

Geochemical Fingerprinting of Oil-Impacted Soil and Water Samples In Some Selected Areas in the Niger Delta

Geokemični kazalniki z nafto nasičenih vzorcev zemljin in vode na nekaterih izbranih področjih delte reke Niger

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Abstract

With over 50 years of oil exploration and exploitation in the Niger Delta, there has been an increasing rate of environmental degradation due to hydrocarbon pollution. This study is aimed at tracing the sources of the oil spills and the distribution of pollutants in selected communities in the Niger Delta using geochemical techniques. A total of sixteen samples made up of ten crude oil-impacted soil samples taken at a depth of 30 cm and six water samples (two from boreholes, two from burrow pits and two from surface water – one from a river and the other from rain harvest as control) were collected. The identification and quantification of aliphatic hydrocarbons (AHs) and polycyclic aromatic hydrocarbons (PAHs) in the samples were performed with an Agilent 7890B gas chromatography flame ionisation detector (GC-FID). The AHs including pristane and phytane, together with seventeen priority PAHs, were identified. The values of AHs and PAHs in the water samples ranged from 0.13 mg/l to 5.78 mg/l and 0.09 mg/l to 1.109 mg/l, respectively, while that for the soil samples ranged from 22.52 mg/kg to 929.44 mg/kg and 10.544 mg/kg to 16.879 mg/kg, respectively.

Key words: PAH, aliphatic hydrocarbon, fingerprinting

Povzetek

Z več kot petdesetimi leti raziskovanja in pridobivanja nafte na območju delte reke Niger narašča stopnja degradacije okolja zaradi onesnaževanja z ogljikovodiki. Namen raziskave je slediti virom razlitij nafte in porazdelitev onesnaževal v izbranih skupnostih v delti reke Niger z uporabo geokemičnih pristopov. Skupno je bilo odvzetih 16 vzorcev, od tega 10 vzorcev z nafto nasičenih zemljin iz globine 30 cm ter 6 vzorcev vode, od tega dva iz vrtin, dva iz jame ter dva iz površinske vode (en vzorec iz reke in en iz deževnice). Z detektorjem plamenskega ioniziranja s plinskim kromatografom Agilent 7890B (GC-FID) je bila izvedena identifikacija in kvantifikacija alifatskih ogljikovodikov (AH) in policikličnih aromatskih ogljikovodikov (PAH). Identificirani so bili AH z vključujočim pristanom (pristane) in fitanom (phytane) skupaj s 17 PAH. Vrednosti AH in PAH v vzorcih vode se gibajo med 0.13 mg/l do 5.78 mg/l in 0.09 mg/l do 1.109 mg/l. Vrednosti AH in PAH v vzorcih zemljine se gibajo med 22.52 mg/kg do 929.44 mg/kg in 10.544 mg/kg do 16.879 mg/kg.

Ključne besede: PAH, alifatski ogljikovodik, kazalniki

Introduction

The Niger Delta is one of the major hydrocarbon provinces of the world, with an estimated reserve of about 23 billion barrels of oil and 183 trillion cubic feet of natural gas with ongoing exploration in the province for over 50 years

[1]. Much of the oil industries located within this region have contributed immensely to the growth and development of the nation.

However, oil exploration activities have rendered the Niger Delta region one of the most severely degraded ecosystems in the world [2]. Crude oil spills are common in the

region with an estimated total of over 7,000 oil spill accidents reported over 50 years [3]. Studies have shown that the quantity of oil spilt over this period amounts to 9–13 million barrels, which is equivalent to 50 Exxon Valdez spills [4].

These spills occur through equipment failure, operational mishap, haulage, oil bunkering and/or vandalism of pipelines leading to the destruction of aquatic and terrestrial flora and fauna of the Niger Delta region [5].

Geochemical or Oil fingerprinting is one of the ways of assessing and evaluating petroleum pollution. It involves the analysis of the released oil with gas chromatography (GC) and measurement of the hydrocarbon compound contents [6]. From the qualitative method (visual comparison of chromatograms) as well as quantitative determination of polycyclic aromatic hydrocarbons (PAHs) diagnostic ratio, *n*-alkane distribution and statistical analysis of data obtained are used for source identification and interpretation of chemical data from oil spills. An assessment and evaluation of hydrocarbon pollution are therefore essential to curb the growing rate of environmental degradation in the

region as well as its social, economic and health impacts. This assessment includes; determination of sources, characterisation, distribution, and fate of organic pollutants such as PAHs and aliphatic hydrocarbons (AHs) in the Niger Delta. The objective is to evaluate the AH and PAHs which are said to be source-specific.

