UJMR, Vol. 8 No. 2, December, 2023, pp. 99 - 109 *E-ISSN: 2814 – 1822; P-ISSN: 2616 – 0668*

https://doi.org/10.47430/ujmr.2382.012

Received: 09 September 2023 **Accepted:** 16 December 2023

Toxicological Risk Evaluation of Polycyclic Aromatic Hydrocarbons in Soils from a Petroleum Spillage Site at Kokori in the Niger Delta Region of Nigeria

Sule, A.M[1]*., Tijani, M.B[2]., Atta, H.I[2] and Isa, M.T[3]

1. Department of Industrial and Environmental Pollution, National Research Institute for Chemical Technology, Zaria, Kaduna State, Nigeria.
2. Department of Microbiology, Ahmadu Bello University, Zaria, Kaduna State, Nigeria.
3. Department of Chemical Engineering, Ahmadu Bello University, Zaria, Kaduna State, Nigeria.

Correspondence Author Email: asmaikano8319@gmail.com; Tel: +2348063981084

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental contaminants that are produced by the incomplete combustion of organic sources and are widely found in soils. This present research was carried out to evaluate the concentrations and toxicological risk assessment of the United States Environmental Protection Agency's sixteen priority polycyclic aromatic hydrocarbons (16 priority PAHs) in soils from the vicinity of an oil spillage site in Delta State of Nigeria. The level of pollution and potential toxicological health hazards of the PAHs were assessed in surface soil samples using soxhlet extraction of and Gas Chromatography-Mass Spectrometry (GC-MS). Thirteen out of the sixteen USEPA priority PAHs were detected in the soil sample. The concentrations of PAHs in the petroleum-contaminated soils in this investigation ranged from 0.01181 ppm to 1.16054 ppm, with the total estimated concentration of the 16 priority PAHs being 5.6713 ppm. Furthermore, the distribution of the PAHs in the study area was predominated by LMW PAHs (62%) over HMW PAHs (38%). Additionally, the total toxicity equivalency quotients TEQ (B[a]Peq) result of the carcinogenic potency of the USEPA priority PAHs was calculated as 0.08689 ppm (8.689%) and was discovered to be within the Canadian TEQ (B[a]Peq) threshold of 0.6 ppm. This suggests that the soil in the study area is safe based on the Canadian TEQ (B[a]Peq) standard and does not constitute a carcinogenic risk. However, the long-term bioaccumulation of these low quantities of PAHs in human has been found to constitute a potential health concern due to bioaccumulation in living systems.

Keywords: Polycyclic aromatic hydrocarbons, toxicity equivalency quotient, carcinogenic potency, petroleum spillage.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and other harmful compounds have been released into the environment as a result of petroleum spills in Nigeria, where petroleum exploration is a major economic activity (Nwankwoala *et al.*, 2020). According to Iwegbue *et al.* (2016), the volume of petroleum spillages is projected to be over 600,000 metric tons per year. Also, Emoyan (2020) stated that the discharge of petroleum to the environment, whether unintentionally or as a result of human activities such as oil bunkering resulting in petroleum spillages, is a major cause of soil contamination caused by petroleum. This frequently results in major environmental issues that endanger both human health and beneficial microbial communities in the soil (Li *et al.*, 2018). The discharge of petroleum into the soil by spillage has the implication that the soil may remain unsuitable for agricultural practices until the hydrocarbons are degraded to an acceptable level (Kadili *et al.*, 2021). This is because petroleum hydrocarbons in soils produce conditions that enable vital nutrients to be unavailable to plants (Bi *et al.*, 2016). Furthermore, the accumulation of PAHs in food crops and other biota via food chains may pose a risk to human health (Keyte *et al.*, 2016; Li *et al.*, 2018).

PAHs are released into the environment by both natural (such as oil seeps, forest fires, and volcanic activity) and anthropogenic sources, such as petroleum exploration and other petrochemical industrial/combustion operations (Itodo *et al.*, 2018). They are primarily caused by petroleum spills and/or incomplete combustion of organic matter such as wood, fossil fuels, and petroleum products (Kadili *et al.*, 2021).

Due to their ubiquity, stability, and long-term enrichment in soils, PAHs and other kinds of organic pollutants are frequently regarded as suitable reservoirs in the soil system (Keyte *et al.*, 2016). According to Nam *et al.* (2009), large amounts of PAHs have been identified in numerous surface soils around the world, posing potential hazards to the ecological environment and human health. Furthermore, Sun *et al.* (2018) revealed that PAHs are rapidly absorbed by organic matter in soil and difficult to breakdown in the terrestrial environment. Additionally, Bandowe *et al.* (2019) stated that the special attention paid to PAHs is due to their toxicity and other properties, such as low water solubility, high affinity for lipids, ability to convert into alkylated compounds and tendency to be adsorbed to particulate matter. These properties accounts for the persistence and toxicity of PAHs in the environment (Okedere and Elehinafe, 2022).

The Agency for Toxic Substances and Disease Registry (ATSDR, 2017) has classified PAHs as ubiquitous, hydrophobic, and persistent priority pollutants that pose a health risk to humans and animals when exposed to PAH-contaminated air, water, or soil. These effects include neurological, respiratory, and reproductive effects (Adeniyi *et al.*, 2021). Furthermore, PAHs are of environmental and human concern due to their toxic, carcinogenic, and mutagenic qualities (Afegbua, 2015; Raji, 2016; Davie-Martin *et al.*, 2017). The World Health Organization and the United States Environmental Protection Agency currently classify sixteen PAHs as priority PAHs (Keith, 2015; Szopiska *et al.*, 2019).

Despite the health hazards associated with PAHs, Olayinka *et al.* (2018) stated that public awareness of their nature, toxicity, and presence in the Nigerian environment, particularly in the Niger Delta region where petroleum exploration is taking place, is still very low. This may be related to the lack of a regulatory framework on the permissible limits of PAHs in various aspects of Nigeria's environment, as well as the few publications in the literature on the assessments and negative impact of PAHs in the oil-rich Niger Delta region (Chikere *et al.*, 2018). As a result, this study was carried out in order to evaluate the concentrations and toxicological risk assessment of the16 USEPA priority PAHs in soils from the vicinity of an oil spillage site in Delta State of Nigeria.

