

Original Article

Pollution investigation and risk assessment of polycyclic aromatic hydrocarbons in soil and water from selected dumpsite locations in rivers and Bayelsa State, Nigeria.

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Abstract

The transfer ratio of polycyclic aromatic hydrocarbons (PAHs) from soil dumpsite to borehole water is dependent of polluting source and exposure matrices that causes immerse health risk to man and environment over a period of time. PAHs were assessed in selected soil dumpsite and borehole water located at Rivers state (Eleme, Elioizu, Eneka, Oyigbo, and Woji) and Bayelsa state (Yenagoa), Nigeria. Soil samples were collected at four different points 30 m (North, South, East and West) locations at a depth of 15 cm for each dumpsite using soil auger while control samples were collected 200 m away (farmland), where there were little anthropogenic activities and no presence of active dumpsites. Borehole water samples were collected from 300 m distance, which were packaged in an amber container, labeled, and transported to the laboratory for analysis. Standard analytical methods were employed. PAHs concentrations were analyzed using gas chromatography- mass spectrometry (GC-MS) after extraction of water and soil using liquid-liquid and soxhlet extraction methods respectively and clean-up of the extracts, thereafter the laboratory data generated were subjected to statistical analysis. Total PAHs (Σ PAHS) concentrations in soil samples from the study sites ranged from 2.4294 mg/kg in Yenagoa to 5.1662 mg/kg in Eleme while in water samples the total PAHs ranged from 1.3935 mg/L in Woji to 3.009 mg/L in Eleme. The total PAH concentrations in the soil were above the Agency for Toxic Substances and Disease Registry levels of 1.0 mg/kg for a considerably contaminated site except for the control sites. The total concentration of carcinogenic PAHs ranged from 0.0038 to 1.1301mg/kg in soil samples and 0.0014 to 0.9429 mg/L in borehole water samples, therefore raising concern of human exposure via food chain. The results indicate that low molecular weight PAHs were more dominant than high molecular weight PAHs in both soil and water samples, however molecular diagnostic ratio shows that pyrogenic activities are major sources of PAHs as compared to petrogenic origin. Multivariate analysis (principal component analysis and Pearson correlation) showed strong negative correlation implying that they were from dissimilar sources and different migratory route. Cancer and non-cancer risk showed that children were more at risk compared to adults, where inhalation exposure were major contribution as compared to ingestion and dermal exposure, as such there is a need to implement regulatory laws on indiscriminate release of PAHs contaminants to maintain sustainability.

Keywords: PAHs contaminants, Soil dumpsite, Molecular diagnostic ratio, Cancer risk, Hazard index, Southern Nigeria

Introduction

Globally, there has been an increase in the amount of waste generated as a result of growing rate of industrialization, urbanization and population growth [1,2]. Studies have shown that excessive anthropogenic activities (which include gas flaring, fossil fuel combustion, oil spill and inappropriate disposal of industrial wastes) in the form of environmental pollution causes major harm to the environment leading to severe soil degradation, poor water quality and polluted atmosphere in relation to the aesthetic view [3,4]. In Nigeria, the desire to develop and carry out a long-term waste management plan based on public health principles has led to large number of open dumpsites that are not managed appropriately as these dumpsites are incinerated openly, thus leading to release of harmful chemical pollutants to the

environment [5,6]. It is a known fact that poor management of waste dumpsites endangers the groundwater supply as infiltration of chemical leachates from dumpsites through the soil and the aquifers pose a risk to the environment and human health [7-9].

Polycyclic aromatic hydrocarbons, PAHs are cluster of organic compounds with two or more fused benzene rings in various structural configurations and do not contain hetero atom derived from the incomplete combustion of organic matters including coal, oil, gas, wood, garbage, or other organic substances, such as tobacco and charbroiled meat [10,11]. Primary sources of PAHs in the environment are mainly from the incomplete combustion of various organic matters such as fossil fuels (e.g., coal, gasoline, and diesel) and biomass fuels (e.g., straw, firewood), garbage, petroleum product spillage, various industrial, commercial, domestic and agricultural activities [12]. Due to the ubiquitous nature of PAHs, they are found in a wide range of environment including soils, sediments, ground waters, and the atmosphere. It is estimated that 90% of the total environmental PAHs load is found in terrestrial ecosystems, and more specifically, the top 20 cm of the soil horizon [11,13]. PAHs present in soil may exhibit a toxic activity towards different plants, microorganisms, and invertebrates [14,15]. Yang et al. [16] found soils as sink for large number of PAHs, as some of them pose threats to human health. PAHs are pollutants of great concern which are widespread in various ecosystems because of their potential toxicity to aquatic life as several PAHs components are suspected human carcinogens, mutagens, and endocrine disrupters [17-19].

The US Environmental Protection Agency has classified 16 PAHs as priority pollutants, eight of which are possible human carcinogens which include benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz (a,h)anthracene, indeno(1,2,3-cd)pyrene [20,21]. The light PAHs (2-3 rings) such as naphthalene, fluorene, phenanthrene and anthracene have significant acute toxicity to aquatic organisms, while heavy PAHs (4-6 rings) such as chrysene and coronene do not but are carcinogenic [21]. According to USEPA, [22,23] human exposure of PAHs occurs via inhalation of particulate matter, dermal adsorption during contact to contaminated soil and water, and oral ingestion of soil and water. Oral ingestion can also result in tandem with inhalation of particulates from impaction onto mucus membrane in tracheobronchial tract, movement up the tract by cilia to pharynx, and swallowing [24,25]. Exposure of PAHs increases across large radius from close proximity index via leachate for water sources in respect to passer-by and people living within a given vicinity, where these wastes are present may be of greater exposure risk through inhalation due to constant burning of dumpsites [15,25,26].

Consequently, there is a need to assess the PAHs concentration with a mandate to enlighten public health expert, environmental policy makers and regulatory agencies on the relationship between health issues and environmental pollution over a given period. Therefore, the study aims to assess the concentrations and human health risk of PAHs in soils and water boreholes from the selected active waste dumpsites in Rivers and Bayelsa States, South-South Nigeria.

Materials and Methods

Description of study site

In this study, six (6) major waste dumpsites, five (5) located in Rivers State (Eleme, Elioju, Eneka, Oyigbo, Woji) and one (1) located in Bayelsa state (Yenagoa), South-South, Nigeria were selected as shown in Figure 1. The study site is characterized by tropical dry seasons (November to February) and wet seasons (March to October) with a mean annual rainfall increasing from 2000 mm around the northern border to about 4500 mm around the coastal margin [27]. The dumpsites are surrounded by residential houses, factories, gasoline stations, auto spare parts market and auto repair workshops as these expose residents, rag-pickers passer-by including infants to soil and water contaminants by inhalation, ingestion and dermal contacts.



Eleme

Latitude: 04°79'94"N
Longitude: 06°54'48.7"E



Elioze

Latitude: 04°54'16.4"N
Longitude: 07°11'98"E



Eneka

Latitude: 04°53'34.1"N
Longitude: 06°54'48.7"E



Oyigbo

Latitude: 04°53'07.4"N
Longitude: 07°00'50.1"E



Woji

Latitude: 04°82'83"N
Longitude: 07°05'79"E



Yenagoa

Latitude: 04°58'59.20"N
Longitude: 06°19'18.2"E

Figure 1. Active waste dumpsites in Rivers and Bayelsa State, Nigeria [1].

Sample collection of soil and water

Soil samples were collected from selected dumpsites in a 30 m quadrant route (West, East, South and North) with soil auger and a spatula at a depth of 15 cm after removing the overlying wastes, while control site soil sampling was done at 200 m distance from the dumpsites that is a farmland with minimal human activity. The quadrant samples from each dumpsite were homogenized into a composite sample in tandem to the control site also. The composite soil samples were air-dried at room temperature for 48 hours before ground using a porcelain pestle and mortar to reduce the surface area and sieved with a 2 mm nylon mesh to give the fine earth fraction. The samples were stored in pre-labeled polythene bags and were taken to the laboratory for further chemical evaluation.

