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Research article

Preliminary investigation of polycyclic aromatic hydrocarbons (PAHs) concentration, compositional pattern, and ecological risk in crude oil-impacted soil from Niger delta, Nigeria

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ABSTRACT

Crude oil contamination could serve as an important source of polycyclic aromatic hydrocarbons (PAHs) in the environment. Determining the concentration and distribution of PAHs and their ecological risk could provide clues for appropriate remediation. The present study investigated the concentrations, composition pattern, and ecological risk of PAHs in crude oil-contaminated soil collected from the Niger Delta, Nigeria. The concentrations of Σ_{29}PAHs and 16 priority US-EPA PAHs (Σ_{16}PAHs) in the soil ranged from 24230.68 to 40845.32 ng/g (average: 29953.47 ng/g) and 7361.66–14141.49 ng/g (average: 9819.96 ng/g), respectively. The concentrations of Σ_{16}PAHs US-EPA in all the studied locations far exceeded the safety value of 1000 ng/g set by the soil quality guidelines of Switzerland and above which is regarded as being highly contaminated for Agricultural soils of Poland. The percentage composition of 2-, 3-,4-, 5-, and 6-ring in the soils were 33.69%, 56.31%, 9.47%, 0.52%, and 0.02% of the total PAHs, respectively, indicating the predominance of low molecular weight PAHs typical of petrogenic origin. Ecological risk assessment indicated a high risk to the soil biota and ecosystem in the studied soil samples as presented by individual PAH and total PAHs. 2-, 3- and 4-ring PAHs in the soil contributed significantly to the ecological risk burden in the soils. This research work provides useful information on the ecological risk associated with crude oil contamination and consequently would assist the government in formulating precise, targeted, and effective remediation measures for soil contaminated with crude oil.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic pollutants consisting of two or more fused aromatic rings without heteroatoms [1,2]. The occurrence of PAHs in the environment is of concern globally because the PAHs are carcinogenic, mutagenic, and toxic to humans [3,4]. PAHs containing four-to seven-ring are extremely mutagenic and carcinogenic while two- or three-ring PAHs are considered less mutagenic but with the possibility of high toxicity [5]. Many PAHs have been associated with breast, lung, colon cancers, and neuro-, reproductive, and developmental toxicities [6]. PAHs are released into the environments mainly through pyrolytic and petrogenic sources. The pyrolytic PAHs are considered to originate principally from incomplete

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combustion of fossil fuel and other organic materials while petrogenic PAHs are derived primarily from crude oil and allied products.

Globally, environmental pollution resulting from crude oil and allied products has become a major concern. At least 0.08–0.4% of the internationally produced oil has been estimated to be spilled into the marine ecosystem as pollutants [7]. Nigeria is the 6th largest producer of crude oil in the world and has recorded the highest number of oil spill incidents since 1970 [8]. The Niger Delta region is home to the country's approximately 37 billion barrels of reserve crude oil and 180 trillion cubic feet of natural gas [9]. It also accommodates major oil refineries and many other manufacturing industries. The region has an intricate and widespread system of pipelines running across the region, thereby leading to huge volumes of oil spill incidences [10]. An estimated average of 1.5 million tons of oil has been spilled into the Niger Delta ecosystem over the past 50 years. Amounts that are 50 times higher than the estimated volume of Exxon Valdez spilled oil in Alaska in 1989 [10]. Ahiamadu et al. [11] reported that the national oil spill detection and response agency (NOSDRA), quoted approximately 7581 crude oil spill incidents between 2008 and 2018 in the Niger Delta region of Nigeria. The region is credited with the largest un-remediated oil-polluted areas in the Gulf of Guinea [8,12,13]. Crude oils are often seen floating on water surfaces and are usually dispersed to shorelines by wind and wave actions, thus affecting the soil environment [14]. Apart from oil spills emanating from pipeline failure or vandalism, other sources of oil spills in the region may be oil well blow-outs, seepages, tanker accidents, and intentional damage to operational facilities [15,16]. These activities have led to the release of different pollutants, including heavy metals and various organic pollutants like PAHs into the environment [11,17–21]. There is a high possibility of PAHs and other organic pollutants building up along the food chain in the Niger Delta. The majority of the residents of the region engage in fish farming; thereby making aquatic dwellers readily available for human consumption. In addition, the region's location on the globe with several rivers directly emptying into the Atlantic Ocean (Fig. 1) has necessitated the need to monitor the pollution status of the region.