MATERIALS AND METHODS

Sampling area and sample collection

The soil samples for this investigation were collected from an oil spillage site at Kokori-Erhoike petroleum flow station area in Ethiope East Local Government Area of Delta State, Nigeria, with coordinates of 5°38'30.85"N and 6° 3'58.16"E (Figure 1). Kokori has a land mass that is about 196 square kilometers in size. Composite sampling technique adopted by Raji (2016) was used for the purpose of sample collection.

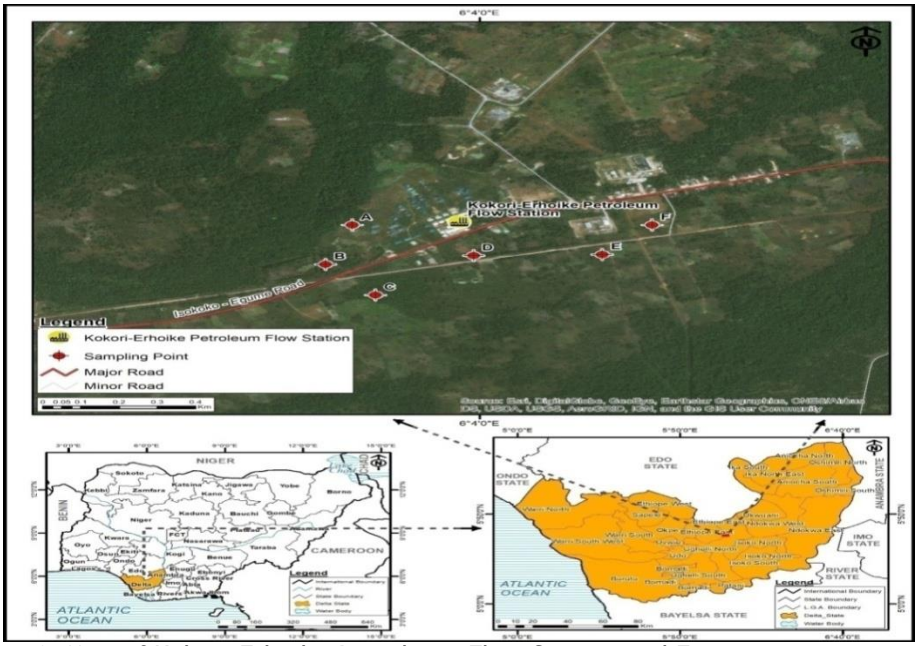

Figure 1: Map of Kokori-Erhoike Petroleum Flow Station and Environs Showing Sampling Points

Source: Map Gallery, Department of Geography, Ahmadu Bello University, Zaria (2021).

Sample preparation

The method used by Olayinka *et al*. (2017) was adopted for sample preparation. Rock particles, sticks and pebbles were removed from the soil sample before being air dried in the laboratory for 72 h at room temperature. To acquire a fine texture, the sample was pounded with a pestle and mortar and sieved through a 2 mm mesh sieve. Prior to examination, the sieved soil was transferred into sterile amber-colored glass vials that were carefully sealed and labeled prior to analysis.

PAHs extraction and clean-up from soil samples

Soil sample for the determination of polycyclic aromatic hydrocarbons (PAHs) was processed using soxhlet extraction method as described by Anyakora *et al*. (2005). The extract was collected in a clean amber glass vial for cleaning to remove contaminants that could interfere with analysis in the gas chromatography column (GCMS). To remove non-polar aliphatic hydrocarbons, the column was washed with 10 mL of hexane, and the polycyclic aromatic hydrocarbon was collected by eluting 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 watched until the extract in the round bottom flask was decreased to around 1mL. Upon 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 carefully open to release the system from the reduced pressure. The round bottom flask was then removed from the rotavap and the extract was transferred into an amber vial for GC-MS analysis of polycyclic aromatic hydrocarbons (PAHs) compounds.

GCMS identification and quantification of PAHs

The qualitative and quantitative analysis of polycyclic aromatic hydrocarbons in soil samples was performed using the external standards approach described by Oluseyi *et al*. (2011). A standard mixture of the United State Environmental Protection Agency (USEPA) 16 priority polycyclic aromatic hydrocarbons (2000 µg/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 soil extract sample were analyzed using a gas chromatography-mass spectrometry Agilent GC: 7890 MS: 5975C instrument equipped with a CTC A200S autosampler and a 30 m, 0.25 ID fused silica capillary column at the American University of Nigeria, Yola, Adamawa State, Nigeria. Helium was employed as the carrier gas, and the column head pressure was kept at 10 psi to achieve an estimated flow rate of 1 mL/min. The injector port and transfer line were kept at 290 °C and 250 °C, 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 °C for 4 minutes before gradually increasing to 300 °C. Finally, the temperature was kept at 300 degrees Celsius 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 acquire 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 petroleum-contaminated soil sample were detected using a retention time and mass spectral match against the calibration standard. Similarly, the external standardization method of the generated calibrations curve of the USEPA sixteen (16) priority PAHs standard combination was used to quantify the USEPA sixteen (16) priority PAHs present in the sample.

Estimation of carcinogenic potency of the soil samples collected from a petroleum spillage site

The carcinogenic potency of PAHs was estimated by calculating the concentrations of individual carcinogenic PAHs in terms of benzo(a)pyrene equivalent (BaPeq), also known as the total BaP equivalent quotient (TEQ), and multiplying by the corresponding toxic equivalency factor (TEF) values proposed by Nisbet and LaGoy, (1992), as shown in Equation 1.

$$\text{Total BaP Equivalent Quotient (TEQ)} = \Sigma(Ci \times TEFi) \quad 1$$

Where:

Ci= Concentration of individual PAHs.

