Original Article

ASSESSMENT OF PAH CONTAMINATION AND ECOLOGICAL RISK IN WASTE DUMPSITES OF BAYELSA STATE, NIGERIA

Chijioke Ifeanyi Obiakor, Nkechi Chiamaka Nwosu and chechukwu Emmanuel Nwogwugwu

Department of Chemistry,
Abia State College of Education,
Abia State, Nigeria

DOI:https://doi.org/10.5281/zenodo.15438395

Abstract : This study investigates the levels, distribution and ecological risk of polycyclic aromatic hydrocarbons (PAHs) in surface soils of some selected wastes dumpsites in Bayelsa State, Nigeria. Polycyclic aromatic hydrocarbons (PAHs) are petty pollutants frequently seen in quite a lot of vicinity that threaten the populace living in close proximity to them. True representative samples of the study and control areas were collected and analyzed for PAHs using Gas Chromatography–Mass Spectrometer (GC–MS). The analyzed PAHs concentrations varies from 40.256 mg/kg for Swali, 10.63549 mg/kg for Opolo, 60.91517 mg/kg for Tombia Round About, and 19.3009 mg/kg for Igbogene wastes dumpsites respectively. Moreover, the total PAHs concentrations in a given station were seen to be higher than the Dutch guideline maximum limits of 40 mg/kg although not for an individual PAHs. The obtained results equally showed the first and second highest single concentration of PAHs composite detected at an individual site for indeno [1,2,3-cd]pyrene (IcdP) to be 22.55850 mg/kg and 8.784 mg/kg for fluoranthene at Tombia round about, this astronomic rise maybe due to its commercial nerve midpoint in Yenagoa Metropolis.

Keywords: Level, Distribution, Ecological risk, Bayelsa, Dumpsites, PAHs , Multiple transfusions, Beta-Thalassemia major

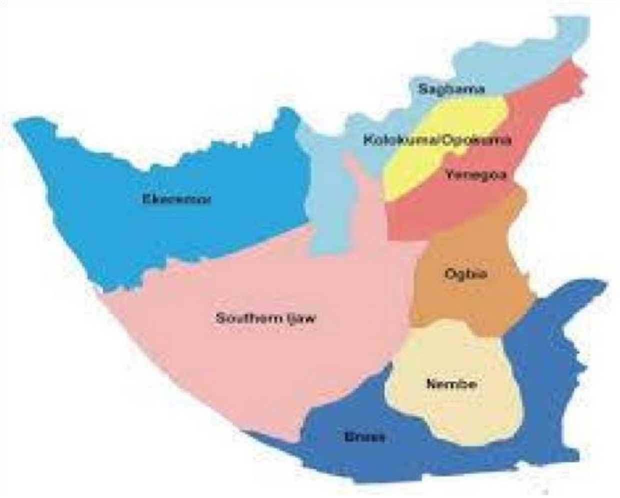
Introduction

Urban renewal drive greeted with increasing human population and economic boom, couple with advanced technology, industrialization, agricultural, municipal and domestic activities, have emanated into billions of wastes debris littered all over the globe. PAHs are emergent organic compounds that have attained global acceptance due to its carcinogenic, mutagenic and teratogenic organic constituents containing several benzene rings. Thus, (4–6 rings) PAHs are categorized as high and (2–3 rings) as low-molecular weight groups. Furthermore, PAHs are generally classified as relatively persistent organic and environmental pollutants. Hence, 2–3 rings PAHs threaten our surrounding through domestic heating, traffic jam, refineries operations and other industrial proceedings (Amolo and Egede 2023). Whereas, 4–6 benzene rings PAHs are basically hazardous complex mixtures, bioaccumulative and semi-volatile, and persistently stockpile in the environment (soil, air, sediments, water, etc.) Ortega et al., 2022. Though 7,8 rings PAHs can be produced either by anthropogenic or naturally means, including forest fires, volcanic exhalations, diagenesis, industrial emissions, burning of biomass and combustion of fossil fuels, and petroleum spills. 9–11 The Σ16PAH contents have been widely reported in global soil, e.g., in London (400– 67 000 ng g−1),12 Glasgow (48–51 822 ng g−1),13 Moscow (208–9604 ng g−1),14 Seville (89.5– 4004 ng g−1),15 Beijing, China (219–27 825 ng g−1),16 and Delhi, India (81.6–45 017 ng g−1). Soil is a major environmental matrix that sustains the lives of several organisms, through a direct or indirect means, and is a major sink for PAHs due to large areas and retention times, emanating into soil quality degradation globally. High molecular weight PAHs are relatively immovable, and moderately insoluble in water. PAHs are essentially found in the bottom sediments, thus accumulating to greater concentrations, which could be lethal to bottom feeders organisms like crustacean cum the environment. PAHs occur at low environmental concentrations due to their low biodegradability and elimination problems. Evidentially, PAHs contains bioeffects, such as interactive effects on hematological parameters and developmental toxicity (Edori et al., 2019). Their emissions may be due to natural or anthropogenic sources. Experimentally over 500 different PAHs have been detected in the air. Moreover, only 16 priority PAHs have been classified by the United States Environmental Protection Agency (U.S. EPA) as pollutants due to their high carcinogenic, mutagenic and teratogenic properties. They include: naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP), and indeno [1,2,3-cd]pyrene (IcdP). Underground/Surface soil are usually contaminated with PAHs via leaching from landfills, untreated wastes, petroleum spills, and fossil fuel combustion, which are the main contributor to the array of public healthcare disease outbreak globally. Humans living in close proximity to a waste dumpsites are inadvertently exposed to PAHs contamination through toxic wastes disposal at unlined dumpsite via leachates as reported by (Tang et al,. 2005). The goal of this study was to adopt Opolo, Swali, Igbogene and Tombia round about waste dumpsites as reference point to the detrimental effects of electronic and other wastes been stock in the environment daily. These dumpsites are open/unlined wastes dumpsite, not fit for wastes disposal or dumpage, due to its poorly structured plan for wastes reception, a typical scenario for waste disposal in Nigeria where prompt and adequate measures are not considered at the point of decision making, either as a result of poor budgetary allocation or oversight. Pollution of surface/underground soil, through improper wastes disposal has gain momentum since they are not regularly monitored thereby posing invasive public health nuisance to commuter and residences living within such vicinity. There is a rising need for Government at all levels from time to time to comprehensively conduct a thorough investigation as a way of reducing the heinous health implications associated with improper wastes disposal. Hence, this research work was tailored to determine the levels, distribution and ecological risk of PAHs in surface soil at some selected wastes dumpsites. PAHs exist in the atmosphere as vapor particle-bound phase, and a greater portion of it are scavenged by vegetation via dry and wet deposition. Invariably, the use of vegetation, especially trees, in the assessment of atmospheric PAHs concentrations has attained an enviable height for a holistic approach. Moreover, due to their high spatial and chronological distribution, the use of trees provides the possibility of building high-resolution maps of air pollution to detect risk areas in urban areas. Consequently, the merit in their capability to hoard PAHs between tree species has been identified. The restriction of pollutants by trees take place mainly in the upper portion of the tree, such as leaves, stems, and barks. Customarily, several research works have been successfully carried out by notable authors in addressing the use of leaves/needles from diverse species of tree to determine the presence of PAHs in urban settlement. Stomata and outer cuticular lamellae are the main vessel for uptake of PAHs in the vapor phase, whereas particle-bound PAHs are heap up on the surface of leaf, Other vegetative parts of the tree, such as bark, have been undergoing series of studies, meanwhile recent findings have shown its efficacious ability to heap up PAHs due to its prominence in lipid content, permeability and almost inert surface. The assessment of the atmospheric PAH concentrations using the leaves and barks of different tree species are achievable due to recent analytical procedures. Although, quite a numbers of this procedures propounded in the literature vary, due to complexity of the sample matrix. However, quite a lot of steps in those protocols are similar, including sample pre-treatment, extraction, clean-up, pre-concentration, and chemical analysis. In addendum, the mechanism of carrying out this analysis is diverse. Considering the sample pretreatment, some studies include the use of drying techniques such as freeze drying, stoves and ovens. Moreover, crushing techniques using mortars, high-speed grinders or liquid nitrogen is welcomed. Nevertheless, there are many works where the intact samples are used, without any prior drying or crushing treatment. The pre-treatment step has been shown to be a tailback in achieving adequate recoveries. Consequently, it is imperative to pay attention to how the samples are prepared, when employing some of these methods because it may greatly reduce their recoveries. Regarding PAHs extraction, ultrasonic extraction, Soxhlet extraction, accelerated solvent extraction and microwave-assisted extraction are the most widely used method, which involve the use of different organic solvents for better yields.