Water samples were collected from borehole water source at 300 m proximity to an active waste dumpsite, which was done in four sample locations (Eleme, Eneka, Woji, and Control Site 1). The water was collected from four residential home equipped with installed borehole water system at close proximity to each other, which was thereafter mixed to form a composite sample into 500 mL sampling amber glass bottles. The samples were labeled, thereafter kept in a refrigerator pending laboratory analysis.

Quality control process

Sample blank solutions were prepared using the same procedure described for the samples. Same quantities of reagents were used for sample and blank. All reagents used were of analytical grade. The reliability and reproducibility of the measurements were ensured by calibrating the instruments used and procedural blanks determined.

Determination of polycyclic aromatic hydrocarbons (PAHs) in soil samples

Soil PAHs extraction and clean-up

The United States Environmental Agency, USEPA-8100 extraction method was used for the preparation of soil samples for analysis. 10 g of soil sample was measured out and quantitatively transferred into a 250 mL separating funnel. A 20 mL of Dichloromethane was added to the soil sample in the funnel and sonicated for 10–15 minutes at about 70 °C (This was done in triplicates to extract all analyte present in the sample) [28]. After sonication, 10 g of anhydrous sodium Sulphate was added to the samples to remove any residual water molecules. This was allowed to stand for about 10-15 minutes. It was then set to shake continuously for 30 minutes at 300 rpm and finally allowed to stand for 5 minutes to sufficiently separate the phases. A 10 mL of the supernatant was carefully taken and dried over 2 g anhydrous magnesium sulphate through filter paper into 50 mL round bottom flask. This was then concentrated to about 2mL using the rotary evaporator and made ready for silica clean up step. The clean-up was done according to method described by USEPA [28].

Soil PAHs determination using gas chromatography/mass spectrometry

The final extracts were analyzed by gas chromatograph- agilent HP 5890 series II model equipped with auto sampler and Ni electron capture detector (ECD) that allowed the detection of contaminants even at trace level concentrations (in the lower µg/g and µg/kg range) from the matrix to which other detectors do not respond. The GC conditions used for the analysis were capillary column coated with VF-5 (30 m + 10 m EZ guard column x 0.25 mm internal diameter, 0.25 µm film thickness). The injector and detector temperature were set at 250 °C and 300 °C respectively. The oven temperature was programmed as follows: 60 °C held for 2 min, ramp at 25 °C/ min to 180 °C, held for 1 min, and finally ramp at 5 °C/ min to 310 °C. Helium was used as carrier gas at constant flow rate of 1.4 °C / min and detector make-up gas of 29 mL / min. The injection volume of the GC was 1.5 mL with total run time for each sample was 31.4 min. Results obtained were presented as mg/kg concentration per analyte.

$$\text{PAHs concentration (mg/kg)} = \frac{\text{Concentration (mg/kg)} \times \text{Final volume (1.5 mL)}}{\text{Sample weight (10 g)}} \quad (1)$$

Determination of polycyclic aromatic hydrocarbons (PAHs) in water samples

Extraction of PAHs from water samples

The United States Environmental Protection Agency (USEPA) Method 3510 for aqueous matrix for the analysis of semi-volatile and non-volatile organics was modeled [28]. After filtration, 100 mL portion of the water sample was transferred into a 2 L capacity glass-separating funnel. Then 30 mL of saturated sodium chloride (NaCl) was added to produce a salt out effect. It was thoroughly mixed by inverting the flask three to four times. 100 mL of dichloromethane as extraction solvent was added and this was vigorously shaken manually for 2-3 minutes and releasing the pressure at irregular intervals. The phases were then allowed to separate for 5 minutes, and the dichloromethane extract (upper organic layer) was collected from the aqueous layer in a round bottom flask. The extraction was repeated with 100 mL of dichloromethane and the organic layers were put together and dried over anhydrous magnesium sulphate. The extracts from water samples were then concentrated on rotary vacuum evaporator to about 2 mL and subjected to clean up.

Water PAHs determination using gas chromatography/mass spectrometry

One gram of silica gel that previously had been activated at 130 °C for 10 hours was carefully packed into 10 mL polypropylene cartridge column and 6 mL Dichloromethane was used to condition the cartridge. The concentrated extract was then loaded onto the column and 50 mL pear shape flask was placed under the column to collect the eluate. A 10 mL dichloromethane was used to elute the column afterwards, and the total filtrate collected concentrated to just dryness using the rotary evaporator set at 38 °C. The residue was re-dissolved in 1 mL methanol and transferred into a 2 mL standard vial prior to quantification by gas chromatography. The GC conditions used for the analysis were capillary column coated with VF-5 (30 m + 10 m EZ guard column x 0.25 mm internal diameter, 0.25 µm film thickness). The injector and detector temperature were set at 250 °C and 300 °C respectively. The oven temperature was programmed as follows: 60 °C held for 2 min, ramp at 25 °C/ min to 180 °C, held for 1 min, and finally ramp at 5 °C/ min to 310 °C. Helium was used as carrier gas at a flow rate of 1.4 °C / min, Inlet Mode: Splitless, Linear velocity: 30 cm/sec and detector make-up gas of 29 mL / min. Results obtained were presented as mg/L concentration per analyte.

$$\text{PAHs concentration (mg/L)} = \frac{\text{Concentration (mg/L)} \times \text{Final volume (1.5 mL)}}{\text{Sample weight (100 mL)}} \quad (2)$$

Statistical analysis

Laboratory data attained from soil and water samples were subjected to analysis Microsoft Excel 2016 software to determine mean±standard deviation (SD), multivariate analysis (principal component analysis, pearson correlation) was done to derive useful information on soil to water interaction across sample locations.

Health and exposure risk assessment model

Health and exposure risk assessment was determined using the United States Environmental Agency's risk models that assesses the health implication of PAHs exposure to humans (adults and children) across different exposure medium that is ingestion, dermal and inhalation accordingly. The risk assessment model utilized chronic daily intake (CDI) calculation of carcinogenic and non-carcinogenic PAHs via diverse exposure medium as shown below [29,30].

Chronic daily intake of soil sample

$$CDI - \text{ingestion (mg/kg/day)} = \left(\frac{CS \times IRS \times \frac{10^{-6}\text{kg}}{\text{mg}} \times EF \times ED \times RBA}{THQ^{**} \times BW \times AT \times TR^*} \right) \quad (3)$$

$$CDI - \text{dermal (mg/kg/day)} = \left(\frac{CS \times SA \times AF \times ABS_{sk} \times 10^{-6}\text{kg/mg} \times EF \times ED}{BW \times AT \times THQ^{**} \times GIABS \times TR^*} \right) \quad (4)$$

$$CDI - \text{inhalation (mg/m}^3) = \left(\frac{CS \times \frac{1}{VF} \times \frac{1}{PEF} \times EF \times ET_{ih} \times \frac{1\text{day}}{24\text{hr}} \times ED \times 10^6\text{kg/mg}^*}{AT \times THQ^{**} \times TR^*} \right) \quad (5)$$

where CS is PAHs concentration in dumpsite soil (mg/kg), IRs is soil ingestion rate (mg/day) (100 mg/day for adults and 200 mg/day for children), EF is exposure frequency (350-day year-1), ED is exposure duration (26 years for adults and 6 years for children), TR* is target risk (1×10^{-6} mg/mg) for carcinogen calculation only, THQ**: target hazard quotient 0.1 for non-carcinogen calculation only, BW is body weight (80 kg for adults and 15kg for children), AT is average time (non-carcinogens = ED × 365 days), (carcinogen = 70×365), SA is skin surface area (6032 cm²/day for adults and 2373 cm²/day for children), AF is water adherence factor: (0.2 mgcm⁻² for adults and 0.07 mgcm⁻² for children), ABS_{sk} is fraction of chemical absorbed through the skin (unit-less) (0.13 for adults and children), GIABS is fraction of contaminant absorbed in gastrointestinal tracts (unit-less) (1.0 for adults and children), ET_{ih} is Exposure time (9 hrs/days for adults and 6 hrs/day for children), VF is Volatilization factor (0.00001 m³/kg for adults and children) for non-carcinogen calculation; 0.006 for carcinogen calculation, PEF is Particulate emission factor (1.36×10^9 m³/kg for adults and children), 10^{6*} kg/mg for carcinogen calculation only.

