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Occurrence And Exposure Risk Of Mono-Aromatic Hydrocarbons In Selected Petroleum Product Jetty Impacted Soils From The Niger Delta, Nigeria

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Abstract

This study evaluated the occurrence and human exposure risk of mono-aromatic hydrocarbons (MAHs) such as benzene, toluene, ethylbenzene, and o,p-xylene (BTEX) in soils from petroleum product jetty from the Niger Delta, Nigeria. Samples were collected from the top (0-15 cm), sub (15-30 cm), and bottom (30-45 cm) soil depths. The MAHs components were determined using Headspace gas chromatography-mass spectrometer (HS-GCMS). The individual and ΣMAHs concentrations ranged from not detected (ND) to 1528 µg kg^{-1} and ND to 2512 µg kg^{-1} respectively. The total cancer risks were within the low category**.** The source identification indicated that the origin *MAHs* species are attributed to solvent, paints, and gasoline-diesel spill and particulate emission from gasoline/diesel combustion exhaust in the vicinity of the petroleum product jetty. *T*his depicts the presence of low molecular weight petroleum fractions such as gasoline and kerosene that could exhibit toxicological and carcinogenic effects to organisms in soils within the jetty. *Clean-up actions* should be carried out to prevent the accumulation of MAHs in soil-plant uptake and the potential ecological and human exposure risks of MAHs in the surrounding soil and aquatic ecosystem.

***Keywords*:** MAHs, petroleum product jetty, exposure risk, soil pollution, Niger Delta

Introduction

Benzene, toluene, ethylbenzene, and o, m, p-xylenes (BTEX) are four related volatile mono-aromatic hydrocarbons (MAHs) that are environmentally ubiquitous and classified as priority pollutants and human carcinogen [1-3]. Naturally, MAHs compounds are constituents of natural gas, crude petroleum, coal tar, and gaseous emissions from forest fires and volcanoes. Anthropogenic sources of MAH are spills from petroleum products, emissions from solid and liquid fossil combustion processes, consumer products such as thinners, cigarette smoke, adhesives, inks, cosmetics, and paints [4]. The introduction and accumulation of MAHs onto soil could alter the general soil ecosystem functions; contaminate the nearby surface and groundwater aquifer, the food chain through plant-animal uptake, and direct human exposures [5-7].

The activities of oil exploitation, exploration, and marketing have contributed to the environmental pollution of the Niger Delta. These activities has led to the deposition of environmental pollutants and damaged the quality of the environment, particularly around petroleum and allied installations [8-11]. Oghara is an urban settlement in the Niger Delta Nigeria; it hosts several administrative commercial and petroleum product handling facilities. The tank-farms at Oghara are connected to the jetty by the bank of the Ethiope River where vessels berth to discharge petroleum products. The deposition of petroleum products containing MAHS constituents in the jetty environment could occur due to spillage during product offload, equipment failure, and spilled chemical used for maintenance of the jetty. The spilled petroleum product could contribute to the ΣMAHs load in the soil matrix around the jetty [12]. Thus, characterizing the concentrations origin and exposure risk of MAHs in soil depths from petroleum product jetty is critical to the establishment of operations compliance and MAHs pollution load arising from the activities of petroleum product haulage and its subsidiary at the jetty. Therefore, this study determined the occurrence profile, sources, and human health hazards of MAHs in soils from selected petroleum product haulage jetty.

Materials and methods

Study area description and Sample collection

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The study area is the petroleum product jetty located by the bank of the Ethiope River at Oghara, with a geographical coordinate between longitude 6°06'0.60" E and latitude 5°35'11.99" N in Delta State, Nigeria, Figure 1. Oghara is an urban settlement with an average human population of 150,000. Oghara is host to over 300,000,000 liters petroleum products storage tanks owned by different petroleum marketing subsidiaries [13]. Using stainless steel auger, soil samples were collected at the top sub and bottom soil depths from the vicinity of petroleum product jetty. The collected samples were labelled, stored in aluminium foil, and kept in an ice chest. In the laboratory, the samples were sieved through 2 mm mesh, air-dried in the dark, and stored below 4 °C before analysis.