Materials and methods

Study area

Bayelsa State has eight (8) LGAs, it extends between latitude 4^0 15’ and 5^0 23’ N and longitude 5^0 15’ and 6^0 45’ E. Bayelsa State is located in the South-South Region of Nigeria, being the only homogeneous Ijaw speaking State bounded to the North by Delta state, to the East by Rivers State and to the South and West by the Atlantic Ocean. The state capital occupies an area of about 21,100 Km2. A swampy, mangrove and tropical rain forest, it is the traditional home for the Ijaw peoples, a renowned fishing group, major exporters of palm oil and kernels, high Agricultural outputs and heavy exploitation of petroleum and Natural gas in large deposits. Who are prone to several health diseases and poverty (The daily times, 2022). The poor sanitary hygiene behavior of this region informed the decision to conduct this research work within the scope of four government approved wastes dumpsites located in Yenagoa conurbation. For this reason, the follow wastes dumpsites was preferred to be precise; Swali, Opolo, Tombia round about, Igbogene.



Sample Collection

Surface soil samples was collected from four Government Approved wastes dumpsites situated within Yenagoa Metropolis using soil auger after removing the covering wastes. A global positioning system (GPS) was used throughout the sampling procedure to meticulously record the sampling sites' geographical coordinates in the field. These samples were collected at the depth of 0-10cm Using a cleaned stainless-steel scoop, at each sampling site 3 subsamples were collected and then mixed together to form a true representative sample of the bulk and immediately place in an ice-cold box, each composite sample weighed was about 200 grams and coated straight away with aluminum foil, stored separately, and sealed in labeled polythene bags. The samples were subsequently frozen before they were transported to the laboratory. Ahead of extraction, the samples were sealed and frozen at −18 °C until pre-treatment within 15 days. During the extraction and chemical analysis, the samples were defrosted, air-dried, and sieved through a <2 mm mesh sieve.

Chemical analysis, Analytical procedures, and Sample preparation

Soil samples were analyzed for the 16 USEPA priority PAHs: acenaphthene (Ace), benzo (ghi)perylene (BghiP), anthracene (Ant), acenaphthylene (Acy), benzo(a)anthracene (BaA), benzo(b)fluoranthene (BbF), chrysene (Chr), dibenzo(a,h)anthracene (DahA), benzo(k)fluoranthene (BkF), fluorene (Flo), fluoranthene (Fluo), indeno (1,2,3-cd) pyrene (IcdP), benzo(a)pyrene (BaP), naphthalene (Nap), pyrene (Pyr) and phenanthrene (Phe). Analytical procedures and sample preparation methods during this study were compared to the Dutch guideline maximum limits of 40 mg/kg, DPR and other notable reports. The samples were quantitatively analyzed by gas chromatography-mass spectrometry (GC-MS, Agilent 6890N GC5975 MSD) for the 16 PAHs.

Sample preparation

The method used by Olayinka et al., (2017) was adopted for sample preparation. Pebbles, rock particles and sticks were removed from surface soil sample prior to being air dried in the laboratory for 72 h at room temperature. To obtain a superior quality, the sample was pounded with a pestle and mortar and sieved through a 2 mm mesh sieve. Preceding the analysis, the sieved soil was eluted into disinfected amber-colored glass vials that were cautiously sealed and labeled before the analysis.