Chronic daily intake of water

$$CDI - \text{ingestion (mg/kg/day)} = \left(\frac{CS \times IRW \times EF \times ED \times TF \times THQ^*}{BW \times AT} \right) \quad (6)$$

$$CDI - \text{dermal (mg/kg/day)} = \left(\frac{CS \times SA \times AF \times ABS_{sk} \times ET_w \times EF \times ED \times TF \times THQ^*}{BW \times AT} \right) \quad (7)$$

where CS is PAHS concentration in water (mg/L), IRw is daily water ingestion rate (L/day) (2.5 L/day for adults and 0.78 L/day for children), EF is exposure frequency (350-day year-1), ED is exposure duration (26 years for adults and 6 years for children), TF is target risk (1×10^{-6} mg/mg) for carcinogen, THQ*: target hazard quotient 10 for non-carcinogen calculation only, BW is body weight (80 kg for adults and 15 kg for children), AT is average time (non-carcinogens = ED ×365 days), (carcinogen = 70 × 365), SA is skin surface area (19652 cm² for adults and 6365 cm² for children), AF is water adherence: (0.2 mgcm⁻² for adults and children), ABS_{sk} is fraction of chemical absorbed through the skin (unit-less) (0.001 for adults and children), ET_w is exposure time during work event (1 h/event for adults and children).

Carcinogenic risk assessment

$$\text{Cancer risk}_{total} = \text{Risk}_{ing} + \text{Risk}_{der} + \text{Risk}_{inh} = ([CDI(Ing) \times OSF] + [CDI(der) \times CSF] + [CDI(Inh) \times IUR]) \quad (8)$$

where cancer risk is the possibility of an adult or child developing cancer over a lifetime, CDI (E) is the chronic daily intake for any exposure matrix (ingestion, dermal and inhalation), CSF is cancer slope factor of PAHs (mg/kg/day)⁻¹, OSF is oral slope factor (mg/kg/day)⁻¹, IUR is inhalation unit risk (mg/m³)⁻¹.

Non-carcinogenic risk assessment

$$HI = HQ_{ing} + HQ_{der} + HQ_{inh} = \left(\left[\frac{CDI(ing)}{RfD} \right] + \left[\frac{CDI(Der)}{RfD} \right] + \left[\frac{CDI(inh)}{RfC} \right] \right) \tag{9}$$

where HI is hazard index that is the sum of all hazard quotient (HQ) of multiple exposure pathway, HQ is probable condition that can lead to adverse health effect, CDI (E) is the chronic daily intake for any exposure matrix, RfD is reference dose (mg/kg/day), RfC is reference inhalation constant (mg/m³).

The reference table for carcinogenic and non-carcinogenic risk assessment are presented in Table 1.

Table 1. Reference value for polycyclic aromatic hydrocarbons (PAHs)

PAHs	Ingestion		Dermal		Inhalation	
	OSF	RfD	CSF	RfD	IUR	RfC
Naphthalene (Nap)	NA	0.04	NA	0.02**	0.034	0.003
Acenaphthene (Ace)	0.073*	0.006	0.073*	0.02**	0.011*	0.88**
Acenaphthylene (Acy)	0.0073*	0.06	0.0073*	0.06**	0.0011*	0.88**
Fluorene (Flu)	NA	0.04	NA	0.04**	NA	NA
Phenanthrene (Phen)	NA	0.04	NA	NA	NA	NA
Anthracene (Ant)	NA	0.3	NA	0.3**	NA	NA
Fluoranthene (Flt)	0.073*	0.04	0.073*	0.04**	0.011*	0.88**
Pyrene (Pyr)	0.73*	0.03	0.73*	0.03**	0.11*	0.88**
Benzo[a]anthracene (BaA)	0.73*	0.03	0.73*	0.03**	0.11*	0.88**
Chrysene (Cry)	0.0073*	0.03	0.0073*	0.03**	0.0011*	0.88**
Benzo[b]fluoranthene (BbF)	0.73*	0.03	0.73*	0.03**	0.11*	0.88**
Benzo[k]fluoranthene (BkF)	0.0073*	0.03	0.0073*	0.03**	0.011*	0.88**
Benzo[a]pyrene (BaP)	7.3*	0.03	7.3*	0.03**	1.1*	0.88**
Dibenzo[a,h]anthracene (DBA)	7.3*	0.03	7.3*	0.03**	1.2*	0.88**
Indeno[1,2,3-cd] pyrene (IND)	0.73**	0.03	0.73*	0.03**	0.11*	0.88**
Benzo[ghi]perylene (BghiP)	0.073*	0.03	0.073*	0.03**	0.011*	0.88**

*[31,32], **[29,33]. CSF: cancer slope factor (mg/kg/day), OSF: oral slope factor (mg/kg/day), IUR: inhalation unit risk (mg/m³), RfD: reference dose, RfC: reference concentration.

Results and Discussion

PAHs composition in soil dumpsites

Figures 2 and 3 show the percentage stark column of PAHs in soil dumpsite and borehole water. As we can see in soil dumpsite (Figure 2), there was presence of naphthalene, acenaphthene, fluorene, benzo(k)fluoranthene in all locations, while pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-cd) pyrene and benzo(g,h,i)perylene were absent accordingly. Phenanthrene was present in Eleme, Eneka, Yenagoa, while absent in Elioizu, Oyigbo, Woji, control site 1 and 2, while for acenaphthylene was absent in control site 2 and present in all locations. In decreasing order, the cumulative PAHs concentration showed that Eleme > Oyigbo > Elioizu > Woji > Eneka > Yenagoa > control site 1 > control site 2 (Figure 3) depict presence of 16 PAHs components except benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd) pyrene and benzo(g,h,i)perylene respectively. A review on the percentage stark column showed that Eleme contributed a commemorate PAHs concentration in comparison to other locations (Eneka, Woji and control site 1).

The results of the concentrations of polycyclic aromatic hydrocarbons (PAHs) for soil and borehole water matrix are presented in Tables 2 and 3, respectively. Twelve and eleven PAHs were detected out of the sixteen priority PAHs analyzed in the soil and borehole water respectively with varying concentration from one location to the other. These PAHs include naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a) pyrene and dibenz(a,h)anthracene . The four PAHs that were not detected in the soil samples were benzo(ghi)perylene, dibenzo(a,h)anthracene, pyrene and indeno(1,2,3-cd)pyrene while five PAHs were not detected in the water samples which include Benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)anthracene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene. The total PAHs concentrations found in the soil ranged from 0.1049 to 5.1662 mg/kg (Table 2) while the total PAHs found in the borehole water ranged from 0.1060 to 3.009 mg/L (Table 3). The highest PAHs concentration in the soil (5.1662 mg/kg) was detected in soil samples

located at Eleme dumpsite. Naphthalene (1.8751±0.0003 mg/kg) and acenaphthylene (0.7706±0.0002 mg/kg) were found in highest concentration at Eleme dumpsite. The highest PAHs concentration in borehole water samples (3.009 mg/kg) was detected in the bore water located at Eleme area. The occurrence of high levels of PAHs in this study area has negative impacts on humans living within the vicinity the area. The high concentration of PAHs observed at Eleme dumpsite in this study could be as a result of open burning and oil /petrochemical industries located in Eleme which discharge their wastes at these dumpsites. According to Mohammed et al. [34], municipal waste and waste discharge from industrial sites are part of the factors causing a high concentration of PAHs in dumpsites soil. The lowest concentration (0.1060) mg/kg was detected in the control sample located far away from the dumpsites and industrial activities. The accumulation of PAHs in all soil samples followed the order; Eleme > Oyigbo > Elioizu > Woji > Eneka > Yenagoa dumpsite while the accumulation of PAHs in all the borehole water samples followed the order; Eleme > Eneka > Woji locations.