Location and geology of the study area

The study area lies within the Niger Delta region between latitudes $5^{\circ}37'00''\text{E}$ – $5^{\circ}47'00''\text{E}$ and longitudes $5^{\circ}53'00''\text{N}$ – $6^{\circ}02'30''\text{N}$ (Figure 1) and cuts across Sapele and Ethiope West Local government, Delta State, Nigeria. Stratigraphically, the Niger Delta consists of three formations, notably; Akata Formation, which is the oldest unit and constitutes under compacted shales, turbidites and silts. This is overlain by the paralic Agbada Formation, made up of alternating sequences of sandstone and shale which contains most of the hydrocarbon reservoirs in the basin while the youngest unit is the Benin Formation, which is made up of continental sands [7]. The area is

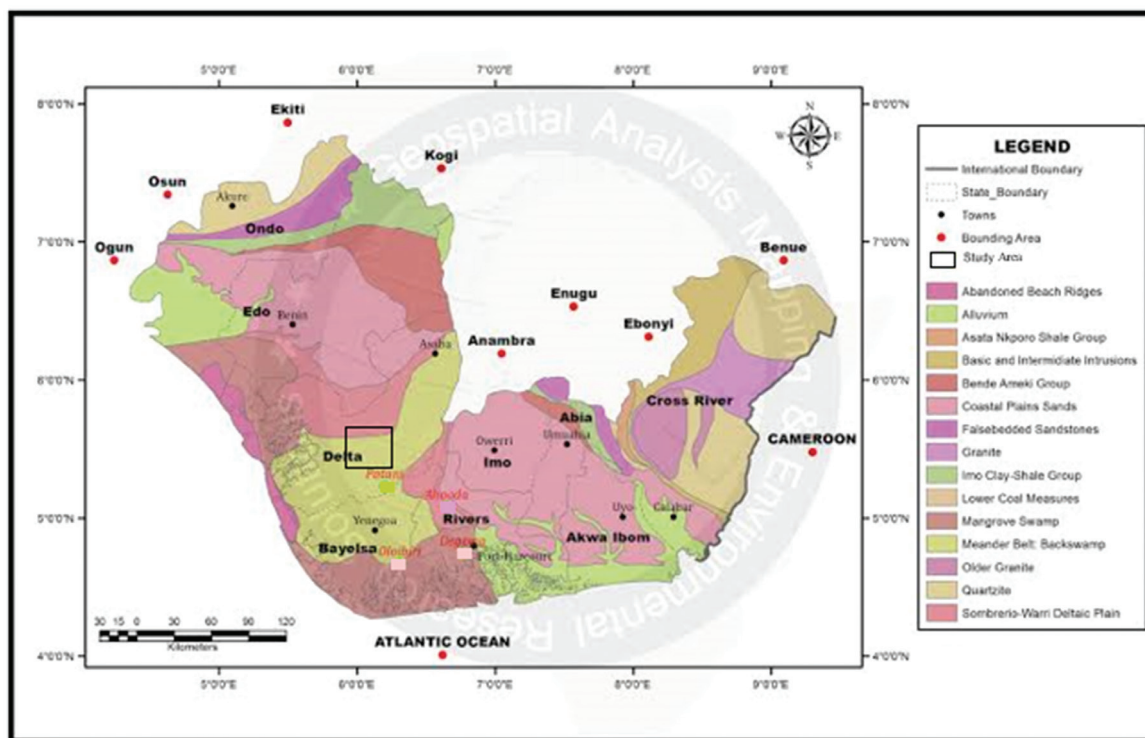


Figure 1: Geological map of the Niger Delta region showing the study area (modified after Geological Map of Niger Delta [8]).

characterised by an even topography. It is situated in the tropics and experiences a fluctuating climate characterised by rainy and dry seasons. The area is drained by minor rivers which are tributaries of the major River Ethiope with a dendritic pattern.