PAHs extraction and clean-up from soil samples

Determination of surface soil sample for polycyclic aromatic hydrocarbons (PAHs) were extracted using soxhlet extraction method as described by Edori & Iyama (2019). The extract was collected in a clean amber glass vial for cleaning to remove contaminants that could obstruct the analysis while using a gas chromatography column (GC-MS). To get rid of non-polar aliphatic hydrocarbons, the column was rinse with 10 mL of hexane, and the polycyclic aromatic hydrocarbon was collected by pouring the column with hexane- dichloromethane (8 mL of hexane and 5 mL of dichloromethane mixed together in the ratio of 3:2). The extract-containing round bottom flask was connected to the rotavap and then lowered into the water bath. The vacuum pump and rotation were turned on, and the setup was monitored until the extract in the round bottom flask reduce to about 1mL. At completion, the rotation was tuned off and the round bottom flask was raised out of the water bath. The vacuum pump was tuned off and the tap was cautiously open to release the system from the reduced pressure. The round bottom flask was then detached from the rotavap and the extract was eluted into an amber vial for GC-MS analysis of PAHs compounds. GC-MS identification and quantification of PAHs. The qualitative and quantitative analysis of polycyclic aromatic hydrocarbons in soil samples were carried out using the external standards approach described by Amolo and Victor (2023). A standard mixture of the United State Environmental Protection Agency (USEPA) 16 priority polycyclic aromatic hydrocarbons (2000µg/mL): naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, Pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene and indeno[123-cd] pyrene was purchased from Sigma-Aldrich Lagos, Nigeria). The PAHs in the surface soil extracted sample were extracted using a gas chromatography-mass spectrometry Agilent GC:7890 MS. Helium was employed as the carrier gas, and the column head pressure was kept at 10 psi to accomplish an estimated flow rate of 1 mL/min. The injector port and transfer line were kept at 290^0C and 250^0C, respectively. A measure of 1 µL volume was set as the injection volumes in a splitless mode. The initial column temperature was held at 70^0C for 4 minutes while it was steadily increasing to 300^0C. In conclusion, the temperature was kept at 300^0C for 10 minutes. A 70 eV electron beam was used to ionize PAHs. Ions were separated using a single quadrupole and detected using an electron multiplier detector. The detector was set to obtain ions using the selected ion monitoring (SIM) mode. The mass range of 50-400 m/z was used to produce all spectra. The PAHs in the wastes dumpsite unhygienic soil sample were analyzed using a retention time and mass spectral match against the calibration standard. Correspondingly, the external standardization method of the generated calibrations curve of the USEPA sixteen (16) priority PAHs standard blend was used to quantify the USEPA sixteen (16) priority PAHs there in the sample. Evaluation of carcinogenic strength of the soil samples collected from each waste dumpsite. The carcinogenic potency of PAHs was estimated by calculating the concentrations of individual carcinogenic PAHs in stipulations of benzo(a)pyrene equivalent (BaPeq), otherwise called total BaP equivalent quotient (TEQ), and multiplying by the corresponding toxic equivalency factor (TEF) values proposed by Nisbet and LaGoy, (1992), as derived in Equation 1.

Total BaP Equivalent Quotient (TEQ) $=\Sigma(Ci \times TEFi)$ 1 Where:

Ci= Concentration of individual PAHs.

TEFi= Corresponding toxic equivalency factor (TEF).

Original Article

Sampli ng Point	Swali	Opolo	Tombia	Igbogene	Depth Cm	CN	Min	Max	Mean	STD
Nap	ND	ND	ND	ND	0-10 Cm	ND	0.000	0.000	0.000	0.000
Acy	9.2285e-1	ND	ND	2.9646e-1	0-10 Cm	0.056	2.9646e-1	9.2285e-1	6.097e-1	4.429
Ace	ND	ND	ND	ND	0-10 Cm	ND	0.000	0.000	0.000	0.000
Flu	6.6757e-1	ND	ND	ND	0-10 Cm	ND	0.000	6.6757e-1	0.000	0.000
Phe	2.1915	ND	4.7226e-1	2.3646e-2	0-10 Cm	ND	2.1915	4.7226e-1	3.093e-1	1.414
Ant	2.8239e-1	ND	ND	ND	0-10 Cm	ND	0.000	2.8239e-1	0.000	0.000
Fluo	0.2428	ND	8.7835e-1	6.6774e-2	0-10 Cm	ND	0.2428	8.7835e-1	5.235	4.449
Pyr	0.7929	ND	0.1422	ND	0-10 Cm	ND	0.1422	0.7929	0.468	0.461
BaA	7.8114e-1	4.0619	2.7137e-1	ND	0-10 Cm	0.134	2.7137e-1	7.8114e-1	4.862e-1	2.025
Chr	7.8343e-1	ND	6.9843e=1	ND	0-10 Cm	0.123	6.9843e=1	7.8343e-1	7.409e-1	0.601
BbF	2.1703e-1	4.3362	ND	ND	0-10 Cm	0.004	2.1703e-1	4.3362	3.253e-1	1.532
BkF	1.1919	2.2374	1.7329	ND	0-10 Cm	0.009	1.1919	2.2374	1.721	0.522
BaP	5.6109e-1	ND	4.6260e-1	ND	0-10 Cm	0.045	4.6260e-1	5.6109e-1	5.118	0.696

BghiP	1.3509	ND	7.4607e-1	ND	0-10 Cm	0.008	1.3509	7.4607e-1	4.406e-1	4.321
DahA	1.5419	ND	1.1907	ND	0-10 Cm	0.014	1.1907	1.5419	1.366	0.248
IcdP	0.0746	ND	22.5585	7.2944	0-10 Cm	0.023	0.0746	22.5585	9.976	11.479

Table 1 Concentration (mg/kg) of PAHs in the soil samples

where naphthalene (Nap), acenaphthylene (Apt), acenaphthene (Aph), fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo(a)anthracene (Ban), chrysene (Chy), benzo(b)fluoranthene (Bbf), benzo(k) fluoranthene (Bkf), indeno(1,2,3-cd)pyrene (Idp), dibenzo(a,h)anthracene (Dbh), standard deviation (STD),

minimum (Min), maximum (Max).