Soils contaminated with PAHs can pose serious health challenges to humans, livestock, and wildlife, as well as an Ecological risk to the soil microbes, soil functions, plants, the quality of air, and aquatic life [22]. The composition of the PAH mixtures in the environment depends on their sources [22]. However, the original composition of PAHs mixtures could be altered by post-emission transport, transformation, and other processes which are in turn controlled by compound properties, soil properties, vegetation, and other ambient conditions [22–24]. This transformation may practically influence PAHs source identification, abundance, spatial distribution, and risk impact assessment.

Studies on the abundance, sources, composition patterns, and health risk of PAHs in anthropogenic impacted soils from the oil-producing Niger Delta region have been reported by previous authors [11,20,25–27]. However, some of these studies mainly collected samples from the host communities and adjoining communities to the flow station and producing oil field. Moreover, for the current study, samples were collected from locations along the pipeline conveying the crude oil. The choice of these locations was necessitated owing to the frequent pipeline vandalisation by miscreants. Therefore, for a better understanding of PAHs distribution and

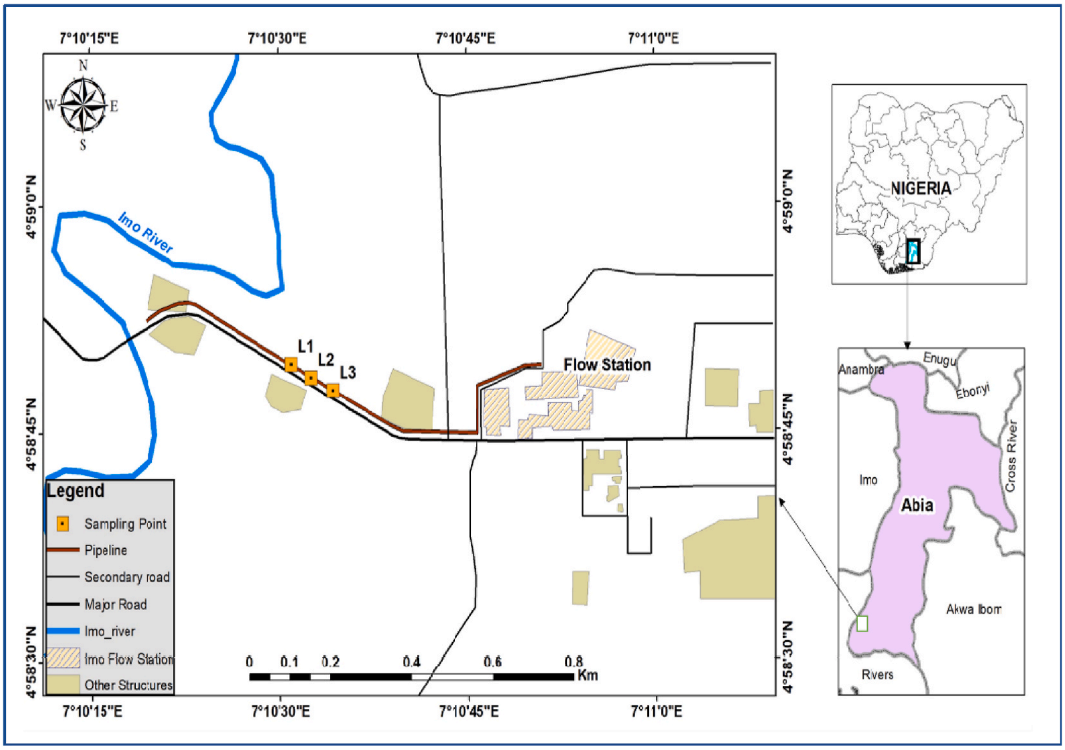

Fig. 1. Map of the study area showing the sampling locations along the oil pipeline and oil flow station in Owaza, Abia State, Nigeria modified after [21].

their immediate ecological risk as a result of crude oil contamination, this study investigated the concentration, distribution, and ecological risk of PAHs in crude oil-contaminated soil in the Niger Delta of Nigeria.