TEF_i= Corresponding toxic equivalency factor (TEF).

RESULTS

PAHs content from soil samples

Result of the concentration mean values of USEPA 16 Priority PAHs detected in the soil sample collected from an oil spillage site is presented in Table 1.

The mean concentration of the USEPA 16 priority PAHs detected in this study ranged from 0.01181 ppm (dibenzo[ah]anthrathene) to 1.16054 ppm (naphthalene). Benzo(ghi)perylene, Indeno(123-cd)pyrene and Benzo(b) fluoranthene were not detected in this study. Furthermore, the sum total of the PAHs (Σ16 PAHs= 5.6713 ppm) recorded in this study was found to exceed the DPR (2002) target value of 1 ppm but still within the intervention value of 40 ppm for soil contaminated with petroleum hydrocarbon. Similarly, the concentration levels of naphthalene (1.1605 ppm), anthracene (1.0766 ppm) and phenanthrene (1.1079) were found to exceed the maximum permissible standard of 0.690 ppm, 0.340 ppm and 1.060 ppm respectively set aside by the Dutch government for petroleum contaminated soils. Using Analysis of Variance (ANOVA), there was a significant difference (p-value= 0.000) among the USEPA 16 Priority PAHs ($P \leq 0.05$).

The percentage distribution of PAHs concentrations (with respect to LMW and HMW PAHs) in the study area is as presented in Figure 1. The 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 petroleum contaminated soils. Using Analysis of Variance (ANOVA), there was a significant difference (p-value= 0.000) among the USEPA 16 Priority PAHs ($P \leq 0.05$).

The percentage distribution of PAHs concentrations (with respect to LMW and HMW PAHs) in the study area was presented in Figure 2. The result indicates that the concentrations distribution of USEPA 16 priority PAHs in the study area was dominated by LMW PAHs with a percentage distribution of 62% while the percentage distribution of HMW was 38%.

Table 1: Mean values of USEPA sixteen (16) priority PAHs present in petroleum contaminated soil

Polycyclic Aromatic Hydrocarbon	Number of Rings	Relative Abundances (ppm) ± SE	Regulatory Standard			ANOVA P- value
			MIWM Standard (ppm)*	DPR Standard**		
				Target Value (ppm)	Intervention Value (ppm)	
Naphthalene	2	1.1605± 0.004	0.690[E]	1.000	40.000	0.000
Acenaphthylene	3	0.1035± 0.001	0.170			
Acenaphthene	3	0.0267± 0.019	0.680			
Fluorene	3	0.0192± 0.003	1.600			
Anthracene	3	1.0766± 0.006	0.340 [E]			
Phenanthrene	3	1.1079± 0.001	1.060 [E]			
Σ 2-3Ring PAHs (LMW)		3.4944				
Fluoranthene	4	1.0874± 0.018	4.800			
Pyrene	4	0.8212± 0.002	1.800			
Benzo(a)anthracene	4	0.0158± 0.005	0.900			
Chrysene	4	0.1063± 0.017	1.600			
Benzo(b)fluoranthene	5	0.000± 0.000	0.790			
Benzo(k)fluoranthene	5	0.0183±0.001	0.790			
Benzo(a)pyrene	5	0.1161±0.004	0.160			
Dibenzo(ah)anthrathene	6	0.0118±0.002	0.180			
Indeno(123-cd)pyrene	6	0.000±0.000	0.380			
Benzo(ghi)perylene	6	0.000±0.000	0.490			
Σ 4-6 Ring PAHs (HMW)		2.1769				
Σ16PAH		5.6713				

Key: MIWM*: Ministry of Infrastructure and Water Management, (MIWM, 2017); DPR**: Department of Petroleum Resources, (DPR, 2002); E: Concentrations exceeding MIWM standard; LMW: Low Molecular Weight PAHs; HMW: High Molecular Weight PAHs.

Correspondingly, result of the assessment of the carcinogenic potency of USEPA 16 priority PAHs present in the soil sample is 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 estimated from the TEF values ranges from 0.00002 ppm (fluorene) to 0.05905 ppm (Dibenzo (a,h) anthrathene). The result also revealed that the TEQ (ΣB[a]Peq) of the USEPA 16 priority PAHs within the period of investigation was 0.08689 ppm (8.669%) which was found to be less than the Canadian TEQ (ΣB[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) ($P \leq 0.05$).

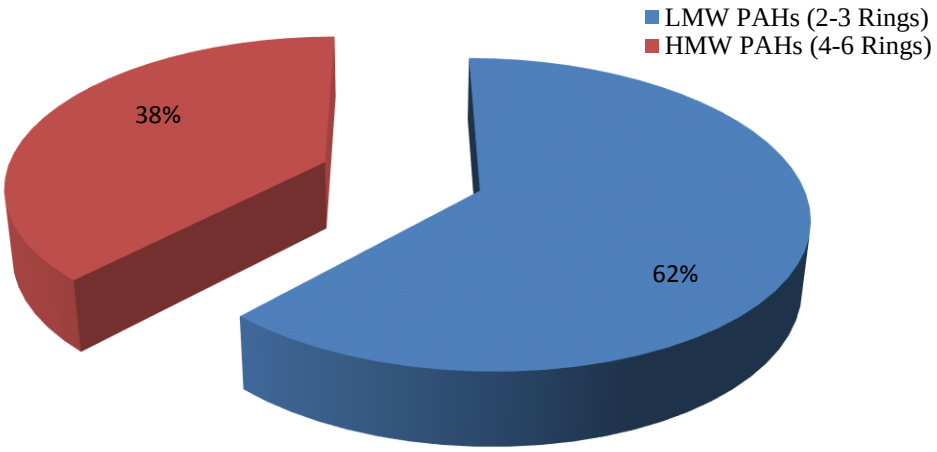

Figure 2: Concentrations and distribution of low and high molecular weight polycyclic aromatic hydrocarbons in a petroleum contaminated soil
Key: LMW: Low molecular weight PAHs, HMW: High molecular weight PAHs