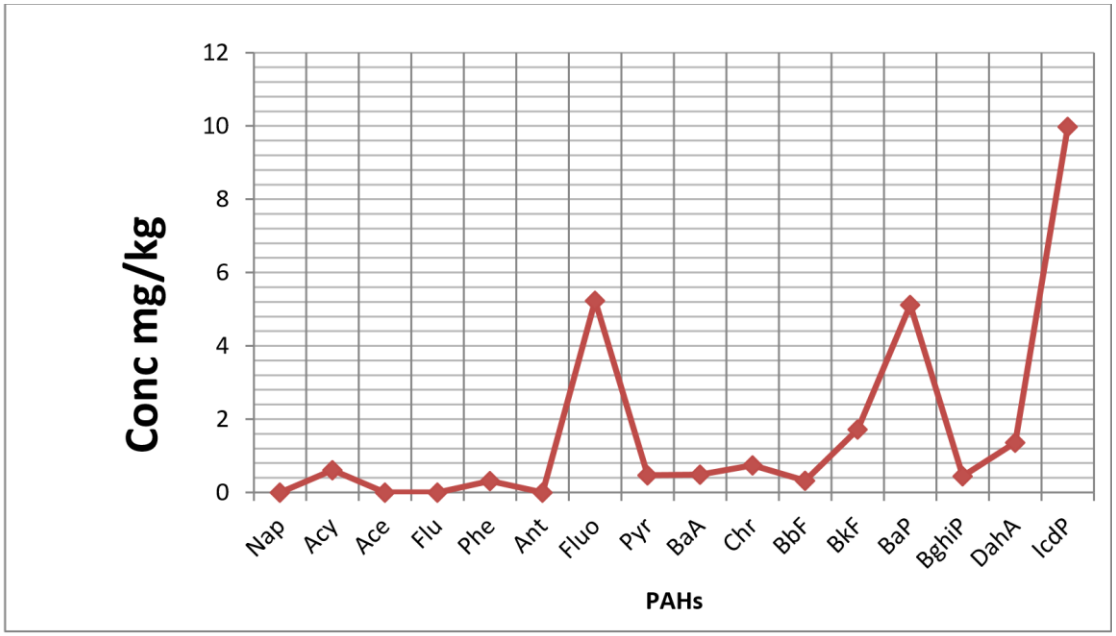


Fig 2 Mean Values of the various PAHs obtained from the study

RESULTS

The experimental PAHs results obtained for surface soil samples was given in their mean concentration of the USEPA 16 priority PAHs analyzed across the wastes dumpsite as shown in Table 1. The mean concentration of the USEPA 16 priority PAHs analyzed during this study varied from 0.24280 ppm (Fluoranthene) to 22.55850 ppm (Indeno(123-cd)pyrene). Naphthalene, Anthracene, Acenaphthylene, Acenaphthene, Benzo(ghi)perylene, and Benzo(b) fluoranthene etc, were not detected in most cases during this study. Furthermore, the sum total of the PAHs ($\sum$16 PAHs=131.1076 ppm) recorded in this study was found to exceed the DPR (2002) target value of 1 ppm but above the intervention limit of 40 ppm for soil contaminated along wastes dumpsite. Correspondingly, the concentration levels of Acenaphthylene (9.2285 ppm), chrysene (7.8343 ppm), fluorene (6.6757 ppm) and Benzo(a) pyrene (5.6109 ppm)) were found to surpass the maximum permissible limits of 0.690 ppm, 0.340 ppm and 1.060 ppm respectively set aside by the Dutch government for wastes dumpsite soils. Using Analysis of Variance (ANOVA), there was a momentous difference (p-value= 0.000) among the USEPA 16 Priority PAHs ($P \leq 0.05$). The fraction circulation of PAHs concentrations (with respect to LMW and HMW PAHs) within the study vicinity could be accessible in Figure 3.