Generally, higher molecular weight (HMW) PAHs display considerable propensity than the lower molecular weight PAHs (LMW) and remain sorbed to soils rather than remain in the water or air and in addition have the greater capacity to bio-accumulate in organisms. In the present study, the distribution of low molecular weight (LMW) PAHs and high molecular weight (HMW) PAHs in the soil and borehole water samples (Tables 2 and 3) shows that ΣLMW are the dominant in the dumpsite soils and the borehole water. The dominance of the low molecular weight PAHs in this study suggests a recent release of PAHs to the environment from different sources due to the LMW PAHs are more biodegradable, less lipophilic and are not to be sorbed as strongly as the HMW PAHs [35]. The presence of low molecular weight PAHs in the environment usually results from the emission of oil spills, domestic coal burning and noncombustible matter, while high molecular weight PAHs results from emission of incomplete combustion of organic matter and solid wastes and industrial plants emission [36]. The results were similar to study carried out by Ekpete et al. [37] and Mohammed et al. [34] to determine the concentration of PAHs from selected dumpsites within Port Harcourt metropolis, where they attributed the dominance of 2- 3 membered rings in majority of the dumpsites and concentrations of leachates from a popular dumpsite in Lagos state respectively, but was not in agreement to the result of Adedosu et al. [36] in Balogun-Biro dumpsite, Nigeria where high molecular weight PAHs dominants to the low molecular weight PAHs.

The total PAHs concentrations in the soil across the study area were observed to be above the Agency for Toxic Substances and Disease Registry levels of 1.0 mg/kg for a significantly contaminated site, due to the total PAHs concentration across the study areas was within 1 and 10 mg/kg, since levels of the total of PAHs between 0.0 and 0.1 mg/kg are considered as non-contamination, values that fall between 0.1 and 1 mg/kg indicates slight contamination, while values between 1 and 10 mg/kg are indication of significant contamination [20,38]. When comparing the total concentration of PAHs in the dumpsites soil of this study, it was found that the values were similar to the report in Balogun-Biro dumpsite, Nigeria (5.6491 mg/g) [36] but lower than the values reported in Sapele municipality, Nigeria (584.44 µg /g) [39]. When comparing the total concentration of PAHs in the borehole water of this study, it was observed that the values recorded were higher than the report of Elelenwo River at different stations (0.230±0.037 mg/L) [40], but lower to the report of Edori and Iyama [41] in the coastline areas of the new Calabar River at the effluents discharge point) and study in the Niger Delta area (1.96 to 10.9 µg/L) by Anyakora and Herbert [42]. The values of PAHs observed in the different borehole water samples were lower than the acceptable limit of 10 mg/L stipulated by Federal ministry of environment for drinking water [43]. Although, the values were lower than the above acceptable limit, people living within the area stand the risk of being affected by the PAHs, hence, posing great health challenges [44]. From observation of the results, incomplete combustion of waste at the studied dumpsites, presence of chemical and petrochemical industries using power generating plants within the studied area, may have contributed to the quantity of PAHs observed in the different dumpsites.

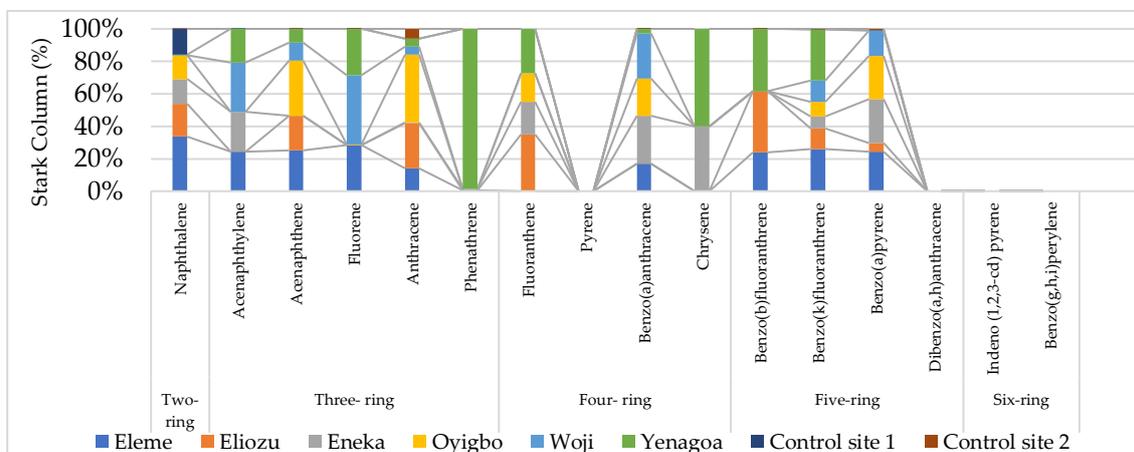


Figure 2. Percentage stark column of PAHs in soil dumpsite.

Table 2. PAHs concentrations (mg/kg) in soil dumpsites.

PAHs	Eleme	Eliozu	Eneka	Oyigbo	Woji	Yenagoa	Control site 1	Control site 2
Two- ring								
Naphthalene	1.8751±0.0003	1.1164±0.0001	0.8683±0.0003	0.8163±0.0003	0.006±0.002	0.011±0.0026	0.8862±0.0002	0.0003±0.0002
Three- ring								
Acenaphthylene	0.7706±0.0002	0.0009±0.0003	0.7709±0.0001	0.0008±0.0003	0.9622±0.0003	0.6605±0.0002	0.001± 0.001	ND
Acenaphthene	0.6537±0.0024	0.5592±0.0002	0.0013±0.0003	0.8853±0.0001	0.2854±0.0003	0.2254±0.0002	0.0001±0.0001	0.0002±0.0001
Fluorene	0.388±0.0032	0.001 ± 0.001	0.0009±0.0001	0.0051±0.0002	0.5891±0.0002	0.3891±0.0001	0.0002±0.0001	0.0004±0.0001
Anthracene	0.2269±0.2947	0.4564±0.0002	0.0052±0.0003	0.6765±0.0001	0.0821±0.0002	0.0751±0.0002	ND	0.1002±0.0002
Phenanthrene	0.0004±0.0002	ND	0.0007±0.0002	ND	ND	0.0843±0.0001	ND	ND
Four- ring								
Fluoranthene	ND	0.0014±0.0004	0.0008±0.0001	0.0007±0.0002	ND	0.0011±0.0002	ND	ND
Pyrene	ND	ND						
*Benzo(a)anthracene	0.5641±0.0001	0.0095±0.0004	0.9865±0.0003	0.7675±0.0002	0.9395±0.0004	0.0861±0.0003	0.0004±0	0.0002±0.0002
*Chrysene	ND	ND	0.0004±0.0004	ND	ND	0.0006±0	ND	ND
Five-ring								
*Benzo(b)fluoranthene	0.5386±0	0.8555±0.0117	ND	0.0009±0.0002	0.0006±0.0002	0.8643±0.0011	0.0002±0.0001	0.0004±0.0002
*Benzo(k)fluoranthene	0.0264±0	0.0126±0.0001	0.0076±0.0005	0.009±0.0002	0.0132±0.0002	0.0319±0.0001	0.0001±0	0.0002±0.0001
*Benzo(a)pyrene	0.1224±0.0005	0.0264±0.0001	0.1356±0.0004	0.1355±0	0.0773±0.0004	ND	0.0027±0.0003	0.003±0.0002
*Dibenzo(a,h)anthracene	ND	ND						
Six-ring								
*Indeno (1,2,3-cd)pyrene	ND	ND						
Benzo(g,h,i)perylene	ND	ND						
Σ LMW PAHs	3.9147	2.1339	1.6473	2.384	1.9248	1.4454	0.8875	0.1011
Σ HMW PAHs	1.2515	0.9054	1.1309	0.9136	1.0306	0.984	0.0034	0.0038
Σ 16 PAHs	5.1662	3.0393	2.7782	3.2976	2.9554	2.4294	0.8909	0.1049
Σ Carcinogenic PAHs	1.2515	0.904	1.1301	0.9129	1.0306	0.9829	0.0034	0.0038

*Values are mean±standard deviation of triplicate determination. ND= Not Detected; detection limits for all the PAHs were 0.001 mg/kg.

