	0.75

Ant denotes anthracene; Phen denotes phenanthrene; LMW denotes low molecular weight PAHs; HMW denotes high molecular weight PAHs; B(a)A denotes benzo(a) anthracene; Chry denotes chrysene.

Taking the reports of [6] into consideration, it would be safe to state that the result of Table 2 shows that the sources of contamination of the soil samples at P1 was more pyrolytic than petrogenic. This observation compares very favourably with the findings of [21]. Such observations of the sources of investigated PAHs in the soil samples at P1, was similarly shown in the soil samples at P2 and the control. This therefore indicates that the soil samples around sites P1 and P2 withessed little or no spillage of the hydrocarbon (fuel) at either discharge or dispensing, hence, the evaporated hydrocarbons resulted in an insignificant contribution to the contamination of the soil samples with PAHs compared to the contamination of the soils from the combustion and degradation of organic materials in the studied environments.

4. CONCLUSION

Most of the investigated PAHs were present in the soils situated around fuel stations in Nibo, Awka South L.G.A., Anambra State. The mean levels of the investigated PAHs in the soil samples at sites P1, P2 and control showed significance respectively. The investigated PAHs were within the recommended permissible limits in the soil samples at sites P1, P2 and control. The soil samples were predominantly contaminated with high molecular PAHs than the low molecular weight PAHs. The soil samples at P1, P2 and control were predominantly contaminated with PAHs from pyrolytic sources than petrogenic sources. It is important that indiscriminate burning of organic and inorganic materials on the soils meant for agricultural purposes should be discouraged and equally, unplanned siting of petrol filling stations near residential and agricultural farmlands should be frowned upon in order to limit the undue exposure to PAHs by the people from food and non-food items.

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Conflicts of interests

The authors declare that there are no conflicts of interests.

Data and materials availability

All data associated with this study are present in the paper.

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