Materials and methods

Sampling and sample preparation

The field study involved the collection of soil and water samples from selected points as shown in Figure 2. A total of sixteen samples made up of ten crude oil-impacted soils taken at a depth of 30 cm and six water samples (two from boreholes, two from burrow pits plus and two from surface water – one from a river and the other from rain harvest as control) were collected. The water and soil samples were collected in clean, well-labelled glass jars and aluminium foils, respectively, and taken to the laboratory for analyses. Due to the

relatively high volatility and instability of AHs and PAHs, the soils were not prepared using conventional soil preparation techniques such as grinding and sieving. However, the soil samples were dried by mixing the samples with 5 g of anhydrous sodium sulfate.

Analytical methods

Organic pollutants were separated from the soil and water samples using an ultrasonic extraction and a separatory funnel, respectively. The extracts were fractionated into the AH and PAH fractions by eluting with *n*-hexane and dichloromethane, respectively. The identification and quantification of AHs and PAHs were performed with an Agilent 7890B gas chromatography flame ionisation detector (GC-FID). The gas chromatographic column has a detection limit of 0.01 ppm. Separation occurs as the constituents of the vapour partition between the gas and liquid phases and oven temperature was programmed from 60°C

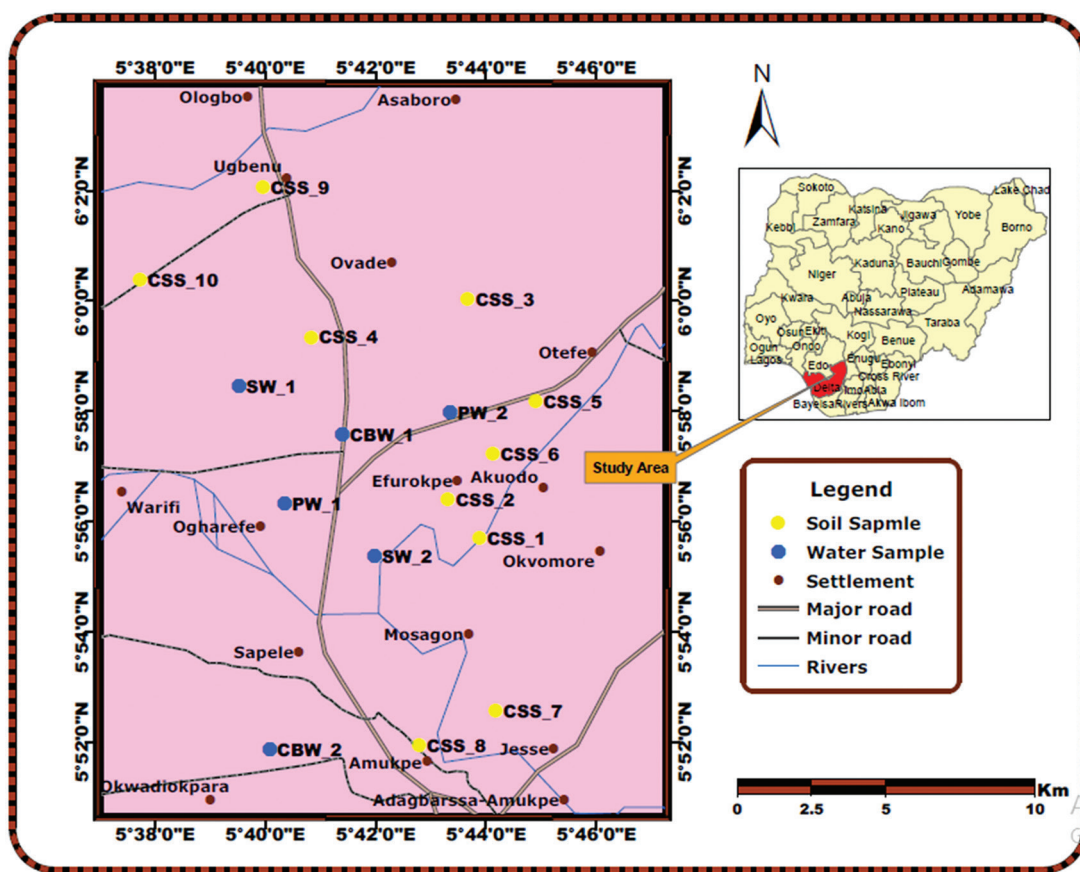


Figure 2: Map of study area showing the sample points (insert: map of Nigeria showing the Niger Delta region).

to 180°C. Identification of analytes was done by comparing the retention time of an individual compound to that of a reference standard.