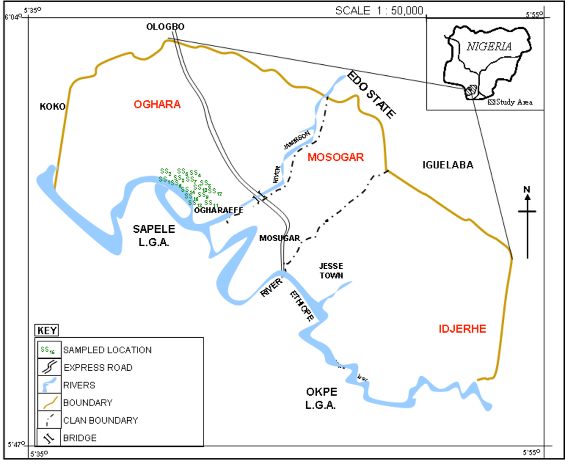

Figure 1: Map of Nigeria showing the study area and sample sites

Determination of soil physicochemical properties and MAHs in soil

The electrical conductivity, pH and total organic carbon (TOC) were determined using conductivity meter, pH meter (Lie-ci PXSJ-216F, lie-ci, purchased from Shanghai, China) in 1:2 soil to water suspension and the Walkley and Black dichromate-based wet oxidation digestion method as described in Emoyan et al. [14]. Using the American Standard Testing Method (EPA) 8260, 2 ml of 99.8% methanol (purchased from Sigma-Aldrich, St. Louis, Missouri, USA) was added into a 20 mL septum sealed vial containing 5 g of the soil sample. The septum sealed vial was placed into the auto caroused of headspace sampler (Dani HSS 82.50, Italy); thereafter, the vial was allowed to move to a heated zone (Headspace Incubator) while maintaining the temperature at 100 °C; a sample of the headspace gas was drawn with an automated gas-tight syringe of the headspace sampler by direct transfer into already calibrated GC-MS. The analysis was allowed to run and data was quantified using equation (1).

$$\text{Concentration}\left(\frac{\text{mg}}{\text{kg}}\right) = \frac{\text{Instrument Reading} \times \text{Volume of Extract} \times \text{Dilution Factor}}{\text{Weight of sample}} \quad (1)$$

Assessment of health-risk from MAHs exposure in soil

The health risk from human exposure to MAHs in the soils was assessed using the carcinogenic risk and non-carcinogenic risk expressed as total cancer risk and hazard index (HI) models.

Total cancer risk from MAHs exposure in soil

The total cancer risk was evaluated as the ratio of chronic daily intake to oral slop of individual MAHs. The carcinogenic risk was evaluated using the United States Environmental Protection Agency model in equations 2-5

$$\text{Total Cancer Risk} = Risk_{ing} + Risk_{inh} + Risk_{derm} \quad (2)$$

Where, Risk_{ing}, Risk_{inh} and $\text{Risk}_{\text{derm}}$ are the risk through ingestion, inhalation and dermal routes respectively.

$$\text{Risk}_{\text{ing}} = \frac{Csoil \times IngR \times EF \times ED \times CF \times SFO}{BW \times AT} \quad (3)$$

$$\text{Risk}_{\text{inh}} = \frac{Csoil \times EF \times ED \times IUR}{PEF \times AT*} \quad (4)$$

$$\text{Risk}_{\text{derm}} = \frac{Csoil \times SA \times AF \times ABS \times EF \times ED \times CF \times SFO \times GIABS}{BW \times AT} \quad (5)$$

Hazard index from MAHs exposure in soil

The HI is the total of the individual hazard quotients (HQs) of the individual exposure route as presented in equations 6-10.