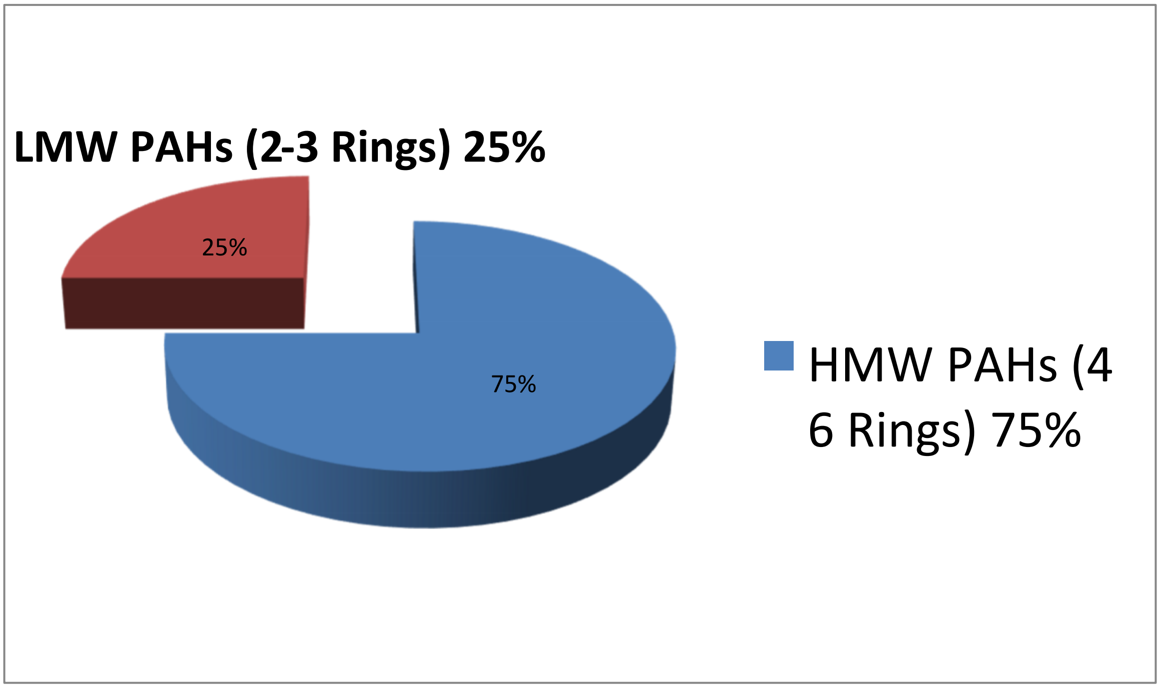


Fig 3. The percentage distribution of PAHs concentrations

The obtained result indicates that the concentrations of naphthalene (1.1605 ppm), phenanthrene (1.1079 ppm) and Anthracene (1.0766 ppm) were found to exceed the maximum permissible standard of 0.690 ppm, 1.060 ppm and , 0.340 ppm respectively set aside by the Dutch government for wastes dumpsite contaminated soils. Using Analysis of Variance (ANOVA), there was a significant difference (p- value= 0.000) among the USEPA 16 PriorityPAHs ($P \leq 0.05$). The percentage distribution of PAHs concentrations (with respect to LMW and HMW PAHs) in the study area was presented in Figure 3. The result indicates that the concentrations distribution of USEPA 16 priority PAHs in the study area was dominated by HMW PAHs in percentage distribution of 75% whilst the percentage distribution of LMW was 25%. Correspondingly, the estimation of carcinogenic potency of USEPA sixteen (16) PAHs analyzed from four wastes dumpsites surface soil sample were presented in Table 2. The result revealed that, the individual TEQ values (B[a]Peq) of the USEPA 16 Priority PAHs analyzed in this study anticipated from the TEF values ranges from 0.00047 ppm (Pyrene) to 6.83 ppm (Dibenzo (a,h) anthrathene). The result also revealed that the TEQ (∑B[a]Peq) of the USEPA 16 priority PAHs within the period of investigation was 8.95178 ppm (895.178%) which was observed to be higher than the Canadian TEQ (∑B[a]Peq) standard of 0.6 ppm. There was a significant difference (p-value= 0.000) among individual TEQ values (B[a]Peq) of the USEPA 16 priority PAHs investigated in this study using analysis of variance (ANOVA) ($P \leq 0.05$).

Table 2: Estimation of carcinogenic potency of USEPA sixteen (16) PAHs analyzed from four wastes dumpsites

PAHs	Numb	Molecul	TEF	TEQ	TEQ%	Canadian	ANOV

Original Article

er of Rings (ppm)	ar Weight Standard	TEQ(∑B[a]Peq) value	A P-

Naphthalene	2	128.2	0.001	0.00000	0.000	0.6	0.000
Acenaphthylene	3	152.2	0.001	0.00609	0.609		
Acenaphthene	3	154.2	0.001	0.00000	0.000		
Fluorene	3	166.2	0.001	0.00000	0.000		
Phenanthrene	3	178.2	0.001	0.00309	0.309		
Anthracene	3	178.2	0.01	0.00000	0.000		
Fluoranthene	4	202.3	0.001	0.00524	0.524		
Pyrene	4	202.3	0.001	0.00047	0.047		
Chrysene	4	228.3	0.001	0.00741	0.741		
Benzo(a)anthracene	4	228.3	0.01	0.04862	4.862		
Benzo(k)fluoranthene	5	252.3	0.1	0.1721	17.21		
Benzo(b)fluoranthene	5	253.3	0.1	0.3253	32.53		
Benzo(a)pyrene	5	252.3	0.1	0.5118	51.18		
Indeno(123cd)pyrene	6	276.3	0.1	0.9976	99.76		
Dibenzo(a,h)anthrathene	6	278.4	5	6.83	68.3		

Benzo(ghi)perylene	6	276.3	0.01	0.04406	4.406
Total TEQ (∑ B[a]Peq)				8.95178	895.178

Key: TEF: Toxic Equivalency Factor (TEF); TEQ: Total BaP Equivalent Quotient (∑B[a]Peq);: Canadian TEQ (∑B[a]Peq) standard Yu et al. (2020); TEF values by Nisbet and LaGoy, (1992).**