Results and discussion

Concentration of AH and PAH

The results of the AH and PAHs in this study are shown in Table 1. The concentrations of the AHs and PAHs found in the studied samples are low when compared with values from other areas in the Niger Delta (Table 2). However, in this study, the concentrations are higher than the regulatory limits given by the United Nations Environment Programme (UNEP) [9].

Occurrence, distribution and sources of PAHs

The distribution of seventeen priority PAHs in the water and soil samples in the study area is presented in Table 3. The main PAH pollutants in the studied areas were found to be Chrysene, Acenaphthene, Methyl-naphthalene, Naphthalene, Anthracene, Benzo(g,h,i) perylene, Fluorene, Indeno(1,2,3-cd) perylene

and Phenanthrene. It is important to note that the sum of the PAHs in the contaminated soil samples is 10.54–16.89 times higher than the standard level (1 mg/kg) of heavy [10]. The level of PAH pollution in the control sample (Sw-1) is very low as compared with those from the other samples studied. The spatial distribution of PAHs in this study is shown in Figure 3 and indicates a predominance of three-ring PAHs which suggests recent deposition according to Jiao et al. [11]. The abundance of three-ring PAHs in the study area is in agreement with studies of some oil-polluted sites in the Niger Delta [12]. The four-ring PAHs are also abundant and they indicate the persistence of high molecular weight (HMW) PAHs in the environment. According to Li et al. [13], petrogenic sources are those PAHs derived from petroleum spills while pyrogenic sources are generated by incomplete combustion of fossil fuel such as coal, crude oil and natural gas plus biomass. Diagnostic ratios such as Phenanthrene/Anthracene, Fluorene/Pyrene, Benz(a)pyrene/Chrysene, Naphthalene/Acenaphthene, Anthracene/(Phenanthrene + Anthracene), Fluoranthene/(Fluoranthene +

Table 1: Results of concentration of the AHs and PAHs present in the soil and water samples

Sample name	Sample medium	AHs	PAHs
Css_1	Soil	37.59 mg/kg	16.88 mg/kg
Css_2	Soil	25.70 mg/kg	11.66 mg/kg
Css_3	Soil	34.43 mg/kg	14.72 mg/kg
Css_4	Soil	22.52 mg/kg	14.77 mg/kg
Css_5	Soil	929.44 mg/kg	14.54 mg/kg
Css_6	Soil	79.55 mg/kg	15.91 mg/kg
Css_7	Soil	36.85 mg/kg	13.11 mg/kg
Css_8	Soil	34.86 mg/kg	10.54 mg/kg
Css_9	Soil	44.73 mg/kg	12.15 mg/kg
Css_10	Soil	41.93 mg/kg	15.81 mg/kg
Cbw_1	Water	0.22 mg/l	0.09 mg/l
Cbw_2	Water	0.13 mg/l	0.29 mg/l
Pw_1	Water	5.78 mg/l	0.86 mg/l
Pw_2	Water	5.14 mg/l	1.11 mg/l
Sw_1	Water (control)	0.61 mg/l	0.17 mg/l
Sw_2	Water	2.08 mg/l	0.86 mg/l

AH, aliphatic hydrocarbon; PAHs, polycyclic aromatic hydrocarbons.

Table 2: Comparison of AH and PAH present in the studied samples with those found in some other areas in the Niger Delta and some regulatory standards

Sample medium	Reference	AHs (mg/l)	PAHs (mg/l)
Contaminated soil	Present study	22.52–929.44	10.54–16.88
	Olawoyin et al. [14]	7,878.8–76,510.9	31.4–132.0
	Adedosu et al. [12]	575.96–1,202.47	7.40–78.30
	Udoetok and Osuji Leo [24]	77.64–3,946.58	8.16–3,756.81
	United Nations Environment Programme (UNEP) [9]	10	No limit
	Department of Petroleum Resources (DPR) [15]	No limit	1.00
	United States Environmental Protection Agency (USEPA) [10]	No limit	1.00
Borehole	Present study	0.13–0.22	0.09–0.29
	Olawoyin et al. [14]	No limit	119.90–450.58
	Ibezue et al. [29]	0.03–0.422	0.002–0.007
	WHO	0.0002	0.0002
	Department of Petroleum Resources (DPR) [15]	No limit	0.1
Surface water	Present study	0.61–2.08	0.17–0.86
	Inyang et al. [30]	2.5–183.0	No limit
	European Union Environmental Protection Agency (EUEPA) [25]	0.3	No limit
	Department of Petroleum Resources (DPR) [15]	No limit	0.0001
	WHO	No limit	0.05
Contaminated water	Present study	5.14–5.78	0.86–1.11
	Inyang et al. [30]	2.5–183.0	No limit
	European Union Environmental Protection Agency (EUEPA) [25]	0.3	No limit
	WHO	No limit	0.05