Table 2: Estimation of carcinogenic potency of USEPA sixteen (16) PAHs detected from the sampling site

PAHs	Number of Rings	Molecular Weight	TEF	TEQ	TEQ%	Canadian TEQ (ΣB[a]Peq) Standard (ppm)	ANOVA P- value
Naphthalene	2	128.2	0.001	0.00116	0.116	0.6**	0.000
Acenaphthylene	3	152.2	0.001	0.00010	0.010		
Acenaphthene	3	154.2	0.001	0.00003	0.002		
Fluorene	3	166.2	0.001	0.00002	0.002		
Phenanthrene	3	178.2	0.001	0.00111	0.111		
Anthracene	3	178.2	0.01	0.01077	0.676		
Fluoranthene	4	202.3	0.001	0.00109	0.109		
Pyrene	4	202.3	0.001	0.00082	0.082		
Chrysene	4	228.3	0.001	0.00011	0.011		
Benzo(a)anthracene	4	228.3	0.01	0.00001	0.001		
Benzo(k)fluoranthene	5	252.3	0.1	0.00183	1.833		
Benzo(b)fluoranthene	5	253.3	0.1	-	-		
Benzo(a)pyrene	5	252.3	0.1	0.01161	1.161		
Indeno(123-cd)pyrene	6	276.3	0.1	-	-		
Dibenzo(a,h)anthrathene	6	278.4	5	0.05905	5.605		
Benzo(ghi)perylene	6	276.3	0.01	-	-		
Total TEQ (Σ B[a]Peq)				0.08689	8.689		

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

DISCUSSION

Owing to their abundance, stability, and long-term enrichment in soils, PAH compounds are thought to be an excellent reservoir of organic pollutants, including the soil system (Bandowe *et al.*, 2021). Despite the fact that there are many PAHs, the United States Environmental Protection Agency (USEPA) identified 16 of them as priority pollutants in the mid-1970s based on their toxicity, persistence in the environment, and ability to be tested or detected from samples (Keith, 2015). Furthermore, Andersson and Achten (2015) said that the sixteen PAHs are routinely targeted for monitoring and assessment, and have thus established a de facto global standard.

The PAHs in the soil sample analyzed in this study were found to be lower in quantity when compared to PAHs concentrations reported by Ehis-Eriakha *et al.* (2020) in their study on crude oil polluted soil sample from an aged spill site located at Komkom community of Rivers State, Niger Delta region of Nigeria, but higher in quantity when compared to concentrations reported by Ekanem *et al.* (2019) in their study on polycyclic aromatic hydrocarbons (PAHs) contamination of soils around Eket metropolis, Akwa Ibom State, Niger Delta, Nigeria. The concentration levels of naphthalene (1.1605 ppm), anthracene (1.0766 ppm), and phenanthrene (1.1079) were found to surpass the maximum allowed standard set aside by the Dutch government using the Dutch Government (NMHE, 1994) standard. This raised serious concerns because previous research by Nisbet and LaGoy (1992); Ramesh *et al.* (2004); Korashy and El-Kadi (2006) and Obayori *et al.* (2017) found that these individual PAHs have the potential to cause cancer and bioaccumulation in living cells at high concentrations. In addition, the significantly high abundance of the aforementioned PAHs (naphthalene, anthracene, and phenanthrene) suggested that they were primarily from low and moderate temperature combustion processes, as previously reported by Guo *et al.* (2011). What's more, the percentage ring wise distribution of PAHs in this analysis shows a predominance of LMW PAHs (62%) over HMW PAHs (38%), indicating recent deposition of these compounds. Also, Li *et al.* (2006) found that LMW PAHs are frequently related with petroleum spillages (petrogenic sources), which is the situation in this study.

The abundance of three-ring PAHs in the studied area is consistent with Adedosu *et al.* (2013) investigation of an oil-polluted site in Nigeria's Niger Delta region. It was reported by the author that unlawful refining of petroleum products could be a significant contributor to the occurrence of LMW PAHs as also recorded in this study. In a similar report also by Jiao *et al.* (2017), they attribute the occurrences of HMW PAHs in the environment to incomplete combustion of fossil fuels such as crude oil and natural gas (pyrogenic sources). As a result, the PAHs found in the current study region were both petrogenic and pyrogenic in nature, as previously reported by both Neff *et al.* (2003) and Itodo *et al.* (2019).

According to Kadili *et al.* (2014), PAHs often accumulate in surface soil as a result of adsorption due to their persistence and affinity for soil organic matter. Similarly, Andersson *et al.* (2003) and Iwegbue *et al.* (2016) observed that low molecular weight (LMW) PAHs are absorbed into the soil by water due to their higher water solubility than high molecular weight (HMW) PAHs. Furthermore, the persistence of oil spillages observed in the current study region, as well as other human activities such as illegal refining of petroleum products, may account for the greater percentage of LMW PAH reported in this study. Similar findings have been reported by Kadili *et al.* (2014) and Ana *et al.* (2009). Despite the high levels of LMW PAHs concentration reported in the current study, these concentrations were found to be relatively low when compared to PAHs concentrations reported in other studies in Nigeria by Kadili *et al.* (2014); Ameh, (2014); Ana *et al.* (2009); Anegbe *et al.* (2016) and other parts of the world by Guo *et al.* (2011); Rabajczyk and wiercz, (2018). This is most likely owing to the presence of PAH degrading bacteria in the study site, as LMW PAHs are easier to use as an energy source during biodegradation than HMW PAHs (Li *et al.*, 2010).