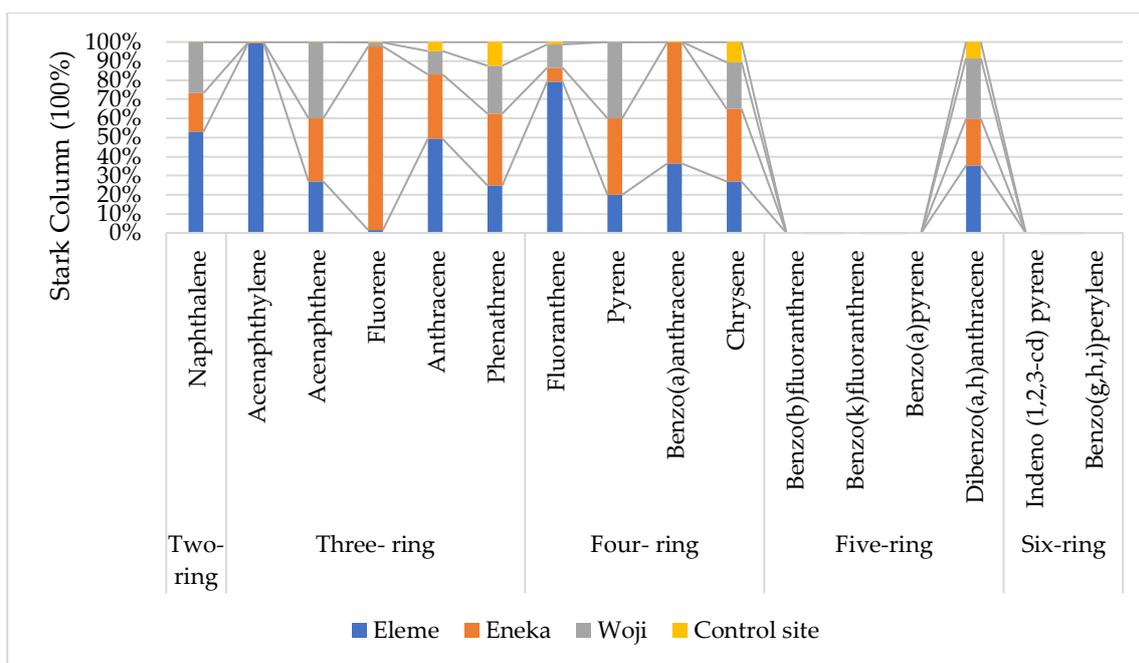


Figure 3. Percentage stark column of PAHs in borehole water.

Table 3. PAHs concentrations (mg/L) in borehole water.

PAHs	Eleme	Eneka	Woji	Control site 1
Two- ring				
Naphthalene	1.7762±0.0003	0.6791±0.0003	0.8893±0.0004	0.0021±0.0003
Three- ring				
Acenaphthylene	0.233±0.0002	0.001±0.0002	<0.001±0.0002	<0.001±0
Acenaphthene	0.1875±0.0003	0.2287±0.0002	0.2763±0.0003	<0.001±0.0001
Fluorene	0.006±0.0002	0.3891±0.0001	0.0096±0.0005	<0.001±0.0001
Anthracene	0.0032±0.0003	0.0022±0.0003	<0.001±0.0002	<0.001±0
Phenanthrene	0.2008±0.0001	0.3007±0.0001	0.2004±0.0004	0.1004±0.0002
Four- ring				
Fluoranthene	0.0571±0.0005	0.0052±0.0003	0.0087±0.0003	<0.001±0.0002
Pyrene	<0.001±0.0001	<0.001±0.0002	<0.001±0.0002	<0.001±0
*Benzo(a)anthracene	0.5411±0.0054	0.9395±0.0004	0.0038±0.0002	<0.001±0.0001
*Chrysene	<0.001±0	0.0014±0.0002	0.001±0.0001	<0.001±0.0001
Five- ring				
*Benzo(b)fluoranthene	ND	ND	ND	ND
*Benzo(k)fluoranthene	ND	ND	ND	ND
*Benzo(a)pyrene	ND	ND	ND	ND
*Dibenzo(a,h)anthracene	0.0029±0.0002	0.002±0.0003	0.0026±0.0002	0.0007±0.0002
Six- ring				
*Indeno (1,2,3-cd)pyrene	ND	ND	ND	ND
Benzo(g,h,i)perylene	ND	ND	ND	ND
Σ LMW PAHs	2.4067	1.6008	1.3771	0.1036
Σ HMW PAHs	0.6023	0.9485	0.0164	0.0024
Σ 16 PAHs	3.009	2.5493	1.3935	0.1060
Σ Carcinogenic PAHs	0.545	0.9429	0.0073	0.0014

Values are mean±standard deviation of triplicate determination. ND= Not Detected; detection limits for all the PAHs were <0.001 mg/L>.

Molecular diagnostic ratio of PAHs

Molecular diagnostic ratio is a widely used method to ascertain the sources of PAHs present in different environmental matrix; as several studies such as Adedosu et al. [36], Ekpete et al. [37], Bucheli et al. [45], and Shamilishvily et al. [46] have been used to derive ratios of specific PAHs isomers to differentiate pyrogenic (combustion) and petrogenic (discharge of petroleum product e.g., oil spillage) PAHs sources. The individual compound ratios are identified to provide precise and consistent estimations of the sources of PAHs [35]. The results of the calculated diagnostic ratios are shown in (Table 4), where the determination of PAHs sources using the diagnostic ratios showed that the ratio of Anth/ (Anth + Phe) values in the soil and borehole water samples across the study areas were all greater than 0.1 which is indicative of pyrogenic source [45]. All the values Flua/Pyr+Flua were beyond detectable limits across the studied soil dumpsites whereas the values recorded for Flua/Pyr+Flua in all the borehole water sampling sites were greater than 0.5, which indicates that the PAHs are due to diesel emissions, grass, wood, and coal combustion [47]. This is possibly due to use of generating plants use by industries around the study areas. The ratio of BaA/(BaA+Chr) less than 0.2, 0.2-0.35 and greater than 0.35 are indication of petrogenic, mixed and pyrogenic sources respectively [48]. The value of BaA/(BaA+Chr) for all the sampling sites is greater than 0.35 indicating a pyrogenic source (combustion of coal, wood, and vehicular emissions). Petrogenic sources are characterize with the predominance of low molecular weight hydrocarbons containing (2-3 fused aromatic rings) PAHs over the high molecular weight (4-6 fused aromatic rings) PAHs. The ratio of low molecular weight PAHS to high molecular weight PAHs greater than 1 indicates a petrogenic source [49,50], thus values recorded for the ratio of low molecular weight to high molecular weight (LMW/HMW) for all the sampling sites is more than 1 and is indicative of petrogenic sources. The ratio of (Phen/Ant) greater than 15 is an indication of petrogenic while (Phen/Ant) less than 10 is pyrogenic source [51]. All the values in the studied samples are less than 10 indicating a pyrogenic source. The use of the different source of diagnostic ratios of PAHs has shown that pyrogenic source (incomplete combustion of organic materials such as combustion of fossil fuel, wood, and coal) on most of the studied dumpsites predominates than petrogenic sources.

Table 4. Molecular diagnostic ratio of PAHs in the soil dumpsites and borehole water.