AH, aliphatic hydrocarbon; PAH, polycyclic aromatic hydrocarbon.

Pyrene), Benzo(a)anthracene/(Benzo(q)anthracene + Chrysene), Indeno(1,2,3-cd)perylene/(Indeno(1,2,3-cd)perylene + Benzo(g,h,i)perylene) and low molecular weight (LMW) hydrocarbon/HMW hydrocarbon have been utilised in deducing the source of pollution [18, 20, 23, 26, 28]. From the source diagnostic indices as presented in Table 4, most PAHs in the study area are from petrogenic sources with a minor contribution from pyrogenic sources.

Normal alkanes and isoprenoids distribution and sources

Although some components of the PAHs and AHs in the study area have been degraded, the majority of the other components still persist in

the environment which may affect groundwater, rivers and soils. This may be injurious to both human and animal health. Some sources of the PAH and AH studied are pyrolytic, i.e. from combustion/bush fire occasioned by explosion of oil tankers, oil installations, leakages from oil pipes and pipelines explosion during oil bunkering or pipeline vandalism. All these have bearing on agriculture, water supply settlement and the biodiversity within the study area.

Cancer risk assessment

PAHs are known to be injurious to health. The eight PAHs typically considered as possible carcinogens are Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene,

Table 3: Occurrence and spatial distribution of PAHs in the soil and water samples

PAHs	Water samples (mg/l)						Soil samples (mg/kg)									
	Cbw_1	Cbw_2	Pw_1	Pw_2	Sw_1	Sw_2	Css_1	Css_2	Css_3	Css_4	Css_5	Css_6	Css_7	Css_8	Css_9	Css_10
Nap	BDL	0.04	0.098	0.043	BDL	0.046	0.814	0.819	0.809	0.758	1.228	1.004	0.913	0.807	0.746	0.788
Mnap	BDL	BDL	0.066	0.176	BDL	0.064	1.814	1.007	1.356	1.106	3.249	1.548	1.264	1.093	1.235	1.350
Acep	BDL	BDL	0.056	0.037	BDL	0.066	3.352	1.148	1.666	0.683	1.459	2.311	1.672	1.340	1.740	1.830
Ace	BDL	0.07	0.081	0.087	BDL	0.073	1.404	1.437	1.420	1.558	3.020	1.536	1.401	1.410	1.376	1.433
Fl	BDL	BDL	0.036	0.173	BDL	0.042	0.768	BDL	0.697	1.216	1.085	0.959	0.706	0.697	0.769	0.771
Phe	BDL	0.06	0.061	0.048	BDL	0.057	0.985	1.041	1.032	1.027	0.174	1.509	0.961	0.803	0.801	0.958
Ant	BDL	0.01	0.010	0.133	0.166	0.017	0.364	0.274	0.375	0.744	0.111	1.632	0.336	0.222	0.233	0.265
Flu	BDL	0.05	0.046	0.040	BDL	0.057	0.924	0.906	1.156	0.841	0.088	0.301	1.027	0.759	0.747	0.927
Pyr	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.146	0.250	BDL	BDL	BDL	BDL
BaA	BDL	BDL	0.133	0.050	BDL	0.015	0.299	BDL	0.313	0.707	0.259	0.134	0.292	0.124	0.104	0.269
Chr	0.02	0.05	0.205	0.137	BDL	0.033	1.217	0.296	0.758	1.265	0.108	0.483	0.620	0.241	0.491	0.082
BbF	0.02	0.01	0.010	0.042	BDL	0.105	1.592	0.728	0.506	2.668	0.085	0.447	0.501	0.108	1.149	0.066
BkF	0.02	0.01	0.018	0.010	BDL	0.018	0.860	0.320	0.199	0.434	0.269	0.169	0.393	0.157	0.242	0.248
BaP	0.02	BDL	BDL	0.025	BDL	0.015	0.252	0.215	0.883	0.228	0.091	0.366	0.167	0.413	0.203	0.283
DahA	BDL	BDL	0.026	0.012	BDL	0.014	0.202	0.211	0.290	0.194	0.065	0.151	0.359	0.516	0.263	0.295
InP	0.01	BDL	BDL	0.038	BDL	0.114	0.912	1.895	0.407	0.665	0.562	0.396	0.598	0.659	0.182	3.374
BghiP	BDL	BDL	BDL	0.060	BDL	0.126	1.119	1.362	2.852	0.673	2.545	2.722	1.899	1.193	1.869	2.870
Total	0.09	0.3	0.856	1.109	0.166	0.863	16.879	11.657	14.720	14.768	14.543	15.917	13.108	10.544	12.151	15.807
Mean	0.005	0.02	0.050	0.065	0.010	0.051	0.993	0.688	0.866	0.869	0.855	0.936	0.771	0.620	0.715	0.930