2. Materials and methods

2.1. Sample collection and preparation

Twelve (12) composite oil-contaminated representative soil samples were collected from 3 different locations around oil facilities (L1- N 04°58'49.3, E 007°10'31.5; L2- N 04°58'48.4, E 007°10'32.8; L3 – N 04°58'47.5, E 007°10'34.0) in Owaza, Abia State, Nigeria (Fig. 1) The soils were sampled at 25 × 25 m^2 sampling plots with 5–10 sub-samples [28] at a depth of 0–30 cm each. The collected soil samples were wrapped with aluminium foil and then placed in pre-cleaned polyethylene bags after an incident of oil spillage in the area in November 2012. The total bulk mass of soil sample collected from each sample location was roughly 1 kg. The soils were air-dried at room temperature, ground with a mortar, sieved (212-μm), and kept at 4 °C prior to chemical analysis. 20–50 g of finely powdered soil samples were soxhlet extracted using pre-extracted thimbles, with 200 mL of dichloromethane (DCM) for a minimum of 48 h. Surrogate standards (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and benzo [g,h,i]perylene-d_{12}) were added prior to extraction to determine the accuracy of the employed methods. Activated copper was added to remove inorganic sulphur in the extract. The concentrated extracts were fractionated by a glass column packed with silica-alumina (2:1) column chromatography into aliphatic hydrocarbons and PAHs fractions by successive elution with 20 mL *n*-hexane and 70 mL *n*-hexane/dichloromethane (7:3 v/v), respectively. The PAH fraction was further concentrated with a rotary evaporator at 30 °C to approximately 1 mL, transferred to a 1.5 mL vial, and blown down to 0.5 mL under a gentle stream of nitrogen.

2.2. Instrumental analysis

GC-MS analyses were performed on a Shimadzu Model 2010 GC-MS (Shimadzu, Japan) with an HP-5MS fused silica column (30 m × 0.25 mm i. d., 0.25 μm film thickness) at the State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, China. Ultrapure Helium was used as a carrier gas. The mass spectrometer was operated in electron impact mode (70 eV). The samples were injected in splitless mode at 100 °C with a purge of 1 min after injection. The following temperature program was used for PAH analysis: the initial temperature was 60 °C and heated to 200 °C at 5 °C/min, then to 250 °C at 2 °C/min and further heated to 280 °C at 10 °C/min (held for 20 min) and finally heated to 290 °C at 10 °C/min (held for 5 min). Identification of the target PAHs was based on the comparison of their GC-retention times and mass spectrum with appropriate reference standards, while data acquisition was made in the selective ion monitoring (SIM) mode. Quantification was performed with a conventional internal calibration method.

2.3. Quality assurance and control

All the chemicals used in this study were of analytical grade with high purity (98+ %). The standards with 98+% purity were purchased from Accustandard Incorporated, New Haven, the USA. Appropriate blanks (Field, laboratory, spiked, and replicate) samples were analysed along with field samples [29]. Quantification was performed using the internal calibration method based on eight-point calibration curves for individual compounds. The average recoveries of the surrogate standards from all the blanks ranged from 65.5% to 99.6%. The average recoveries of the same surrogate standards from the soil samples ranged from 70.5% to 100.5%. All the spiked have surrogate recoveries in the range of 75.0%–120%, the matrix also recorded surrogate recoveries in the range of 72.5%–110.9%.

2.4. Risk quotients

The risk quotients (RQ) method is a useful tool when characterising the risk of PAHs to surrounding organisms and ecosystems [2,30,31]. The RQ method can be used to assess the ecosystem risk of $\sum$PAHs sensitively and accurately [2]. RQ of PAHs in the soil was calculated using the following equation [2]:

$$RQ = C_{PAH}/C_{QV} \tag{1}$$

where C_{PAH} is the concentration of each individual PAH in the soil and C_{QV} is the corresponding quality value of each individual PAH in the soil [32]. Thus, the RQ (NCs) and RQ (MPCs) values could be respectively obtained based on the equation as follows [2]:

$$RQ_{(NCs)} = C_{PAH}/C_{QV(NCs)} \tag{2}$$

$$RQ_{(MPCs)} = C_{PAH}/C_{QV(MPCs)} \tag{3}$$

where $C_{QV(NCs)}$ represents the quality value of negligible concentrations (NCs) and $C_{QV(MPCs)}$ maximum permissible concentrations (MPCs) as reported by Cao et al. [2]. MPCs are the concentration of pollutants above which the risk of adverse effects is considered unacceptable to ecosystems while NCs are the concentrations in the environment below which the occurrence of individual PAHs has no adverse effects [33].

$RQ_{\sum PAHs\ (NCs)}$ and $RQ_{\sum PAHs\ (MPCs)}$ values are calculated by adding $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ of each single PAH [2].

$$RQ_{\sum PAHs\ (NCs)} = \sum RQ_{i(NCs)}\ (RQ_{i(NCs)\geq\ 1}) \tag{4}$$

$$RQ_{\sum PAHs\ (MPCs)} = \sum RQ_{i(MPCs)}\ (RQ_{(MPCs)i\ \geq\ 1}) \tag{5}$$

2.5. Statistical analyses

Data analyses were performed with Origin (Pro) version 2021b (OriginLab Corporation, Northampton, MA, USA). The average concentrations of the total PAHs for all the locations were compared using the Bonferroni *t*-test (pairwise multiple comparisons). Differences between locations were considered statistically significant when $p < 0.05$.