Soil dumpsites	Phen/Ant	Ant/Ant+ Phen	B(a)A/B(a)A + Chry	LMW/HMW	Carc. PAHs / Total PAHs	Flua/ (Pyr + Flua)
Eliozu	-	1	1	2.094	0.297	-
Yenagoa	1.122	0.471	0.993	1.468	0.404	-
Eneka	0.135	0.881	0.999	1.674	0.407	-
Oyibo	-	1	1	2.574	0.277	-
Woji	-	1	1	1.862	0.348	-
Eleme	0.0017	0.998	1	3.128	0.2422	-
Control site 1	-	-	1	261.37	0.0038	-
Control site 2	-	1	1	26.60	0.0362	-
Borehole water sites						
Eneka	0.0073	0.9927	0.9985	1.6877	0.369	0.9285
Eleme	0.016	0.9843	0.9981	3.9958	0.181	0.9965
Woji	0.0039	0.9960	0.8085	83.96	0.005	0.9560
Control site 1	0.0029	0.9970	0.4285	43.16	0.013	1.0000

Fluoranthene(Flua), Pyrene(pyr), Anthracene(Anth), Phenanthrene (Phen), Low molecular weight (LMW), High molecular weight (Hmw), Benzo(a)anthracene, B(a)A; Chrysene (Chry).

Relationship of PAHs components across soil dumpsite and borehole water

Multivariate analysis was conducted on soil dumpsite and borehole water to determine Pearson correlation (PC) and principal component analysis (PCA) respectively. Multivariate analysis is widely used to determine the relationship between complex data source thereby deriving crucial information [52], so therefore, the PAHs concentration detected during laboratory analysis in soil dumpsite and borehole water sources was utilized for this study with regards to different locations.

Table 5 shows the PCA conducted for soil dumpsite and borehole water, which produced five factor aggregates, with cumulative variance of 69.96% using rotated varimax. So therefore, Factor 1 produced variance of 19.45 % with presence of Ace-S, BaA-S, BAP-S, Acy-BW, Ant-BW, Pyr-BW, Chry-BW and DBA-BW. Factor 2 gave variance of 12.80 % with PCA component as Acy-S and Phen-S. Factor 3 showed variance of 13.12% with presence of Ant-S, Chry-S, BbF-S and BkF-S. Factor 4, Flu-S was present only at 11.27% variance, while Factor 5 produced variance of Nap-S, Nap-BW, Ace-BW, Phen-BW, Flua-BW accordingly. As for factor analysis conducted, there was presence of positive and negative aggregation, as it depicts that Factor 3 having positive aggregate, while other factor (1,2,4,5) had negative aggregate. BaA-S and BaA-BW were in Factor 1 that means that BaA leachate transfer took place from soil (-0.92) to borehole water (-0.67),

while Flu-S increased from soil (-0.43) to borehole water (-0.66). Factor 5 produced Nap-S leachate transfer decreased from soil (-0.81) and borehole water (-0.74).

Table 5. Principal component analysis of PAHs across soil and borehole water.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Nap-S					-0.81
Ace-S	-0.82		0.41		
Acy-S		-0.94			
Flu-S	-0.43			0.80	
Phen-S		-0.96			
Ant-S			0.88		
Flua-S			0.65	-0.45	
*BaA-S	-0.92				
*Chry-S			0.83		
*BbF-S			0.78		
*BkF-S			0.84		
*BaP-S	-0.72	-0.55			
Nap-BW	-0.63				-0.74
Ace-BW					-0.96
Acy-BW	-0.94				
Flu-BW	-0.66			-0.71	
Phen-BW	-0.64				-0.75
Ant-BW	-0.87				
Flua-BW					-0.93
Pyr-BW	-0.97				
*BaA-BW	-0.67			-0.59	-0.40
*Chry-BW	-0.87				
*DBA-BW	-0.80				-0.51
Eigenvalue	8.325	2.965	3.631	2.484	4.881
Variance (%)	19.452	12.803	13.12	11.266	13.314
Cumulative (%)	19.452	32.255	45.375	56.64	69.955

S-Soil dumpsite; BW-Borehole water; Nap-Naphthalene; Ace -Acenaphthene; Acy-Acenaphthylene; Flu-Fluorene; Phen-Phenanthrene; Ant-Anthracene; Flua-Fluoranthene; BaA-Benzo(a)anthracene; Chry-Chrysene; BbF-Benzo(b)fluoranthene; BkF-Benzo(k)fluoranthene; BaP-Benzo(a)pyrene; DBA-Dibenz(ah)anthracene.

Table 6 gives the correlative potential of PAHs in soil dumpsite and borehole water across all sampling locations, as seen, the PC showed presence of strong (≥ 0.70 PC ≤ 1.00), medium (≥ 0.30 PC ≤ 0.69) and weak (≥ 0.00 PC ≤ 0.29) correlations [52]. Vertical Ace-S produced strong correlation with Flu-S, Nap-BW, Acy-BW, Ant-BW, Pyr-BW, Chry-BW and DBA-BW, also Acy-S correlated strongly with Phen-S (0.89), while BaA-S correlated with Bap-S, Acy-BW, Ant-BW, Pyr-BW, Chry-BW. There was strong correlation as one moves towards borehole water in PAHs components. The correlation (Table 5) conducted produced positive regression that implies PAHs component were from similar pollution source and migratory behavior across soil and borehole water system via leaching route, while negative correlation implies dissimilar or different polluting source [1].

Table 6. Correlation matrices of PAHs in soil and borehole water.

	Nap-S	Ace-S	Acy-S	Flu-S	Phen-S	Ant-S	Flua-S	BaA-S	Chry-S	BbF-S	BkF-S	BaP-S	Nap-BW	Acy-BW	Ace-BW	Flu-BW	Phen-BW	Ant-BW	Flua-BW	Pyr-BW	BaA-BW	Chry-BW	DBA-BW	
Nap-S	1																							
Ace-S	-0.04	1																						
Acy-S	0.48	-0.10	1																					
Flu-S	-0.19	0.79	0.11	1																				
Phen-S	0.32	-0.50	0.89	-0.26	1																			
Ant-S	-0.41	0.25	-0.12	0.36	-0.22	1																		
Flua-S	0.02	-0.10	0.25	-0.26	0.40	0.42	1																	
BaA-S	0.11	0.62	0.24	0.31	0.08	-0.30	-0.14	1																
Chry-S	-0.31	0.43	-0.34	0.15	-0.39	0.81	0.50	0.04	1															
BbF-S	0.21	0.08	0.30	0.23	0.18	0.58	0.63	-0.45	0.35	1														
BkF-S	0.14	0.58	0.38	0.68	0.05	0.68	0.32	0.06	0.50	0.75	1													
BaP-S	0.49	0.40	0.50	0.07	0.35	-0.41	-0.04	0.88	-0.08	-0.31	0.10	1												
Nap-BW	0.52	0.72	0.21	0.57	-0.18	-0.25	-0.43	0.55	-0.13	0.01	0.41	0.59	1											
Ace-BW	0.72	0.36	0.39	0.36	0.04	-0.14	-0.35	0.14	-0.21	0.26	0.49	0.39	0.84	1										
Acy-BW	0.12	0.85	-0.08	0.56	-0.36	-0.28	-0.33	0.80	0.02	-0.28	0.16	0.60	0.80	0.34	1									
Flu-BW	0.11	0.37	-0.39	-0.26	-0.34	-0.14	0.20	0.54	0.46	-0.29	-0.17	0.49	0.18	-0.13	0.49	1								
Phen-BW	0.64	0.64	0.07	0.29	-0.25	-0.26	-0.30	0.53	0.03	-0.03	0.30	0.65	0.92	0.79	0.73	0.47	1							
Ant-BW	0.30	0.73	-0.26	0.29	-0.49	-0.33	-0.33	0.71	0.10	-0.35	0.01	0.59	0.73	0.34	0.90	0.69	0.82	1						
Flua-BW	0.68	0.47	0.35	0.45	-0.03	-0.18	-0.40	0.25	-0.21	0.19	0.48	0.45	0.91	0.99	0.48	-0.10	0.85	0.46	1					
Pyr-BW	0.03	0.82	-0.19	0.46	-0.39	-0.27	-0.24	0.82	0.11	-0.34	0.07	0.59	0.67	0.17	0.98	0.63	0.65	0.91	0.32	1				
BaA-BW	0.48	0.52	-0.15	-0.07	-0.28	-0.20	0.01	0.55	0.32	-0.13	0.10	0.65	0.60	0.40	0.62	0.86	0.84	0.81	0.45	0.65	1			
Chry-BW	0.33	0.74	-0.22	0.30	-0.46	-0.33	-0.32	0.71	0.10	-0.32	0.05	0.62	0.77	0.39	0.91	0.69	0.85	1.00	0.51	0.91	0.83	1		
DBA-BW	0.36	0.79	-0.01	0.58	-0.36	-0.32	-0.49	0.67	-0.11	-0.21	0.22	0.57	0.93	0.60	0.93	0.33	0.86	0.90	0.72	0.86	0.61	0.91	1	