Ace, Acenaphthene; Acep, Acenaphthylene; Ant, Anthracene; BaA, Benz(a)anthracene; BaP, Benzo(a)pyrene; BbF, Benzo(b)fluoranthene; BDL, Below Detection Limit; BghiP, Benzo(g,h,i) perylene; BkF, Benzo(k)fluoranthene; Chr, Chrysene; DahA, Dibenzo (a,h) anthracene; Fl, Fluorene; Flu, Fluoranthene; InP, Indeno (1,2,3-cd) perylene; Mnap, 2-Methylnaphthalene; Nap, Naphthalene; Phe, Phenanthrene; Pyr, Pyrene.

Benzo(a)pyrene, Dibenzo(a,h)anthracene, Indeno(1,2,3-cd)pyrene and Benzo(g,h,i)perylene. In particular, Benzo(a)pyrene has

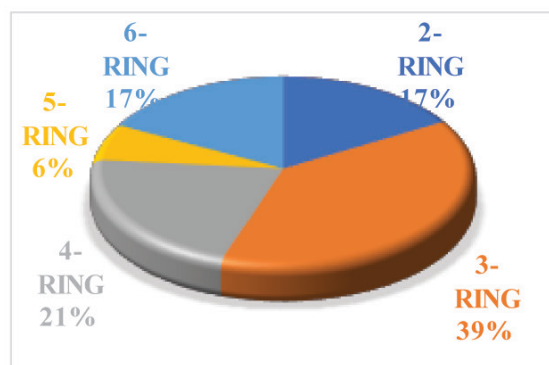


Figure 3: The spatial distribution of the PAH rings in the water and soil samples. PAH, polycyclic aromatic hydrocarbons.

been identified as being highly carcinogenic. The World Health Organization (1993) revealed that Benzo(a)pyrene concentration of 0.7 µg/l corresponds to an excess lifetime cancer risk of 10–5. The BaP-equivalent (BaPE) is used as a way to access carcinogenic risk due to the contamination by PAHs. The BaPE not only includes the risk due to BaP but also calculates all of the carcinogenic PAHs, where each of the PAH is weighed according to its carcinogenicity in relation to the carcinogenicity of BaP, which is measured by 1. This index can be calculated with this equation [17]; $BaPE = BaP + (BaA \cdot 0.06) + (BkF \cdot 0.07) + (BbF \cdot 0.07) + (DahA \cdot 0.06) + (InP \cdot 0.08)$. BaPE ranged from 0 mg/l to 0.042 mg/l and 0.22 mg/kg to 1.16 mg/kg in the water and soil samples, respectively. The highest value of BaPE in the samples is in C_{ss}_3, hence indicating

Table 4: PAH diagnostic ratios of the studied soil and water samples in comparison with that of standard references (after Tobiszewski and Namieśnik [21])