$$\text{Hazard index (HI)} = \sum HQ = HQ_{ing} + HQ_{inh} + HQ_{derm} \quad (6)$$

$$HQ_{ing} = \frac{CDI_{nc}}{RfD}; \quad HQ_{inh} = \frac{CDI_{nc}}{RfCinh};$$

$$HQ_{derm} = \frac{CDI_{nc}}{RfD \times GIABS} \quad (7)$$

$$\text{CDI}_{\text{ing-nc}} = \frac{Csoil \times \text{IngR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}_{nc}} \times 10^{-6} \quad (8)$$

$$CDI_{inh\text{-}nc} = \frac{Csoil \times InhR \times EF \times ET \times ED}{PEF \times 24 \times AT_{nc}} \quad (9)$$

$$CDI_{derm\text{-}nc} = \frac{Csoil \times SA \times AF \times ABS_{d} \times EF \times ED}{BW \times AT_{nc}} \times 10^{-6} \quad (10)$$

The parameters in equation 2-10 are defined in the supplementary material (Table 1 and 2) and Table 1 as described in USEPA, [15, 16]; Iwegbue et al. [17].

Table 1: Variables and definition for estimation of human health risk assessment

Variable	Definition	Variable	Definition
ATca	average time for carcinogen in 19,893 days (54.5yrs × 365 days),	IUR	inhalation unit risk (mg m^{-3}),
ED	exposure duration, 54.5 years was applied based on the assumed average lifespan of Nigerians	SFO	oral slope factor (2.00 mg^{-1} kg^{-1} day^{-1}).
CRing,	incremental lifetime cancer risk through non dietary ingestion	ILCRderm	incremental lifetime cancer risk through dermal contact
ILCRinh.	incremental lifetime cancer risk through inhalation	ABS	dermal absorption factor (0.13 infants and adults),
ATnc	average time (in days) for non carcinogen,	PEF	particle emission factor (1.36 × 10^9 m^3 kg^{-1}),
ET	exposure time (8 hrs day^{-1} for infants and adults),	SA	skin surface area in contact with soil (2800 cm^2 for infants and 5700 cm^2 for adults,
AF	soil-skin adherence factor (0.2 for infants and 0.7 mg cm^{-2} for adults)	BW	average body weight (15 kg for infants and 60 kg for adults).
CF	conversion factor (1 × 10^{-6} kg mg^{-1}),	ED	exposure duration (6 years for infants and 30 years for adults),
IngR	ingestion rate (200 mg day^{-1} for infants and 100 mg day^{-1} for adults),	EF	exposure frequency (350 days $year^{-1}$ for both infants and adults, excluding 15 days holiday period),
CUCL.	UCL 95% concentrations of MAHS in soil samples (µg kg^{-1})	CDIinh-nc,	chronic daily intakes for inhalation, route
CDIing-nc	chronic daily intakes for ingestion route	CDIderm-nc	chronic daily intakes for dermal route

Quality control and data analysis

During sample collection and sample preparations, equipment and containers were cleaned to avoid cross-contamination, and analytical grade reagents were used. The Microsoft Office Excel software was used for all descriptive statistics. A linear regression and ANOVA were used to determine the relationship between TOC and MAHs concentrations.

Results and Discussions

Soil physicochemical properties

The results of the soil physicochemical properties are presented in Table 2. The TOC values ranged from 0.39 to 4.55%, and the highest TOC value was obtained in the topsoil at site SS6 and the lowest value in the bottom soil at site SS1. The EC values ranged from 28.6 to 123 µS/cm. The highest and lowest EC values were observed in the top and bottom soil at sites SS3 and SS11 respectively. The soil pH ranged from 4.20 to 7.60, the highest and lowest pH values were obtained in the top and subsoil depths at SS9 and SS8 respectively. The pH values are of the acidic and neutral range. The soil TOC, EC, and pH content decreased with depth and were comparable to other studies previously reported for some Niger Delta soils [18,19]. Microbial biodegradation of MAHs compounds is limited to bio-available portions [20,21]. Therefore, the observed soil TOC and pH may induce the adsorption of o, *p*-xylene, and ethylbenzene on fine-active soil surfaces and would hinder their mobilization, leaching and onward migration from top to adjacent soil depths, and aquatic environments around the petroleum product jetty [20-22].