¹ S – Soil dumpsite; BW – Borehole water; Nap – Naphthalene; Ace – Acenaphthene; Acy – Acenaphthylene; Flu – Fluorene; Phen – Phenanthrene; Ant – Anthracene; Flua – Fluoranthene; BaA – Benzo(a)anthracene; Chry – Chrysene; BbF – Benzo(b)fluoranthene; BkF – Benzo(k)fluoranthene; BaP – Benzo(a)pyrene; DBA – Dibenzo(a,h)anthracene

² Correlation matrices, p-value ≤ 0.0

Relationship of cumulative PAHs component across locations.

Table 7 gives the PCA analysis conducted for cumulative PAHs component across different locations in tandem to soil dumpsite and borehole water, which produced four factors at 65.85% cumulative variance. Factor 1 gave the high number of aggregates (Eleme-S, Eliozu-S, control site 1, Eleme-BW and Woji-BW) as compared to other factors that is factor 2 (Eneka-S, Woji-S), factor 3 (control site 2) and factor 4 (Yenagoa-S). We can also derive that there was slight increase from Eleme-S (-0.87) to Eleme (-0.96) in relation to Eneka-S (-0.43) and Eneka-BW (-0.56).

Table 7. Principal component analysis of PAHs across locations

	Factor 1	Factor 2	Factor 3	Factor 4
Eleme-S	-0.87			
Eliozu-S	-0.78			-0.41
Eneka-S	-0.43	-0.85		
Oyigbo-S	-0.49		0.67	
Woji-S		-0.91		
Yenagoa-S				-0.94
Control site 1-S	-0.96			
Control site 2-S			0.82	
Eleme-BW	-0.96			
Eneka-BW	-0.56			
Woji-BW	-0.96			
Control site 1-BW			-0.41	
Eigenvalue	4.948	2.04	1.64	1.49
Variance (%)	22.26	16.08	14.13	13.38
Cumulative (%)	22.26	38.34	52.47	65.85

Table 8 shows the correlation matrices conducted for cumulative PAHs component across different study locations, as such there was presence of weak, medium, and strong correlation. Vertical Eleme-S showed strong correlation with Eliozu-S (0.74), control site 1-S (0.85), Eleme-BW (0.79) and Woji-BW (0.82). Eliozu-S and Woji-BW produced correlation (0.70), control site 1-S correlated strongly with Eleme-BW (0.95) and Woji-BW (0.93). Eleme-BW and Woji-BW correlated at 0.91 Therefore, the vertical correlation (Eneka-S, Woji-S, Yenagoa-S) and horizontal correlation (Eneka-S, Oyigbo-S, Woji-S, Yenagoa-S, control site 2, Eneka-BW, control site 1-BW) implies that soil dumpsite and borehole water interact weak and medium pollution source.

Table 8. Correlation of PAHs in soil and borehole water.

	Eleme -S	Eliozu -S	Eneka -S	Oyigbo -S	Woji -S	Yenagoa -S	Control site 1-S	Control site 2-S	Eleme - BW	Eneka - BW	Woji - BW	Control site 1-BW
Eleme-S	1											
Eliozu-S	0.74	1										
Eneka-S	0.69	0.16	1									
Oyigbo-S	0.58	0.53	0.44	1								
Woji-S	0.21	-0.33	0.62	0.15	1							
Yenagoa-S	0.19	0.24	0.03	-0.30	0.35	1						
Control sit 1-S	0.85	0.68	0.51	0.45	-0.20	-0.21	1					
Control sit 2-S	-0.10	0.16	-0.18	0.33	-0.14	-0.14	-0.1	1				
Eleme-BW	0.79	0.60	0.47	0.37	-0.22	-0.23	0.95	-0.16	1			
Eneka-BW	0.26	0.18	0.00	0.05	-0.25	-0.28	0.46	-0.22	0.67	1		
Woji-BW	0.82	0.70	0.40	0.54	-0.24	-0.23	0.93	-0.14	0.91	0.49	1	
Control sit 1-BW	-0.20	-0.19	-0.18	-0.20	-0.22	-0.13	-0.1	-0.10	-0.01	0.10	0.12	1

¹S – Soil dumpsite; BW – Borehole water

²Correlation matrices, p-value ≤ 0.05

Health and exposure risk assessment

The degree of PAHs exposure to humans is due to the influence of chronic daily intake (CDI) across different exposure matrices (ingestion, dermal and inhalation) of soil dumpsite and borehole water that are interconnected via chemical infiltrations and its corresponding biochemical transformations with flora and faunas [2,53]. Health and exposure risk assessment was conducted on PAHs concentration for soil dumpsite and borehole water using USEPA risk models that gives the exposure ratio with regards to health implication (carcinogenic and non-carcinogenic) for adults and children respectively. As seen in Appendix 1 and 2, cancer risk for adults and children were evaluated in soil dumpsite which produced cumulative exposure matrices in Table 9, which implies that adults and children are at serious risk of having cancer related issues over a period of time in tandem with USEPA cancer reference of 0.000001 – 0.0001 (1.0E-06 – 1.0E-04) [54-56] For Appendix 3 and 4, hazard index gave cumulative hazard quotient (non-cancer risk) that were within USEPA hazard range (0 –1) [54,56].

Appendix 4 and 5 shows that cumulative cancer risk of borehole water that were within USEPA cancer reference thus implies there will be no cancer related issues, while for appendix 6 and 7 shows that the sum-total of hazard quotient for ingestion and dermal contact were within USEPA hazard range except for inhalation that was above 1 correspondingly.

The utilization of individual PAHs components with their corresponding cancer slope factor and reference dose has immerse influence of incremental lifetime cancer and non-cancer risk [31], as children is more at risk compared to adults, thereby as PAHs is absorbed into the human body, they act more in cellular functioning negatively leading to tissues degradation, poor organ development and improper functioning of the central nervous system [53]. The effects of carcinogenic PAHs have been reported to be more prominent in certain parts of the body which include the liver, lung gastro-intestine, bladder, and skin (ATSDR, 2013). Even though there is concern over the potential health risk of the populace, most especially the children living close to dumpsite areas due to the possibility of dispersal of PAHs to the entire environment and as well inherent hand to mouth activities leading to long life exposure and residents and resident's detrimental health. As we can see across the entire summarized values of cumulative cancer risk and hazard quotient, there were diverse values that implies that adults and children are at risk over a period of time based on age, exposure period, exposure frequency, as such using USEPA reference age of 70 years for cancer risk evaluation, it shows that inhalation can be detrimental since it contributed more as compared to ingestion (oral) and dermal (skin contact), as such one should expect that inhalation of PAHs into the lungs get absorbed into the blood stream leading to blood cancer and respiratory based cancer [55,57]. For ingestion and dermal exposure can lead to carcinogenesis leading to formation of cellular tumors, DNA degeneration and abnormal genetic changes over a period [58,59]. Although other information has shown that PAHs is removed from the body by urination as hydroxylated PAHs metabolites [57,60].