The total amount of PAHs (16 PAHs= 5.6713 ppm) observed in this study exceeded the target value of 1 ppm but remained within the intervention threshold of 40 ppm set by DPR, 2002 for safe industrial soils. This suggests that the soil sample collected at the petroleum-affected site as a result of oil leakage and illegal refining going on at the site is contaminated with PAHs but not substantially polluted. As a result, the sum total of PAHs (16 PAHs) from this investigation was found to be more than the 0.82 ppm concentration reported in soils from a petroleum polluted site in Abraka, Rivers State, Nigeria by Emoyan *et al.* (2011). Oketola and Akpotu (2015) observed a lower concentration of 16 PAHs of 2.790 ppm in a study done in Nigeria's Niger Delta region. On the contrary, the value (16 PAHs= 5.6713 ppm concentration) reported in this study was found to be lower than the level reported by Nganje *et al.* (2007), where a 16 PAHs of 12.450 ppm

was recorded in soil samples from a petroleum polluted site in Calabar, Cross Rivers State in Nigeria's Niger Delta region. Other studies from the Niger Delta region of Nigeria that showed 16 PAHs levels higher than the current study include Adedosu *et al.* (2015) (5.649ppm), Nduka *et al.* (2013) (6.151 ppm), Nganje *et al.*(2007) (17.3 ppm), and Ekanem *et al.* (2019) (12.9 ppm).

Further ecological evaluation of the impact of PAHs pollution levels in soil for agricultural purpose as classified by Malizewkwa-Kordybach (1996) and adopted by Kadili *et al.* (2014) has classified soil contaminated with PAHs into four categories based on the 16 USEPA priority pollutants (Σ16PAHs) namely; unpolluted (less than 0.2 ppm), weakly polluted (0.2- 0.6 ppm), polluted (0.6- 1 ppm) and severely polluted (1 ppm and above). According to this categorization, the study site is severely polluted with PAHs (16 PAHs= 5.6713 ppm), making it unfit for agricultural use and posing a risk to human health, including cancer as reported Bortey-Sam *et al.* (2014).

PAH-contaminated soils have previously been linked to health risks to humans, plants, livestock, and wildlife, as well as ecotoxicological risks to the soil biome (CCME, 2010; IARC, 2010). Furthermore, Tsai *et al.* (2004) state that the health risk assessment related with PAHs absorption in soil is frequently based on Benzo[a]pyrene (B[a]Peq) concentrations. This is because (B[a]Peq) has been widely examined and found to be extremely carcinogenic (Adeniyi *et al.*, 2021). Furthermore, according to the WHO (2017), a benzo[a]pyrene concentration of 0.7 ppm correlates to a lifetime cancer risk. As a result, the BaP-equivalent (B[a]Peq) is used to assess carcinogenic risk from PAH-contaminated soil (Adeniyi et al., 2021). This is for the reason that B[a]Peq does not only includes the risk due to B[a]P but also calculates all the carcinogenic potencies of other PAHs, where the carcinogenic potency of each PAH is estimated in relation to the carcinogenicity of B[a]P (Adeniyi *et al.*, 2021). As a result, most research identify B[a]P as the primary carcinogenic factor (Halek *et al.*, 2008). In this study, the toxicity equivalency factors (TEFs) developed by Nisbet and LaGoy (1992) and used by Tsai et al. (2004) and Bortey-Sam *et al.* (2014) were used to quantify and estimate the carcinogenic potential of other individual PAHs by multiplying their concentrations by their appropriate TEF values.

The total benzo[a]pyrene equivalent concentration (B[a]Peq) of the detected PAHs in this study during the investigation period was calculated as 0.08689 ppm, indicating a relatively low carcinogenic potency based on the Canadian soil environmental quality B[a]Peq standard of 0.6 ppm stipulated for PAH-contaminated soil, and thus does not pose carcinogenic risk (Yu *et al.*, 2020). Furthermore, the B[a]Peq (0.08689 ppm) obtained in this study was low when compared to analogous investigations conducted in petroleum polluted areas by Cao *et al.* (2019) and Bortey-Sam *et al.* (2014), which revealed 1.245 ppm and 0.158 ppm B[a]Peq values, respectively. The low value of B[a]Peq revealed in this study, however, should not be taken for granted. This is due to the fact that the health risk assessment of the carcinogenic effect of PAHs cannot be based solely on the overall concentrations of the 16 PAHs (B[a]Peq), because each PAH has a different carcinogenic potential, as compiled by Nisbet and LaGoy (1992) and adopted by Kadili *et al.* (2021). Furthermore, since illegal oil refining has continued in the study region for decades and recurring annual instances of oil spillages have been observed there for some time. These activities could raise the amounts of these PAHs, which are not yet disclosed in this study, posing health risk in the future.

Also, the continuous bioaccumulation of these low quantities of PAHs in humans throughout time has been observed in earlier studies conducted by Cao *et al.* (2019); Yu *et al.* (2020); Kadili *et al.*(2021) to pose a health danger in the future due to bioaccumulation in the system. Also, the exposure of soil microorganisms, plants and humans to samples containing mixtures of PAHs and metals can result in synergistic toxic effects as reported by Maliszewska-Kordybach and Smreczak, (2003); Thavamani *et al.*(2012); Wang *et al.*(2015). Additionally, the BaP concentrations are frequently used to predict the health risks related with PAH absorption this is because, almost every investigation cites BaP as the leading carcinogen (Kadili *et al.*, 2021). Finally, investigations from various parts of the world that reported elevated levels of B[a]Peq concentrations in soil samples polluted with PAHs includes; , Lisbon 2.29 ppm (Cachada *et al.*, 2012), Shanghai 2.36 ppm (Wang *et al.*, 2015), Guwahati, India 5.57 ppm (Hussain and Hoque, 2015).

CONCLUSION

The soil sample examined for this investigation contained thirteen of the sixteen USEPA prioritized PAHs. Similar to this, it was discovered that the total amount of the 16 USEPA priority PAHs measured in the soil samples (16 PAHs= 5.6713 ppm) exceeded the DPR (2002) target value of 1 ppm but fell short of the 40 ppm intervention value. Additionally, it was discovered that the concentrations of

naphthalene (1.1605 ppm), anthracene (1.0766 ppm), and phenanthrene (1.1079 ppm) exceeded the Dutch government's maximum permitted standard. However, based on the estimated benzo[a]pyrene equivalent (B[a]Peq] value of 0.08689 ppm from this study, the estimated B[a]Peq value indicated a relatively low carcinogenic potency based on the Canadian soil environmental quality B[a]Peq standard of 0.6 ppm stipulated for soil contaminated with PAHs, therefore does not pose a carcinogenic risk.