PAH diagnostic ratio	Value range	Source	Reference	Value ranges from studied samples	Inferred source
$\Sigma LMW / \Sigma HMW$	<1 >1	Pyrogenic Petrogenic	Zhang et al. [26]	0–2.45	Petrogenic/pyrogenic
Fl(Fl + Pyr)	<0.5 >0.5	Petroleum Emissions Diesel Emissions	Ravindra et al. [20]	0–0.4	Petroleum emissions
Ant(Phe + Ant)	<0.1 >0.1	Petrogenic Pyrogenic	Pies et al. [18]	0–0.21	Petrogenic/pyrogenic
Flu(Flu + Pyr)	<0.4 0.4–0.5 >0.5	Petrogenic Fossil fuel Combustion Grass, wood, coal combustion	De La Torre-Roche et al. [27]	0–0.4	Petrogenic/mixed source of fossil fuel and combustion
BaA/(BaA + Chr)	0.2–0.35 >0.35 <0.2 >0.35	Coal combustion Vehicular emission Petrogenic Combustion	Akyüz and Çabuk [23] Yunker et al. [28]	0–0.31	Coal combustion/petrogenic
InP/(InP + BghiP)	<0.2 0.2–0.5 >0.5	Petrogenic Petroleum Combustion Grass, Wood, Coal Combustion	Yunker et al. [28]	0–0.23	Petrogenic/petroleum combustion

$\Sigma LMW / \Sigma HMW$, the sum of low molecular weight hydrocarbon/the sum of high molecular weight hydrocarbon.

Table 5: The concentrations of AHs in the soil and water samples

AHs	Water samples (mg/l)						Soil samples (mg/kg)									
	Cbw_1	Cbw_2	Pw_1	Pw_2	Sw_1	Sw_2	Css_1	Css_2	Css_3	Css_4	Css_5	Css_6	Css_7	Css_8	Css_9	Css_10
C8	BDL	BDL	BDL	0.11	BDL	0.51	12.76	1.13	0.59	0.30	2.38	BDL	1.32	1.44	1.77	9.42
C9	BDL	BDL	0.02	0.01	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
C10	BDL	BDL	0.81	0.17	BDL	0.01	BDL	BDL	BDL	BDL	0.94	BDL	BDL	BDL	0.29	0.59
C11	BDL	BDL	0.08	0.04	BDL	0.04	1.63	BDL	BDL	BDL	11.06	BDL	BDL	BDL	BDL	0.53
C12	BDL	BDL	0.18	0.11	BDL	BDL	BDL	BDL	BDL	BDL	6.35	BDL	BDL	0.06	BDL	0.04
C13	BDL	BDL	0.23	0.18	BDL	0.14	2.43	0.36	0.46	BDL	11.24	BDL	BDL	0.18	1.28	3.06
C14	BDL	0.02	0.33	0.23	0.03	0.01	0.53	0.77	0.66	0.42	47.91	0.09	BDL	0.17	0.57	0.56
C15	BDL	BDL	0.31	0.23	BDL	BDL	BDL	BDL	BDL	0.06	48.04	0.88	0.13	0.29	BDL	BDL
C16	BDL	0.04	0.33	0.25	0.02	0.01	0.85	0.19	0.12	0.69	29.37	3.90	0.31	0.39	0.95	0.89
C17	BDL	BDL	0.31	0.25	BDL	BDL	BDL	BDL	BDL	BDL	9.39	6.82	BDL	BDL	BDL	BDL
C18	BDL	0.03	0.28	0.23	0.01	0.04	0.45	0.10	0.73	0.60	17.20	7.94	0.13	BDL	0.93	0.64
C19	BDL	0.01	0.21	0.20	0.02	BDL	BDL	0.27	0.22	0.13	16.14	7.08	BDL	0.19	0.14	BDL
C20	BDL	0.02	0.22	0.28	0.03	0.05	0.39	1.18	0.65	0.78	24.05	7.78	1.24	1.36	1.65	0.74
C21	BDL	BDL	0.20	0.19	BDL	BDL	BDL	BDL	BDL	0.12	15.49	6.19	0.04	BDL	BDL	BDL
C22	BDL	BDL	0.26	0.22	0.02	0.02	1.37	0.57	0.28	BDL	15.23	5.27	1.49	1.71	0.45	0.17
C23	0.01	BDL	0.26	0.17	BDL	BDL	0.13	BDL	BDL	0.24	11.69	4.35	BDL	0.42	BDL	BDL
C24	0.01	0.02	0.36	0.23	0.03	BDL	BDL	BDL	0.60	1.62	19.32	4.16	0.38	0.34	BDL	0.05
C25	0.02	BDL	0.30	0.17	BDL	BDL	0.40	BDL	BDL	0.19	13.90	3.17	BDL	BDL	BDL	BDL
C26	0.02	BDL	0.12	0.16	BDL	0.04	0.73	0.66	1.01	0.74	12.47	2.75	1.40	1.14	1.15	0.96
C27	0.02	BDL	0.14	0.14	BDL	BDL	0.59	BDL	BDL	0.31	10.58	2.44	BDL	0.19	BDL	BDL
C28	0.01	BDL	0.11	0.12	BDL	0.03	0.86	0.30	0.71	0.54	18.87	1.93	0.96	1.18	0.80	0.68
C29	BDL	BDL	0.08	0.10	BDL	BDL	0.24	BDL	BDL	BDL	30.88	1.19	BDL	BDL	BDL	BDL
C30	BDL	BDL	0.08	0.05	BDL	BDL	BDL	BDL	BDL	BDL	29.12	0.29	BDL	BDL	BDL	BDL
C31	BDL	BDL	0.08	0.08	BDL	BDL	1.06	BDL	BDL	BDL	15.14	1.11	0.63	0.32	BDL	BDL