3. Results and discussion

3.1. PAHs concentration and composition pattern

The concentrations of 29 target PAHs, the sum of which is defined as $\sum_{29}$PAHs, determined from the oil-contaminated soil are shown in Table 1. The $\sum_{29}$PAHs in the soils ranged from 24230.68 to 40845.32 ng/g with an average value of 29953.47 (Table 1). High concentrations of PAHs were detected in all the locations with location 3 having the highest value. A high abundance of n-alkanes $\sum(nC_{14}$ to $nC_{29})$ with an average concentration value of 24664 μg/g had been previously observed from the same soil samples [21]. This could be attributed to the volume of the spilled oil, and also an indication of little effect of environmental degradation on the impacted soil. The highest value recorded in location 3 may be due to relatively high volume of oil discharged into the area and its closeness to the flow station (Fig. 1). Since most international regulatory bodies and several studies in the literature usually refer to the concentration of the 16 priority US-EPA PAHs in their reports [34], the concentrations of 16 priority US-EPA PAHs (Σ_{16}PAHs) are also indicated in Table 1 for comparison. The Σ_{16}PAHs values in the soil samples ranged from 7361.66 to 14141.49 ng/g (average: 9819.96 ng/g). PAHs pollution levels in soils had been characterised as not contaminated (<200 ng/g), weakly contaminated (200–600 ng/g), contaminated (600–1000 ng/g), and heavily contaminated (>1000 ng/g) [35], according to the classification system suggested for Agricultural soils of Poland. Also, the concentrations of Σ_{16}PAHs far exceeded the precautionary value of 1000 ng/g set by the soil quality guidelines of Switzerland [36]. Based on these classifications, the Niger Delta soil could be classified as heavily contaminated

Table 1
Average concentration (ng/g dry wt.) of polycyclic aromatic hydrocarbons (PAHs) in Niger Delta soil.