DISCUSSION

Leveraging on their abundance, immovability, and durable enrichment in soils, PAH compounds were thought to be an exceptional reservoir of organic pollutants, together with their soil system (Edori et al., 2019). Despite the insinuation that there are over 500 different PAHs, off which the USEPA recognized 16 priority pollutants in 1970s due to their doggedness, noxious effects within the environment and experimental attributes (Krauss, 2005). Recall Ekpete et al. (2019) put forward that the 16 priority PAHs should be routinely beleaguered for assessment and monitoring while affirming de facto global standard. The analyzed PAHs concentrations were moderately lower than those of Ortega et al., 2022 in their study, Determination of polycyclic aromatic hydrocarbons extracted from lichens by gas chromatography–mass spectrometry, but higher in quantity when compared to concentrations reported by Nuerla et al. (2022) during their study, Levels, sources, and risk assessment of PAHs residues in soil and plants in urban parks of Northwest China. The concentration levels of acenaphthylene (9.2285 ppm), chrysene (7.8343 ppm), fluorene (6.6757 ppm) and Benzo(a) pyrene (5.6109 ppm) were found to exceed the maximum permissible limits of the Dutch government using the Dutch Government (NMHE, 1994) standard. This arose tempers and worries when compared with Nisbet and LaGoy (1992); Obayori et al. (2017); Protano et al., (2014); Rodriguez et al. (2010); and Alexandrino et al. (2022) affirmed that these individual PAHs have the prospective to cause cancer thereafter bioaccumulation in living cells of most organisms at an elevated concentrations. In order to buttress, the appreciably soaring abundance of the aforesaid PAHs (naphthalene, anthracene, and phenanthrene) indicates that they were chiefly from low and reasonable temperature incineration processes, as opposed to earlier report by Guo et al. (2011). Paradoxically, the percentage ring shrewd allotment of PAHs in this psychoanalysis showed a prevalence of HMW PAHs (75%) over LMW PAHs (25%), signifying current authentication of these compounds. In the nutshell, Li et al. (2006) establish that LMW PAHs are habitually associated with petroleum spillages (petrogenic sources), which gives credits to this study. In an affirmative report by Amolo and Egede (2023), they attribute the occurrences of HMW PAHs in the environment to unfinished incineration of fossil fuels such as crude oil and natural gas (pyrogenic sources). Thus, the resultant analysis postulation was both petrogenic and pyrogenic in nature, as previously reported by both Edori et al. (2019) and Ekpete et al. (2019). Also recalling, Ekanem et al. (2019), PAHs habitually accumulate in surface soil as a result of adsorption due to their persistence and similarity for soil organic matter. The total amount of the 16 priority PAHs (16 PAHs= 131.1076 ppm) observed in this study exceeded the permissible limits of 1 ppm thereby surpassing the intervention threshold of 40 ppm set by DPR, 2002 for secure industrial soils. These insinuate that the surface soil sample collected at various wastes dumpsite were severely contaminated with PAHs debris littered all over the dumpsite. As a result, the sum total of the 16 priority PAHs (16 PAHs) gotten during this study was observed to be more than the 112.981 ppm concentration reported in Concentrations of polycyclic Aromatic hydrocarbons from selected dumpsites within Port Harcourt Metropolis, Rivers State, Niger Delta, Nigeria by Ekpete et al. (2019). While, Emoyan et al. (2011) observed values were more than the 0.82 ppm concentration reported in soils from a petroleum polluted site in Abraka River, Delta State, Nigeria. Thus, categorized soil pollutions of PAHs into four categories based on the 16 USEPA priority contaminants (∑16PAHs) namely; uncontaminated (less than 0.2 ppm), feebly contaminated (0.2-0.6 ppm), contaminated (0.6- 1 ppm) and sternly contaminated (1 ppm and above). According to this classification, the sampling stations was sternly infected with PAHs (16 PAHs= 131.1076 ppm), inserting it unhealthy for agricultural utilization connoting human health risk, as well as cancerous, as envisaged by Bandowe et al. (2021). PAH-contaminated soils have previously been linked to human health risks, stunted plants growth, aquaculture depletion, livestock disorderliness, and wildlife strain, as well as ecotoxicological risks to the soil biome (CCME, 2010; IARC, 2010). On the side line, Blasco et al. (2022) emphatically agreed to the fact that physical risk condition appraisal unified with PAHs absorption in soil habitually based on Benzo[a]pyrene (B[a]Peq) concentrations. This may be due to the fact that (B[a]Peq) has been extensively analyzed and establish to be tremendously carcinogenic (Liu et al., 2010). Recalling, WHO (2017), a benzo[a]pyrene concentration of 0.7 ppm correlates to a natural life cancer risk. Thus, the BaP-equivalent (B[a]Peq) is used to appraise carcinogenic risk from PAH-contaminated soil (Adeniyi et al., 2021). Depicting that B[a]Peq does not only associate with the risk of B[a]P but equally calculates each carcinogenic potencies of every PAHs, whereas the carcinogenic potency of both PAH is projected in relation to the carcinogenicity of B[a]P (Adeniyi et al., 2021).

Interestingly this findings recognize B[a]P as the chief carcinogenic factor (Sule et al., 2023). Hence, the toxicity equivalency factors (TEFs) developed by Nisbet and LaGoy (1992) and used by Sule et al. (2023) and Edori et al. (2019) were used to quantify and estimate the carcinogenic potential of other individual PAHs by multiply their concentrations by their suitable TEF values. The total benzo[a]pyrene different concentration (B[a]Peq) of the observed PAHs during the research was calculated as 8.95178 ppm, representing an abruptly high carcinogenic potency based on the Canadian soil environmental excellence B[a]Peq standard of 0.6 ppm stipulated for PAHpolluted soil, therefore depicting noxious carcinogenic risk (Amolo et al., 2023). In Conglomeration, as prohibited debris continue to pile up along various unlined wastes dumpsite in the city of Yenagoa for more than the stipulated days is required to stay thereby decaying before evacuation. More and more depleting wastes products will continually litter the city, producing detrimental wastes all over its environed if not adequately check. At the tail end, PAHs contaminations should be routinely beleaguered for assessment and monitoring.

CONCLUSION

The soil sample analyzed during this research indicates that the 16 USEPA priority PAHs were present. Comparably, it was revealed that the total amount of the 16 USEPA priority PAHs measured in the surface soil samples (16 PAHs=60.91517 mg/kg) exceeded the DPR (2002) target value of 1 ppm but fell dumpy of the 40 ppm interference value. Furthermore, it was evidential that the concentrations of Acenaphthylene (9.2285 ppm), chrysene (7.8343 ppm), fluorene (6.6757 ppm) and Benzo(a) pyrene (5.6109 ppm)) were found to surpass the Dutch government's maximum permitted standard. On the other hand, due to the estimated benzo[a]pyrene equivalent

(B[a]Peq] value of 8.95178 ppm obtained during this research, the estimated B[a]Peq value showed an abrupt increase of carcinogenic potency based on the Canadian soil environmental quality B[a]Peq standard of 0.6 ppm maximum permissible limits for wastes polluted soil by PAHs, invariably posing huge carcinogenic risk.

References

Alexandrino, K.; Sánchez, N.E.; Zalakeviciute, R.; Acuña, W.; Viteri, F. (2022). Polycyclic Aromatic Hydrocarbons in Araucaria heterophylla Needles in Urban Areas: Evaluation of Sources and Road Characteristics. Plants.

Adeniyi, A.V., Nton, M.E. and Adebanjo, F.O. (2021). Geochemical Finger Printing pf Oil-

Impacted Soil and Water Samples in Some Selected Areas in the Niger Delta. RMZ – M&G., 67(4):209-219.

Amigo, J.M.; Ratola, N.; Alves, A.(2011). Study of geographical trends of polycyclic aromatic hydrocarbons using pine needles. Atmos. Environ. 45, 5988–5996.

Amolo, I. R.; & Egede, V. P.; (2023). Characteristic, sources and risk assessment of PAHs in surface soil from five wastes dumpsites in Yenagoa Metropolis, Bayelsa State, Nigeria. International Journal of Chemistry and Chemical Processes. 9(4) 2695-1916.

A. J. White , P. T. Bradshaw , A. H. Herring , S. L. Teitelbaum , J. Beyea , S. D. Stellman , S. E. Steck , I. Mordukhovich , S. M. Eng , L. S. Engel , K. Conway , M. Hatch , A. I. Neugut , R. M. Santella and M. D. Gammon , Environ. Int., 2016, 89–90 , 185 —192.