Conflict of Interest

The authors report there are no conflicts of interests to declare.

REFERENCES

Adedosu, T.A., Adedosu, H.O, Sojinu, O.S., Olajire, A.A. (2013): N-Alkanes and Polycyclic Aromatic Hydrocarbons (PAHs) Profile of Soils from some Polluted Sites in Niger Delta, Nigeria. *Environmental Earth Sciences Journal,* **68**:2139-2144. **[Crossref]**

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. **[Crossref]**

Afegbua, S.L. (2015). Importance of Plants and Microorganisms in the Phytoremediation of Brownfield sites. Ph.D. Thesis, University of Birmingham, United Kingdom. pp 65-98.

Agency for Toxic Substances and Disease Registry (ATSDR, 2017). The Priority List of Hazardous Substances. Atlanta, GA: Division of Toxicology and Human Health Sciences, Agency for Toxic Substances and Disease Registry, **pp** 87-95.

Al-Rashdan, A., Helaleh, M. I. H., Nisar, A., Ibtisam, A., & Al-Ballam, Z. (2010). Determination of the Levels of Polycyclic Aromatic Hydrocarbons in Toasted Bread Using Gas Chromatography Mass Spectrometry. International Journal of Analytical Chemistry, **10**: 1–8. **[Crossref]**

Ameh, E. G. (2014). A Preliminary Assessment of Soil Samples Around a Filling Station in Diobu, Port Harcourt, Rivers State, Nigeria. Research Journal of Environmental and Earth Sciences, **6**(2):57–65. **[Crossref]**

Andersson, B.E., Lundstedt, S., Tornberg, K., Schnürer, Y., Öberg, L.G. and Mattiasson, B. (2003). Incomplete Degradation of Polycyclic Aromatic Hydrocarbons in Soil Inoculated with Wood-Rotting Fungi and their Effect on the Indigenous Soil Bacteria. *Environmental Toxicology and Chemistry,* **22**(6):1238-1243. **[Crossref]**

Andersson, J. T., & Achten, C. (2015). Time to Say Goodbye to the 16 EPA PAHs? Toward an Up-to-Date Use of PACs for Environmental Purposes. Polycyclic Aromatic Compounds, **35**(2–4):330–354. **[Crossref]**

Anegbe, B., Okuo, J.M. and Okieimen, F.E. (2016). The Impact of Inorganic and Organic Pollutants in Soil from the Vicinity of Mechanic Workshops in Benin City.
International Journal of Chemical Studies, **4**(3):106-112

Anyakora., C., Anthony, O., Pete, P., Herbert C., Grace, U. and Ogah, C. (2005). GC-MS Analysis of Polynuclear Aromatic Hydrocarbons in Sediment Samples from the Niger Delta Region. *Chemosphere,* **60**:990-997. **[Crossref]**

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. **[Crossref]**

Bandowe, B.A.M., Wei, C., Han, Y.M., Cao, J.J., Zhan, C. and Wilcke, W. (2019). Polycyclic Aromatic Compounds (PAHs, Oxygenated PAHs, Nitrated PAHs and azaarenes) in
Soils from China and their Relationship with Geographic Location, Land Use and Soil Carbon Fractions. *Science of the Total Environment*, **690**:1268-1276. **[Crossref]**

Bi, X., Luo, W., Gao, J., Xu, L., Guo, J. and Zhang, Q. (2016). Polycyclic Aromatic Hydrocarbons in Soils from the Central-Himalaya Region: Distribution, Sources, and Risks to Humans and Wildlife. *The Science of the Total Environment,* **556**:12-22. **[Crossref]**

Bortey-Sam, N., Ikenaka, Y., Nakayama, S., Akoto, O., Yohannes, B.Y., Baidoo, E., Mizukawa, H. and Ishizuka, M. (2014). Occurrence, Distribution, Sources and Toxic
Potential of Polycyclic Aromatic Hydrocarbons (PAHs) in Surface Soils from the Kumasi Metropolis, Ghana. *Science of the Total Environment,* **496**:471-478.

Cachada, A., Pato, P., Rocha-Santos, T., Da-Silva, E.F. and Duarte, A.C. (2012). Levels, Sources and Potential Human Health Risks of Organic Pollutants in

Urban Soils. *Science of the Total Environment*, **430**:184-192. [Crossref]

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.

Cao, W., Yin, L., Zhang, D., Wang, Y., Yuan, J., Zhu, Y. and Dou, J. (2019). Contamination, Sources, and Health Risks Associated with Soil PAHs in Rebuilt Land from a Coking Plant, Beijing, China. *International Journal of Environmental Resources and Public Health*, **16**:670-673. [Crossref]

Davie-Martin, C.L., Stratton, K.G., Teeguarden, J.G., Waters, K.M. and Simonich, S.L.M. (2017). Implications of bioremediation for polycyclic aromatic hydrocarbon Contaminated soils for human health and cancer risk. *Environmental Science and Technology,* **51**:9458-9468. [Crossref]

Department of Petroleum Resources (DPR) and Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN) (2002). Review of the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN) Department of Petroleum Resources: Lagos, Nigeria, 2002.

Ehis-Eriakha, C.B., Chikere, C.B. and Akaranta, O. (2020). Functional Gene Diversity of Selected IndigenousHydrocarbon-Degrading Bacteria in Aged Crude Oil. *International Journal of Microbiology*, **20**:1-11. [Crossref]

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 Nature Applied Sciences*, **1**:447. [Crossref]

Emoyan, O.O., Ejecha, O.O., and Tesi, G.O. 2020. Concentration Assessment and Source Evaluation of 16 Priority Polycyclic Aromatic Hydrocarbons in Soils from Selected Vehicle-Parks in Southern Nigeria. *Scientific African,* **7**:56-79. [Crossref]

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):513-516.