Compound	Abbreviation	L1 (n = 4)	L2 (n = 4)	L3 (n = 4)	^{t}Avg
Naphthalene	Nap	140.30 ± 11.1	155.47 ± 6.3	242.03 ± 2	179.27 ± 4.6
2-Methylnaphthalene	2-MNap	458.05 ± 35.5	367.44 ± 12.6	765.27 ± 6.9	530.25 ± 15.1
1-Methylnaphthalene	1-MNap	271.12 ± 19.4	236.33 ± 8.17	452.52 ± 4.4	319.99 ± 7.8
Biphenyl	Bi	158.47 ± 4.9	117.18 ± 0.5	194.41 ± 1.5	156.69 ± 2.3
2,6-Dimethylnaphthalene	2,6-DMNap	2340.27 ± 114.3	1871.5 ± 0.5	3872.32 ± 29.9	2694.70 ± 59.1
Acenaphthylene	Ace	173.00 ± 9.2	145.91 ± 41.8	291.07 ± 2.4	203.33 ± 21.1
Acenaphthene	Ac	407.02 ± 13	344.39 ± 3.7	514.74 ± 4.9	422.05 ± 5.1
2,3,5-trinaphthalene	2,3,5-TNap	6044.43 ± 108.2	4988.48 ± 0.3	5740.29 ± 37.7	5591.07 ± 54.8
fluorene	Fl	828.47 ± 13.6	532.44 ± 1.0	1310.70 ± 1.2	890.54 ± 7.2
phenanthrene	Phe	2661.64 ± 26.5	1636.11 ± 6.4	4325.46 ± 21.9	2874.40 ± 10.5
anthracene	Ant	2628.14 ± 26.2	1633.57 ± 7.4	4316.34 ± 21.1	2859.35 ± 9.7
2-phenanthrene	2-MPhe	3164.07 ± 25.3	2555.54 ± 12.6	5563.49 ± 19.1	3761.03 ± 6.4
1-methylphenathrene	1-MPhe	3111.99 ± 23.9	2491.4 ± 6.1	5402.14 ± 18.5	3668.51 ± 9.1
2,6-dimethlyphenanthrene	2,6-DMPhe	1803.60 ± 10.2	2508 ± 3.4	4159.96 ± 1.72	2823.85 ± 4.5
fluranthrene	Flu	139.51 ± 5.1	587.79 ± 1.5	523.79 ± 1.52	417.03 ± 2.1
Pyrene	Pyr	120.96 ± 4.2	587.79 ± 1.8	371.75 ± 1.73	360.17 ± 1.4
11H-benzo(*b*)fluorine	11-BbF	41.34 ± 1.8	1092.2 ± 6.7	381.92 ± 3.17	505.15 ± 2.5
benzo(*a*)anthracene	BaA	160.81 ± 12.6	389.29 ± 22.4	994.26 ± 4.64	514.79 ± 8.9
chrysene	Chr	94.50 ± 1.8	1936.51 ± 4.3	1088.25 ± 4.54	1039.75 ± 1.5
benzo(*b*)fluoranthene	BbF	6.45 ± 3.0	9.48 ± 3.7	64.59 ± 1.73	26.84 ± 1.0
benzo(k)fluoranthene	BkF	6.38 ± 3.0	9.38 ± 3.7	6.91 ± 1.71	7.56 ± 1.0
benzo(e)pyrene	BeP	6.16 ± 3.8	7.8 ± 4.1	64.45 ± 2.75	26.14 ± 0.7
benzo(*a*)pyrene	BaP	5.25 ± 4.8	6.57 ± 5	66.04 ± 0.63	25.95 ± 2.5
perylene	Per	8.69 ± 2.5	17.27 ± 10.3	66.35 ± 2.43	30.77 ± 4.5
9,10-diphenylanthracene	9,10-DPha	1.64 ± 0.9	1.84 ± 0.5	25.36 ± 0.43	9.61 ± 0.3
dibenzo (a,h)anthracene	DahA	0.8 ± 0.9	0.32 ± 0.2	16.7 ± 1.5	5.94 ± 0.7
benzo (ghi)perylene	BghiP	0.34 ± 0.5	0.00	8.90 ± 0.04	3.08 ± 0.3
indeno (123-cd) pyrene	IcdP	0.85 ± 0.9	0.47 ± 0.04	13.78 ± 0.11	5.03 ± 0.5
coronene	Cor	0.16 ± 0.2	0.21 ± 0.02	1.53 ± 0.04	0.63 ± 0.1
$\sum_{16}$ US-EPA PAHs		7361.66	7956.73	14141.49	9819.96
$\sum_{29}$PAHs		24784.41	24230.68	40845.32	29953.47

Data are reported in the format average (mean ± standard deviation), ^{t}Avg is the mean concentrations of each target at all the studied locations.

with PAHs. The very high concentrations recorded in this study could be attributed to intense exploration and exploitation activities with incessant pipeline leakages occasioned by vandals in the area. It should also be noted that there is continuous gas flaring in the sample locations as a result of the exploration activities which further increased the PAHs loads in the collected samples. The PAHs displayed noticeable distribution patterns, with 2-, 3-,4-, 5-, and 6-ring accounting for 33.69%, 56.31%, 9.47%, 0.52%, and 0.02% of the total PAHs, respectively (Fig. 2a and b), indicating the predominant of 3- ring PAHs over 2-, 4-, 5- and 6- ring PAHs. The percentage contribution from 6-ring PAHs is insignificant and thus, could not be clearly displayed in the pie chart (Fig. 2b). Such distributions have been attributed to contamination resulting from petrogenic sources [37].

The mean values of the PAHs obtained from the different locations (L1, L2, and L3) (Fig. 3) are statistically compared. The results show significant differences among the locations, however, the difference in the means is not significant at $p = 0.05$ level between L1 and L2. This suggests that the locations have received different input of PAHs from crude oil contamination.

3.2. Comparison with PAH levels from other studies

PAH concentrations in the soils were compared with reported values from other parts of the globe (Table 2). Sojinu et al. [20] and Adedosu et al. [38] have previously reported PAHs concentrations that ranged from 23.8 to 120 and 7.40–78.3 ng/g, respectively (Table 2) in similar soil samples from the region, although, their soil samples for instance, in Sojinu et al. [20] were collected within the host communities where oil facilities were installed and not along pipeline pathways as it is the case in the present study. The concentrations of PAHs obtained in the present study were found to be higher than those reported from other regions of the world with the exception of samples from chemical plant areas in Australia (Table 2). This may reflect the quantity of spilled hydrocarbons in the area under study. The present samples have higher concentrations of PAHs when compared with global distribution patterns of PAHs in soils from oil exploration areas (Fig. 4). The Niger Delta is heavily affected by anthropogenic influences resulting from agriculture, deforestation, and, especially, oil exploration activities. With respect to the latter, the environment of the Niger Delta is intensely damaged by oil spills and contamination by industrial by-products as well as intense natural gas flaring. In early August 2011, the United Nation Environmental Programme (UNEP) released a report on oil spills in Ogoni land in the Niger Delta, Nigeria. The report showed that it will take up to 30 years to fully recover from the devastation done by oil spills in the area, even though oil industry operations have been suspended in the area since 1993.