The total cancer risk and hazard index were summed up in terms of all exposure (Table 10), which shows that Eleme had the highest cancer risk thus implying that adults and children leaving within 500-1000 m in tandem to other activities that is taken place in the vicinity such as oil and gas and chemical industries will experience immerse cancer issues such as cancer of the skin, lungs, bladder, liver, stomach as well as well as reduction in reproductive, immunity, neurologic and bodily development [61-63]. Although one cannot conclude that Eleme contributed to the cumulative PAHs concentration without due diligent to other petroleum exploratory activities (gas flaring, flue-gas venting, effluent release into water body) taken place across offshore and land shore areas in oil-producing area, southern Nigeria [4,15,64]. Therefore, petroleum and chemical industries is assumed to contribute immensely to the total PAHs release in tandem to automobile and heavy duty, residential and natural releases accordingly.

Table 9. Total cancer risk and non-cancer risk of heavy metals across soil and borehole water sources

Sample Location	Exposure Medium	Soil dumpsites				Borehole water samples			
		Total cancer risk		Hazard index		Total cancer risk		Hazard index	
		Adults	Children	Adults	Children	Adults	Children	Adults	Children
Eleme	Ingestion	7.83E-01	1.93E+00	2.17E-02	1.78E-01	8.12E-13	3.00E-09	1.90E-05	3.16E-05
	Dermal	4.13E-03	3.05E-02	1.29E-06	8.89E-05	1.28E-12	4.90E-09	3.77E-05	1.63E-05
	Inhalation	5.27E+03	8.11E+02	5.40E-02	1.11E-01	1.96E-05	4.60E-01	1.09E+04	2.18E+04
Eliozu	Ingestion	3.69E-01	9.08E-01	1.10E-03	9.01E-03	1.89E-10	1.88E-09	3.20E-05	5.33E-05
	Dermal	1.95E-03	1.44E-02	6.38E-07	4.41E-05	2.98E-10	3.06E-09	5.84E-05	2.52E-05
	Inhalation	2.61E+03	4.01E+02	3.21E-02	6.59E-02	4.56E-03	4.52E-01	2.84E+04	5.69E+04
Eneka	Ingestion	7.86E-01	1.94E+00	2.09E-02	1.72E-01	NA	NA	NA	NA
	Dermal	4.15E-03	3.06E-02	7.88E-07	5.45E-05	NA	NA	NA	NA
	Inhalation	4.74E+03	7.29E+02	2.51E-02	5.14E-02	NA	NA	NA	NA
Oyigbo	Ingestion	6.93E-01	1.71E+00	1.08E-03	8.86E-03	NA	NA	NA	NA
	Dermal	3.66E-03	2.70E-02	5.82E-07	4.02E-05	NA	NA	NA	NA
	Inhalation	4.20E+03	6.47E+02	2.36E-02	4.83E-02	NA	NA	NA	NA
Woji	Ingestion	5.89E-01	1.45E+00	2.58E-02	2.12E-01	5.69E-13	1.06E-10	8.50E-06	1.41E-05
	Dermal	3.11E-03	2.29E-02	6.75E-07	4.67E-05	8.94E-13	1.73E-10	2.38E-05	1.03E-05
	Inhalation	3.20E+03	4.92E+02	3.94E-04	8.09E-04	1.37E-05	1.22E-01	2.13E+04	2.85E+04
Yenagoa	Ingestion	3.31E-01	8.15E-01	1.79E-02	1.47E-01	NA	NA	NA	NA
	Dermal	1.75E-03	1.29E-02	5.27E-07	3.65E-05	NA	NA	NA	NA
	Inhalation	1.81E+03	2.78E+02	4.98E-04	1.02E-03	NA	NA	NA	NA
Control	Ingestion	9.00E-03	2.22E-02	3.73E-04	3.06E-03	8.12E-14	2.31E-11	1.49E-07	2.49E-07
Site 1	Dermal	4.75E-05	3.51E-04	2.93E-07	2.02E-05	1.28E-13	3.78E-11	2.51E-07	1.08E-07
	Inhalation	5.31E+02	8.17E+01	2.54E-02	5.21E-02	1.96E-06	3.41E-03	3.37E+01	6.74E+01
Control	Ingestion	9.95E-03	2.45E-02	7.50E-06	6.16E-05	NA	NA	NA	NA
Site 2	Dermal	5.25E-05	3.87E-04	3.22E-09	2.23E-07	NA	NA	NA	NA
	Inhalation	5.41E+01	8.32E+00	8.98E-06	1.84E-05	NA	NA	NA	NA

¹NA: No data**Table 10.** Cancer risk and Hazard index of soil dumpsite and borehole water.

Sample Location	Soil dumpsite				Borehole water			
	Total Cancer risk		Hazard Index		Total Cancer risk		Hazard Index	
	Adults	Children	Adults	Children	Adults	Children	Adults	Children
Eleme	5.27E+03	8.13E+02	7.57E-02	2.89E-01	1.96E-05	4.60E-01	1.09E+04	2.18E+04
Eliozu	2.61E+03	4.02E+02	3.32E-02	7.50E-02	4.56E-03	4.52E-01	2.84E+04	5.69E+04
Eneka	4.74E+03	7.31E+02	4.60E-02	2.23E-01	NA	NA	NA	NA
Oyigbo	4.20E+03	6.49E+02	2.47E-02	5.72E-02	NA	NA	NA	NA
Woji	3.20E+03	4.93E+02	2.62E-02	2.13E-01	1.37E-05	1.22E-01	2.13E+04	2.85E+04
Yenagoa	1.81E+03	2.79E+02	1.84E-02	1.48E-01	NA	NA	NA	NA
Control Site 1	5.31E+02	8.17E+01	2.58E-02	5.52E-02	1.96E-06	3.41E-03	3.37E+01	6.74E+01
Control Site 2	5.41E+01	8.34E+00	1.65E-05	8.02E-05	NA	NA	NA	NA

NA: No data

Conclusions

The study investigated the concentration, sources (molecular diagnostics), health and exposure risk assessment of Polycyclic Aromatic Hydrocarbons (PAHs) from soil and borehole water samples in selected active dumpsites in Rivers and Bayelsa State, Nigeria. PAHs across the studied dumpsites showed significant contamination as Eleme contributed more as compared to other locations. Molecular diagnostics showed that low molecular weight PAHs dominated in comparison to high molecular weight PAHs in both soil and water samples as PAHs were from petrogenic and pyrogenic source, but the pyrogenic activities were predominant. Multivariate analyses were conducted for PAHs and locations gave principal component analysis (PCA) and Pearson correlation that were negative implying that they were from dissimilar polluting source and vice versa for positive across migration route. The results of health and exposure risk indicated that, in both adults and children, the inhalation pathway was the greatest contributor for cancer risk and non-cancer risk implying inhalation-based health issues over a period, as dermal pathway was the least contributor. Also, children were more at risk as compared to adults, as based on the result of this present study, it can be concluded that soils surrounding the dumpsites area are polluted by PAHs contaminants especially with known carcinogens (BaA, BbF, BkF and BaP) that in turn leach into water aquifer system leading to increase PAHs concentration, which poses adverse health threat to man and environment in maintain equitable balance. Therefore, public enlightenment should be created on environmental pollution, treatment and containment measures need to be put in place to avoid possible human exposure.

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Conflict of interest

We declare no conflict of interest as regards this article as the study was self-funded.

CRedit author statement

VIO: Conceptualization, Research design, Supervision; VUO: Methodology, Software, Data curation, Writing- Original draft preparation; DOO: Writing- Original draft preparation, Writing- Reviewing and Editing; ENN: Visualization, Investigation; PLO: Visualization and Investigation

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Supplementary Material

The evaluation of data from health and exposure risk assessment are available as appendix 1 - 8. This material is available online at www.eaht.org.

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