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. [Crossref]

Halek, F., Nabi, G. and Kavousi, A. (2008) Polycyclic Aromatic Hydrocarbons Study and Toxic Equivalency Factor (TEFs) in Teheran, Iran. *Environmental Monitoring Assessment*, **143**:303-311.

Hussain, K., and Hoque, R.R. (2015). Seasonal attributes of Urban Soil PAHs of the Brahmaputa Valley. *Chemosphere***119**:784-802. [Crossref]

International Agency for Research on Cancer (IARC, 2010). Some non-heterocyclic Polycyclic Aromatic Hydrocarbons and some related Exposures. *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*, **92**:18-53.

Itodo, A.U., Sha'Ato, R. and Arowojolu, M.I. (2018) Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Soil Samples from Regions Around Loda-Irele Bitumen Field, Nigeria. *Pakistan Journal of Analytical Environmental Chemistry*, **19**:45-52. [Crossref]

Iwegbue, C.M.A., Obi, G., Aganbi, E., Ogala, J.E., Omo-Irabor, O and Martincigh, B.S. (2016). Concentrations and Health Risk Assessment of Polycyclic Aromatic Hydrocarbons in Soils of an Urban Environment. *Nigeria Journal of Basic and Applied Science*, **21**(2):96-104.

Jiao, H., Wang, Q., Zhao, N., Jin, B., Zhuang, X. and Bai, Z. (2017). Distributions and Sources of Polycyclic Aromatic Hydrocarbons (PAHs) in Soils around a Chemical Plant in Shanxi, China. *International Journal of Environmental Research and Public Health,* **14**(10):1198-1201. [Crossref]

Kadili, J.A., Eneji, I.S., Itodo, A.U. and Sha'Ato, R. (2021). Concentration and Risk Evaluation of Polycyclic Aromatic Hydrocarbons in Soils from the Vicinity of Selected Petrol Stations in Kogi State-Nigeria. *Open Access Library Journal*, **8**:1-21. [Crossref]

Keith, L.H. (2015). The source of USEPA's sixteen PAH priority pollutants. *Polycyclic Aromatic Compound*, **35**(2):147-160. [Crossref]

Keyte, I.J., Albinet, A., and Harrison, R.M. (2016). On-road Traffic Emissions of Polycyclic Aromatic Hydrocarbons and their oxy- and Nitro- derivative

Compounds Measured in Road Tunnel Environments. *The Science of the Total Environment*, **566**:1131-1142. **[Crossref]**

Li, G.C., Xia, X.H, Yang, Z.F, Wang, R. and Voulvoulis, N. (2010*)*: Distribution and Sources of Polycyclic Aromatic Hydrocarbons in the Middle and Lower Reaches of the Yellow River, China. *Environmental Pollution*, **144**:985-993. **[Crossref]**

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. **[Crossref]**

Maliszewska-Kordybach, B. and Smreczak, B. (2003). Habitat Function of Agricultural Soils as affected by Heavy Metals and Polycyclic Aromatic Hydrocarbons Contamination. *Environment International*, **28**:719:729.

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 276-289.

Nganje, T.N., Edet, A., and Ekwere, S.J. (2007). Distribution of PAHs in Surface Soils from Petroleum Handling Facilities in Calabar. *Journal Environmental Monitoring and Assessment*, **130**:27-34. **[Crossref]**

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**:290-300. **[Crossref]**

Nwankwoala, H.O., Amadi, A.N., Omofuophu, E. and Ibrahim, H.A. (2020). Risk evaluation and modeling of soils contaminated with Polycyclic Aromatic Hydrocarbons (PAHs) in parts of Bonny Island, Niger Delta, Nigeria. *Ann Civil Environ Eng.*, **4**:015-026. **[Crossref]**

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 Polluted Site. *Biocatalysis and Agricultural Biotechnology*, **12**:78-84. **[Crossref]**

Okedere, O.B. and Elehinafe, F.B. (2022). Occurrence of Polycyclic Aromatic Hydrocarbons inNigeria's Environment: A review. *Scientific African*, **16**:(4):89-96. **[Crossref]**

Oketola, A. A., and Akpotu, S. O. (2015). Assessment of Solid Waste and Dumpsite Leachate and Top Soil. *Journal of Chemistry and Ecology*, **31**(2):134-146. **[Crossref]**

Olayinka, O.O, Adewusi, A.A., Olarenwaju, O.O., Aladesida, A.A. (2018). Concentration of Polycyclic Aromatic Hydrocarbons and Estimated Human Health Risk of Water Samples around Atlas Cove, Lagos, Nigeria. *J Health Pollution.*, **8**(20):181210. **[Crossref]**

Olayinka, O.O. Akande, O.O., Bamgbose, K. and Adetunji, M.T. (2017). Physicochemical Characteristics and Heavy Metal Levels in Soil Samples obtained from Selected Anthropogenic Sites in Abeokuta, Nigeria. *Journal of Applied Science and Environmental Management*, **21**(5):883-891. **[Crossref]**

Oluseyi, T., Kehinde, O., Babajide, A. and Roger, M.S. (2011). Comparison of Extraction and Clean-Up Techniques for the Determination of Polycyclic Aromatic Hydrocarbons in Contaminated Soil Samples. *African Journal of Environmental Science and Technology*, **5**(7):482-493.

Rabajczyk, A. and Świercz, A. (2018). Contamination of Soils with Polycyclic Aromatic Hydrocarbons Near Petrol Stations in the City of Kielce. *Journal of Environment Protection and Engineering*, **44**:101-115. **[Crossref]**

Raji, H.M. (2016). Characterization and Molecular Diversity of Some Soil Prokaryotes with Potentials for Polycyclic Aromatic Hydrocarbon Degradation. A Ph.D Thesis Submitted to the School of Postgraduate Studies, Ahmadu Bello University, Zaria, Nigeria, pp 94-101.