Benzo(*a*)pyrene (BaP) is the most carcinogenic PAH in the present study with concentrations that ranged from 5.25 to 66.04 ng/g and with an average value of 26 ng/g (Table 1). These values are higher than those reported in soils from communities hosting oil installations in the same region by Sojinu et al. [20] (0.09–2.05 ng/g) and Adedosu et al. [38] (0.02–2.98 ng/g). However, a relatively comparable average value (22 ng/g) was reported from the city of Chiang Mai in Thailand [39]. Hashmi et al. [40] observed relatively higher BaP values between 5 and 270 ng/g with an average concentration value of 55 ng/g from the industrial zones of the Korean Peninsula. This present study shows that the Niger Delta soils have received significant input of BaP contamination when compared with previous studies from the region.

3.3. Ecological risk assessment

The ecological risk of sixteen listed PAHs by the United State Environmental Protection Agency (USEPA) as priority pollutants in the soil samples is assessed in this present study using the risk quotients method. The average values of RQ (NCs) and RQ (MPCs) in the studied soil samples are listed in Table 3. RQ values are interpreted as suggested by Cao et al. [2], where RQ (NCs) < 1.0, indicates that the contamination of individual PAH present in the soil has a very low ecological risk and might be of insignificant concern. RQ (NCs)

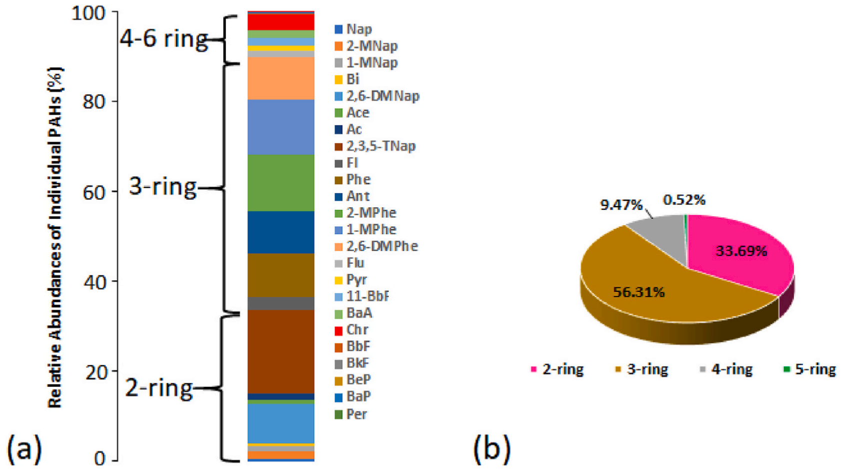

Fig. 2. (a) Relative distribution pattern of individual PAHs in the soil samples; (b) Pie chart of percentage contribution of the four major PAH groups (2-, 3-, 4-, and 5-ring) to the total PAHs in the soil samples.

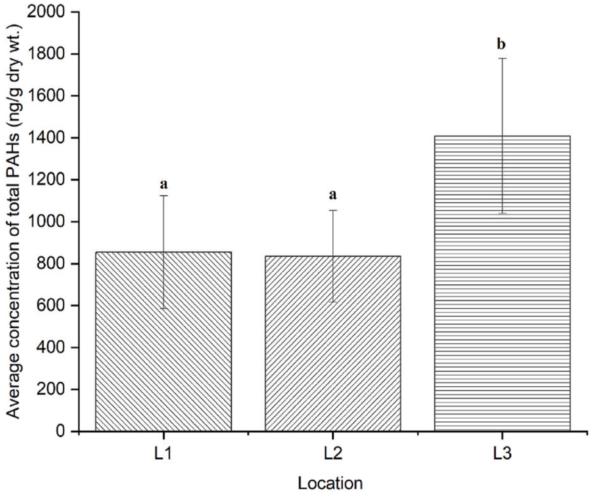

Fig. 3. Average of total 29 PAHs concentrations in each of the sample locations. Values represent Mean ± SD ($n = 29$). Means that do not share a letter are significantly different ($p < 0.05$).