Bandowe, B.M.B., Shukurov, N., Leimer, S., Kersten, M., Steinberger, Y. and Wilck, W. (2021). Polycyclic Aromatic Hydrocarbons (PAHs) In Soils of an Industrial Area in Semi-Arid Uzbekistan: Spatial Distribution, Relationship with Trace Metals and Risk Assessment. Environ Geochem Health, 43:4847-4861.

Blasco, M.; Domeño, C.; López, P.; Nerín, C.(2022). Behaviour of different lichen species as biomonitors of air pollution by PAHs in natural ecosystems. J. Environ. Monit. 13, 2588– 2596.

Canadian Council of Ministers of the Environment (CCME, 2010). Canadian Soil Quality Guidelines for Carcinogenic and other Polycyclic Aromatic Hydrocarbons (Environmental and Human Health Effects). Scientific Criteria Document (revised) PN 1445, Quebec, Canada. www.ccme.ca Accessed January 2020.

Dugay, A.; Herrenknecht, C.; Czok, M.; Guyon, F.; Pages, N. (2002). New procedure for selective extraction of polycyclic aromatic hydrocarbons in plants for gas chromatographic-mass spectrometric analysis. J. Chromatogr. 958, 1–7.

Dybing, E.; Schwarze, P.E.; Nafstad, P.; Victorin, K.; Penning, T.M. (2013). Polycyclic Aromatic Hydrocarbons in ambient air and cancer. Air Pollution Cancer, 161, 75.

Edori, O. S., & Iyama, W. A. (2019). Source Identification of Polycyclic aromatic hydrocarbons in water at point of effluent discharge into the New Calabar River, Port Harcourt, Rivers State, Nigeria. International Journal of Environment and Climate Change, 9(6), 343-349.

Ekanem, A.N., Osabor, V.N. and Ekpo, B.O. (2019). Polycyclic Aromatic Hydrocarbons (PAHs) Contamination of Soils and Water around Automobile Repair Workshops in Eket Metropolis, Akwa Ibom State, Nigeria. Journal of Springer NatureApplied Sciences, 1:447.

Ekpete, O. A., Edori, O. S., & Iyama, W. A. (2019). Concentrations of polycyclic Aromatichydrocarbons from selected dumpsites within Port Harcourt Metropolis, Rivers State, Niger Delta, Nigeria. International Journal Environmental Science Natural Research, 21(4), 556066. DOI: 10.19080/IJESNR.2019.21.55606606.

Emoyan, O.O., Agbaire, P.O., Otobrise, C., and Akporhonor, E.E. (2011). Distribution pattern of Polycyclic Aromatic Hydrocarbons (PAHs) in soils in the vicinity of Fuel Stations in Abraka, Nigeria. Journal of Applied Science and Environmental Management, 15(3):513516.

Environmental Protection Agency (EPA). Compendium Methods for the Determination of Toxic Organic Compounds in Ambient Air: Compendium Method TO-11A. Available online: https://www3.epa.gov/ttnamti1/files/ambient/airtox/to-11ar.pdf (accessed on 4 February 2023).

Fellet, G.; Pošćić, F.; Licen, S.; Marchiol, L.; Musetti, R.; Tolloi, A.; Barbieri, P.; Zerbi, G. (2016).

PAHs accumulation on leaves of six evergreen urban shrubs: A field experiment. Atmos. Pollut. Res. 7, 915–924.

Fernández, R.; Galarraga, F.; Benzo, Z.; Márquez, G.; Fernández, A.J.; Requiz, M.G.; Hernández, J. (2014). Lichens as biomonitors for the determination of polycyclic aromatic hydrocarbons (PAHs) in Caracas Valley, Venezuela. Int. J. Environ. Anal. Chem. 91, 230– 240.

Guo, J., Zhang, L., Haiqing, L., Zhi, T. Xiaoli, Z. and Fengchang, Wu. (2011). Sedimentary Record of Polycyclic Aromatic Hydrocarbons in Lake Erhai, Southwest China. Journal of Environmental Sciences, 23(8):1308-1315.

G. Agapkina , P. Chikov , A. Shelepchikov , E. Brodskiy , D. Feshin , N. Bukhanko and S. Balashova,(2007). Moscow University, Soil Science, Bulleting, 62 , 149 —158.

IARC-International Agency for Research on Cancer. Outdoor Air Pollution/IARC Working Group on the Evaluation of Carcinogenic Risks to Humans. IARC-International Agency for

Research on Cancer: Lyon, France, 2013. Available online:https://publications.iarc.fr/_publications/media/download/4317/b1f528f1fca20965a2b48a220f47447c1d94e6d1.pdf (accessed on 30 September 2019).

Krauss, M.; Wilcke, W.; Martius, C.; Bandeira, A.G.; Garcia, M.V.; Amelung, W. (2005). Atmospheric versus biological sources of polycyclic aromatic hydrocarbons (PAHs) in a tropical rain forest environment. Environ. Pollut. 135, 143–154.

Landis, M.S.; Studabaker, W.B.; Pancras, J.P.; Graney, J.R.; Puckett, K.; White, E.M.; Edgerton, E.S. (2019). Source apportionment of an epiphytic lichen biomonitor to elucidate the sources and spatial distribution of polycyclic aromatic hydrocarbons in the Athabasca Oil Sands Region, Alberta, Canada. Sci. Total Environ. 654, 1241–1257.

Lee, Y.-N.; Lee, S.; Kim, J.-S.; Patra, J.K.; Shin, H.-S. (2019). Chemical analysis techniques and investigation of polycyclic aromatic hydrocarbons in fruit, vegetables and meats and their products. Food Chem. 277, 156–161.

Li, Y.T., Li, F.B., Chen, J.J., Yang, G.Y., Wan, H.F. and Zhang, T.B. (2008). The Concentrations, Distribution and Sources of PAHs in Agricultural Soils and Vegetables from Shunde, Guangdong, China. Environmental Monitoring and Assessment, 139:1-76.

Liu, S., Xia, X., Yang, L., Shen, M., and Liu, R. (2010). Polycyclic Aromatic Hydrocarbons in Urban Soils of Different Land Uses in Beijing, China: Distribution, Sources and their Correlation with the City’s Urbanization History. Journal of Hazardous Materials, 177:1085-1092.