Ramesh, A., Walker, S. A. and Hood, D. B. (2004). "Bioavailability and Risk Assessment of Orally Ingested Polycyclic Aromatic Hydrocarbons". *International Journal of Toxicology*, **23** (5):301-333. **[Crossref]**

Sun, J., Pan, L., Tsang, D. C. W., Zhan, Y., Zhu, L. and Li, X. (2018). Organic Contamination and Remediation in the Agricultural Soils of China: A critical review. *Science of the Total Environment*, **615**:724-740. **[Crossref]**

Szopińska, M., Szumińska, D. and Bialik, R.J. (2019). Determination of Polycyclic Aromatic Hydrocarbons (PAHs) and other Organic Pollutants in Freshwaters on the Western shore of Admiralty Bay (King George Island, Maritime Antarctica). *Environ Sci Pollut Res.*, **26**(18):18143-18161. **[Crossref]**

Thavamani, P., Malik, S., Beer, M., Megharaj, M. and Naidu, R. (2012). Microbial activity and Diversity in Long-Term Mixed Contaminated Soils with Respect to Polyaromatic Hydrocarbons and Heavy Metals. *Journal of Environmental Management*, **99**:10-17. **[Crossref]**

Tsai, P.J., Shih, T.S., Chen, H.L., Lee, W.J., Lai, C.H. and Liou, S.H. (2004) Assessing and Predicting the Exposures of Polycyclic Aromatic Hydrocarbons (PAHs) and their Carcinogenic Potencies from Vehicle Engine Exhausts to Highway Toll Station Workers. *Atmospheric Environment*, **38**:333-343. **[Crossref]**

Wang, Z., Pan, F., Hesham, A., Gao, Y., Zhang, Y. and Yang, M. (2015). Impacts of Produced Water Origin on Bacterial Community Structures of Activated Sludge. *Journal of Environmental Sciences*, **14**:1-8. **[Crossref]**

Yu, Y, Sun, X., Zou, L., Zhang, H, Liu, Y. and Liu, M. (2020). Polycyclic Aromatic Hydrocarbons (PAHs) in Surface Soil from the Guan River Estuary in China: Contamination, Source Apportionment and Health-Risk Assessment. *Science Asia*, **46**:80-86. **[Crossref]**

Adedosu, T. A., Adeniyi, O. K., and Adedosu, H. O. (2015). Distribution, Sources and Toxicity Potentials of Polycyclic Aromatic Hydrocarbons in Soil around the Vicinity of Balogun-Birro Dumpsite of Osogbo, Nigeria. *Malaysian Journal of Analytical Sciences* **19**(3):636-648.

Ana, G.R.E.E., Sridhar, M.K.C. and Emerole, G.O. (2009). Polycyclic Aromatic Hydrocarbon Burden in Ambient Air in Selected Niger Delta Communities in Nigeria, *Journal Air Waste Management Association*, **62**(1):18-25.

Chikere, C.B. and Fenibo, E.O. (2018). Distribution of PAH-Ring Hydroxylating Dioxygenase Genes In Bacteria Isolated From Two Illegal Oil Refining Sites In The Niger Delta, Nigeria. *Scientific African*, **1**:1-10. **[Crossref]**

Itodo, A.U., Akeju, T.T. and Itodo, H.U. (2019). Polycyclic Aromatic Hydrocarbons (PAHs) in Crude Oil Contaminated Water from Ese-Odo Offshore, Nigeria. *Annals of Ecology and Environmental Science*, **3**:12-19. **[Crossref]**

Kadali, R.B., Rathi, N. and Perumal, V. (2014). Evaluation of pedestrian midblock road crossing behavior using an Artificial Neural Network (ANN). Journal of Traffic and Transportation Engineering., 1(2):111-119. **[Crossref]**

Korashy, H.M. and El-Kadi, A.O.S. (2016). "The Role of Aryl Hydrocarbon Receptor in the Pathogenesis Of Cardiovascular Diseases". Drug Metabolism Reviews, **38**(3):411-450. **[Crossref]**.

Li, Z., Romanoff, L.C., Trinidad, D.A., Hussain, N., Jones, R.S., Porter, E.N., *et al.*, (2006). Measurement of Urinary Monohydroxy Polycyclic Aromatic Hydrocarbons Using Automated Liquid-Liquid Extraction and Gas Chromatography/Isotope Dilution High-Resolution Mass Spectrometry. *Anal Chem.*, **78**:5744-5751. **[Crossref]**.

Li, H., Wang, A and Cen, B.Z. (2018). Molecular Detection, Quantification and Distribution of Alkane-Degrading Bacteria in Production Water from Low Temperature Oil Fields. *International Biodeterioration and Biodegradation*, **76**:49-57.

Maliszewska-Kordybach, B. (1996). Polycyclic Aromatic Hydrocarbons in Agricultural Soils in Poland; Preliminary Proposal for Criteria to Evaluate the Levels of Soil Contamination. *Appl. Geochem.*, **11**:121-127. **[Crossref]**.

Nam, J.J., Sweetman, A.J. and Jones, K.C. (2019). Polynuclear Aromatic Hydrocarbons (PAHs) in Global Background Soils. *Journal of Environmental Monitoring*, **11**(1):45-48. **[Crossref]**

Nduka, J.K., Anyakora, C., Obi, E., Obumselu, F.O., Ezenwa, J.E and Ngozi-Olehi, L.C. (2013). Polyaromatic Hydrocarbons (PAHs) and Inorganic Chemical Contaminants at Refuse Dumpsites in Awka, South Eastern Nigeria: A Public Health Implication. *Journal of Scientific Research and Reports*, **2**(1):173-189

Neff, J.M, Boehm, P.D., Kropp, R., Stubblefield, W.A. and Page, D.S. (2003). Monitoring Recovery of Prince William Sound, Alaska, following the Exxon Valdez Oil **[Crossref]**