Table 2
PAHs concentrations in soils from the Niger Delta and from different regions of the world.

Location	Source type	No. of PAHs	∑PAHs (ng/g)	References
Uzbekistan	Industrial area	29	41–2670	[22]
China	Riverbank soils	16	36.9–378	[2]
United States	Highway	14	3000[a]	[44]
United Kingdom	Motorway	7	20000[a]	[45]
China	Urban soils	16	467–5470	[46]
Canada	Highway	17	1400[a]	[47]
Australia	Chemical plant	18	300–79000	[48]
Niger Delta, Nigeria	Gas plant area	16	7.40–78.3	[38]
Niger Delta, Nigeria	Close to oil installation	28	23.8–120	[20]
Niger Delta, Nigeria	Close to oil installation	29	29953.47[a]	This study

[a] Mean values.

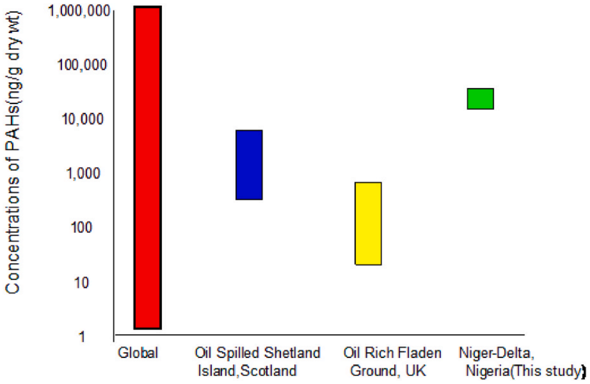

Fig. 4. PAH concentrations in Nigeria (the present study) compared with those reported from other regions of the world. The data for the Shetland Island, Fladen Ground, and Global Range were obtained from Refs. [41–43].

≥ 1 and RQ (MPCs) < 1 indicate the pollution of individual PAH is at moderate risk, while RQ (MPCs) ≥ 1 suggests much more severe contamination and high ecological risk. The RQ∑PAHs(NCs) and RQ∑PAHs(MPCs) values seem to accurately reflect the pollution levels and signify the overall or all-inclusive risk posed by ∑PAHs. RQ∑PAHs (NCs) ≥ 1, <800, and RQ∑PAHs(MPCs) = 0 represent low risk; RQ∑PAHs(NCs) ≥ 800 and RQ∑PAHs(MPCs) = 0, moderate risk$_1$; RQ∑PAHs(NCs) < 800 and RQ∑PAHs(MPCs) ≥ 1, moderate risk$_2$; while RQ∑PAHs(NCs) ≥ 800 and RQ∑PAHs(MPCs) ≥ 1 of high risk.

As shown in Table 3, the RQ (NCs) values are >1 for Nap, Ace, Ac, Fl, Phe, Ant, Flu, Pyr, and BaA in the soil samples, and RQ (MPCs)

Table 3
Average values of $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ of sixteen US-EPA PAHs in soils from Niger Delta, Nigeria.

	NCs(ng/g)[a]	MPCs(ng/g)[a]	RQ (NCs) (ng/g)	RQ (MPCs) (ng/g)
Nap	1.4	140	128.05	1.28
Ace	1.2	120	169.44	1.69
Ac	1.2	120	351.77	3.52
Fl	1.2	120	742.12	7.42
Phe	5.1	510	563.61	5.64
Ant	1.2	120	2382.79	23.83
Flu	26	2600	16.04	0.16
Pyr	1.2	120	300.14	3.00
BaA	3.6	360	143.00	1.43
Chr	107	10700	9.72	0.10
BbF	3.6	360	7.46	0.07
BkF	24	2400	1.11	0.01
BaP	27	2700	0.96	0.01
DahA	27	2700	0.22	0.00
IcdP	59	5900	0.09	0.00
BghiP	75	7500	0.04	0.00
$\sum_{16}$PAHs			4815.25	47.81

[a] Cao et al. [2].

values are all >1. This indicates that this individual PAH presented a high risk for the biota and ecosystem in the area. The RQ (NCs) values for Chr, BbF, and BkF are <1, indicating a moderate risk to the environment. This assessment shows that most of the low molecular PAHs pose a high risk to the environment. Although these PAHs are less mutagenic and carcinogenic, their high ecological risk calls for serious attention. Meanwhile, PAHs such as BaP, DahA, IcdP, and BghiP pose no ecological threat. However, the average values of RQ$\sum$PAHs (NCs) (4815.17) and RQ$\sum$PAHs (MPCs) (47.81) are greater than the minimum threshold values of 800 and 1.0 respectively, indicating a high risk of $\sum$PAHs to the biota and ecosystem in the study area.