Ministry of Infrastructure and Water Management (MIWM, 2017). Environmental quality objectives in the Netherlands: A Review of Environmental Quality Objectives and their Policy Framework in the Netherlands. Risk Assessment and Environmental Quality Division. Directorate for Chemicals, External Safety and Radiation Protection, pp 276289.

Nascimbene, J.; Tretiach, M.; Corana, F.; Schiavo, F.L.; Kodnik, D.; Dainese, M.; Mannucci, B. (2014). Patterns of traffic polycyclic aromatic hydrocarbon pollution in mountain areas can be revealed by lichen biomonitoring: A case study in the Dolomites (Eastern Italian Alps). Sci. Total Environ. 475, 90–96.

Navarro, P.; Cortazar, E.; Bartolomé, L.; Deusto, M.; Raposo, J.; Zuloaga, O.; Arana, G.; Etxebarria, N. (2006). Comparison of solid phase extraction, saponification and gel permeation chromatography for the clean-up of microwave-assisted biological extracts in the analysis of polycyclic aromatic hydrocarbons. J. Chromatogr. 1128, 10–16.

Navarro-Ortega, A.; Ratola, N.; Hildebrandt, A.; Alves, A.; Lacorte, S.; Barceló, D. (2012). Environmental distribution of PAHs in pine needles, soils, and sediments. Environ. Sci. Pollut. Res.19, 677–688.

Nisbet, I.C.T. and LaGoy, P.K. (1992). Toxic Equivalency Factors (TEFs) for Polycyclic Aromatic Hydrocarbons (PAHs). Journal of Regulatory, Toxicology and Pharmacology, 16:290300.

Nuerla A., Naifu Z., Xiaolong Z., Anwar M., Jiali C., Shuangyu C., Zhenyu H., Nanxin Li (2022). Levels, sources, and risk assessment of PAHs residues in soil and plants in urban parks of Northwest China. Scientific Reports, 12:21448. https://doi.org/10.1038/s41598-02225879-8.

Obayori, O.S., Salamb, L.B., Oyetibo, G.O.,Idowua, M. and Amund, O.O. (2017). Biodegradation Potentials of Polycyclic Aromatic Hydrocarbon (Pyrene and Phenanthrene) by Proteus mirabilis Isolated from an Animal Charcoal PollutedSite. Biocatalysis and Agricultural Biotechnology, 12:78-84.

Ortega, L.M.; Uribe, D.M.; Grassi, M.T.; Garrett, R.; Sánchez, N.E.(2022). Determination of polycyclic aromatic hydrocarbons extracted from lichens by gas chromatography–mass spectrometry. MethodsX, 9, 101836.

Pereira, G.M.; da Silva, S.E.; Mota, E.Q.; Parra, Y.J.; Castro, P. (2019). Polycyclic aromatic hydrocarbons in tree barks, gaseous and particulate phase samples collected near an industrial complex in Sao Paulo (Brazil). Chemosphere. 237, 124499.

Protano, C.; Guidotti, M.; Owczarek, M.; Fantozzi, L.; Blasi, G.; Vitali, M. (2014). Polycyclic Aromatic Hydrocarbons and Metals in Transplanted Lichen (Pseudovernia furfuracea) at Sites Adjacent to a Solid-waste Landfill in Central Italy. Arch. Environ. Contam. Toxicol. 66, 471–481.

Ratola, N.; Amigo, J.M.; Alves, A. (2010). Levels and Sources of PAHs in Selected Sites from Portugal: Biomonitoring with Pinus pinea and Pinus pinaster Needles. Arch. Environ. Contam. Toxicol. 58, 631–647.

Ratola, N.; Herbert, P.; Alves, A. (2012). Microwave-assisted headspace solid-phase microextraction to quantify polycyclic aromatic hydrocarbons in pine trees. Anal. Bioanal. Chem. 403, 1761–1769.

Ratola, N.; Alves, A.; Psillakis, E. (2011). Biomonitoring of Polycyclic Aromatic Hydrocarbons Contamination in the Island of Crete Using Pine Needles. Water Air Soil Pollut.215, 189– 203.

Rodriguez, J.H.; Pignata, M.L.; Fangmeier, A.; Klumpp, A. (2010). Accumulation of polycyclic aromatic hydrocarbons and trace elements in the bioindicator plants Tillandsia capillaris and Lolium multiflorum exposed at PM10 monitoring stations in Stuttgart (Germany). Chemosphere, 80, 208–215.

Shukla, V.; Upreti, D.K. (2009). Polycyclic aromatic hydrocarbon (PAH) accumulation in lichen, Phaeophyscia hispidula of DehraDun City, Garhwal Himalayas. Environ. Monit. Assess.

Sule, A.M., Tijani, M.B., Atta, H.I,. Isa, M.T. (2023). Toxicological Risk Evaluation of Polycyclic Aromatic Hydrocarbons in Soils from a Petroleum Spillage Site at Kokori in the Niger Delta Region of Nigeria. UMYU Journal of Microbiology Research. 8(2)10, 99 – 109.

Tham, Y.W.; Takeda, K.; Sakugawa, H. (2008). Polycyclic aromatic hydrocarbons (PAHs) associated with atmospheric particles in Higashi Hiroshima, Japan: Influence of meteorological conditions and seasonal variations. Atmos. Res. 88, 224–233.

Van der Wat, L.; Forbes, P.B.C. (2019). Comparison of extraction techniques for polycyclic aromatic hydrocarbons from lichen biomonitors. Environ. Sci. Pollut. Res.26, 11179– 11190.

World Health Organization–Office for Europe (EURO-OMS). (2000). Air Quality Guidelines, 2nd ed.; WHO Regional Office for Europe: Copenhagen, Denmark.

Wu, C.Y.; Cabrera-Rivera, O.; Dettling, J.; Asselmeier, D.; McGeen, D.; Ostrander, A.; Lax, J.; Mancilla, C.; Velalis, T.; Bates, J.; et al. (2007). An Assessment of Benzo (a) pyrene Air Emissions in the Great Lakes Region. Arbor, 1001, 48104.