Continued

(Continued)

Table 5: Continued

AHs	Water samples (mg/l)						Soil samples (mg/kg)										
	Cbw_1	Cbw_2	Pw_1	Pw_2	Sw_1	Sw_2	Css_1	Css_2	Css_3	Css_4	Css_5	Css_6	Css_7	Css_8	Css_9	Css_10	
C32	BDL	BDL	BDL	BDL	BDL	0.11	BDL	2.47	4.62	0.72	4.53	BDL	BDL	BDL	0.44	5.40	3.79
C33	BDL	BDL	BDL	0.31	BDL	0.40	5.05	8.38	12.62	2.20	13.12	BDL	3.23	4.24	13.73	10.84	
C34	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	15.04	3.88	3.66	BDL	BDL	BDL	
C35	BDL	BDL	BDL	BDL	0.07	BDL	BDL	BDL	11.16	BDL	6.12	BDL	BDL	BDL	BDL	BDL	
C36	0.13	BDL	BDL	0.75	0.03	0.02	8.12	7.66	BDL	6.97	11.78	BDL	9.81	7.43	12.83	11.78	
C37	BDL	BDL	0.15	BDL	0.26	0.65	BDL	BDL	BDL	BDL	5.90	BDL	9.99	11.26	BDL	BDL	
C38	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	2.27	BDL	BDL	BDL	BDL	BDL	
C39	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	
C40	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	
PRISTANE	BDL	BDL	0.27	0.16	BDL	BDL	BDL	BDL	BDL	5.32	392.91	6.70	BDL	BDL	BDL	BDL	
PHYTANE	BDL	BDL	0.04	0.02	0.08	BDL	BDL	1.67	BDL	0.56	61.00	1.64	2.12	2.10	BDL	BDL	
Pr/nC17	0	0	0.90	0.63	0	0	0	0	0	0	41.84	0.98	0	0	0	0	
Total	0.22	0.13	5.78	5.14	0.61	2.08	37.59	25.69	34.43	22.52	929.44	79.55	36.85	34.86	44.73	41.94	

AH, aliphatic hydrocarbon.

Table 6: The AH diagnostic ratios (after Sojinu et al. [22])

Sample	CPI	OEP
Cbw_1	0.29	1.81
Cbw_2	0.06	0
Pw_1	0.76	0.82
Pw_2	0.71	0.79
Sw_1	2.14	0
Sw_2	1.47	0
Css_1	0.44	0.21
Css_2	0.60	0
Css_3	2.46	0
Css_4	0.24	0.27
Css_5	0.85	0.72
Css_6	0.87	0.94
Css_7	0.68	0.006
Css_8	1.09	0.31
Css_9	0.57	0
Css_10	0.48	0
Mean	0.86	0.37

AH, aliphatic hydrocarbon.

that PAHs at this sample point have high carcinogenic effects.

Conclusion

The prevalence of petrogenic-derived PAHs was confirmed in the studied samples. AHs in both media originated from both petrogenic and biogenic. The AHs are products from both terrestrial and marine inputs. The pollution level of the study area is high as compared with USEPA, DPR and WHO standards which poses health hazards. However, the values are lower compared with other areas in the Niger Delta. The PAH and AH diagnostic ratios have proven to be useful in tracking pollution emission sources and have helped in assessing the level of degradation of oils in impacted soils and water.

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