A plot of relative % values of $RQ_{(NCs)}$ for individual PAHs in the soil samples is shown in Fig. 5. 3-ring PAHs contribute to the major environmental risk burden and anthracene provides the largest percentage. This is followed by 2-ring PAHs, and then 4-ring PAHs. It is also noteworthy that Pyr contributes significantly to the ecological risk burden in the soils among the 4-ring PAHs. Therefore, in the event of crude oil spillage, the class of PAHs that require immediate de-contamination are the lower molecular weight PAHs.

4. Conclusion

The average concentrations of Σ_{29}PAHs Σ_{16}PAHs in the investigated crude oil contaminated soil samples were 29953.47 ng/g and 9819.96 ng/g, respectively. The concentrations of 16 priority US-EPA PAHs (Σ_{16}PAHs) far exceeded the threshold values set by the soil quality guidelines of Switzerland and Poland and classified the area under study as heavily polluted. The very high concentrations recorded in this study could be attributed to intense oil exploitation activities and incessant pipeline leakages occasioned by vandals in the areas. The percentage composition of 2-, 3-,4-, 5-, and 6-ring in the soils were 33.69%, 56.31%, 9.47%, 0.52%, and 0.02% of the total PAHs, respectively, indicating the preponderance of low molecular weight PAHs over high molecular weight PAHs. The average values of RQ$\sum$PAHs (NCs) (4815.17) and RQ$\sum$PAHs (MPCs) (47.81) are greater than the minimum threshold values of 800 and 1.0 respectively, indicating a high risk of $\sum$PAHs to the biota and ecosystem in the study area. 2-, 3- and 4-ring PAHs in the soils contribute significantly to the ecological risk burden in the soils. Thus, in the event of crude oil spillage, the immediate decontamination of the low molecular weight PAHs must be considered. Based on the enormous quantity of the PAHs determined in the study area and the high ecological risk of low molecular weight PAHs, preventative and remedial measures should be conducted.

Declarations

Author contribution statement

Oluwabamise L. Faboya: Conceived and designed the experiments; Performed the experiments; Analysed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper. Samuel O. Sojinu: Performed the experiments; Analysed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper. Joseph O. Otugboyega: Analysed and interpreted the data; Wrote the paper.

Data availability statement

Data will be made available on request.

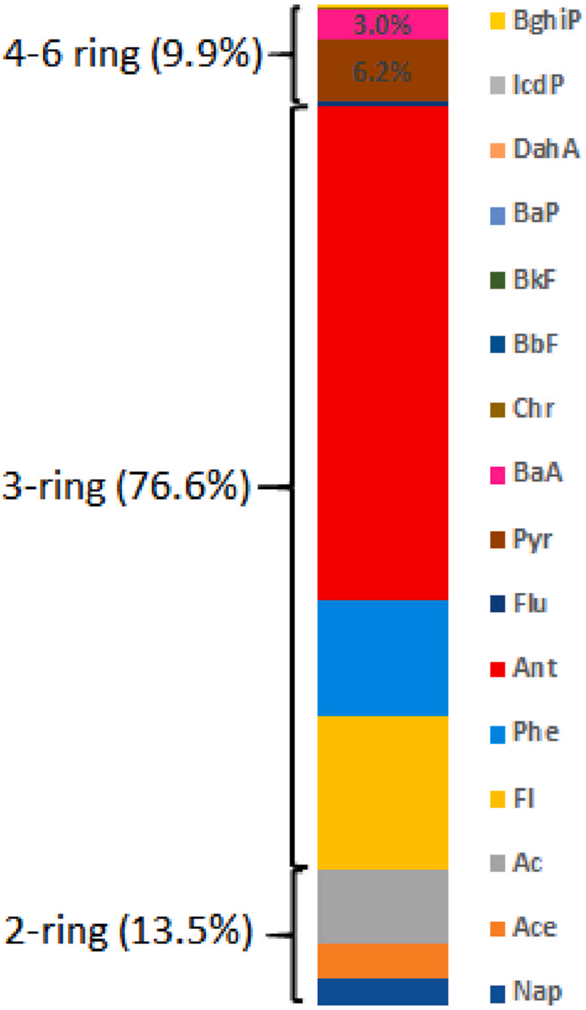

Fig. 5. A plot of relative % values of $RQ_{(NCs)}$ for individual PAH in soils from the Niger Delta.

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The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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