MAHs concentrations in soils

The results of MAHs concentrations in this study are presented in Table 2. The concentrations of the MAHs ranged from ND to 2512 µg kg^{-1}, 8.0 to 2483 µg kg^{-1} and ND to 1911 µg kg^{-1} for the top, sub, and bottom soils respectively. The highest concentration was observed in the topsoil at site SS13. MAHs were not detected in the top and bottom soil depths at sites SS1 and SS8 respectively. The MAHs concentrations at sites SS9 to SS15 surpassed those found at sites SS1 to SS8. The ΣMAHs concentrations suggest the presence of petroleum products with low molecular weight petroleum fractions such as gasoline and kerosene [23]. The MAHs concentration pattern in the soil depths is in the order bottom > top > subsoil and did not show any regular trend. The irregular occurrence of MAHs concentrations concerning soil depth is attributed to the soil mechanical and bioturbation behavior, the difference in soil physicochemical properties, the retention capacity of the different soil layer, nature of soil surfaces, leaching characteristics, the strength of the input sources, biological chemical activities within soil depths, and other environmental variables such as hydrolysis dissociation and redox reactions, sorption, volatilization, and weathering [24].

The observed ΣMAHs concentrations were higher than the concentrations reported for soils around automobile mechanic workshop and lubricant production plants [25,26]. The individual and ΣMAHs concentrations were below the MO intervention threshold range of 2,000-100,000 µg kg^{-1} and the DPR-EGASPIN intervention value of 246,000 µg kg^{-1} [27,28]. However, these concentrations are considerable and could have high toxicological and carcinogenic effects on terrestrial and aquatic organisms when leached to nearby soil and aquatic environments [29].

The compositional patterns of MAHs in soil

The compositional patterns of MAHs varied for all sites and depths, Figure 2. Benzene ranged from ND to 36.4% of the total MAHs. The highest concentration of benzene was observed in the subsoil at site SS1. The concentrations of toluene ranged from ND to 53.5% of the total MAHs. The highest concentration of toluene was found at the topsoil of site SS12. Ethylbenzene constituted ND to 62.3% of the total MAHs. The highest concentration of ethylbenzene was found at the topsoil of site SS14. Ortho xylene concentration ranged from ND to 68.7% of the total MAHs concentrations. The highest concentration of o-xylene was found at the topsoil of site SS13. The concentrations of p- ranged from ND to 52.6% of the total MAHs concentrations. The average compositional patterns of MAHs in the soil depths followed the order of ethylbenzene > o-xylene > p-xylene > toluene > benzene. The dominance of ethylbenzene relative to other MAHs compounds suggest that under undisturbed natural environment, MAHs constituents can migrate through the soil in the order benzene > toluene > *m*-, *p*- and *o*-xylenes > ethylbenzene. Again, ethylbenzene is less soluble in water (152 ppm) when compared to other MAHs compounds, [30,31].

Linear regression correlation between TOC and ΣMAH

The linear regression indicates a weak correlation between soil depths (0.0078 to 0.0775) Figures 3abc. The low correlation between TOC and ΣMAHs in the soil depths could be related to non-equilibrium adsorption behaviour between TOC, ΣMAHs, and fresh pollution occurrence. Also, it depicts that the fate of MAHs in the soil depths is not determined by the organic matter contents and the input of multiple sources of MAHs compounds. A number of studies have demonstrated a negative correlation between TOC and organic pollutants similar to MAHs [32].

The one way ANOVA ($P < 0.05$) implies that there is no significant ($P < 0.05$) variation between MAHs levels and soil depths. Therefore, the impact of soil depth variation on the concentration levels of MAHs did not change considerably. This is attributed to soil physicochemical properties, biological and chemical reactions within the soil profiles, MAHs properties, biological and mechanical disturbances within soil depths [33].

Non-carcinogenic and carcinogenic risks of MAHs in soils

There exist an informal sector consisting of family members that operate petty kiosk for food and consumables within the petroleum product jetty premises. Hence the inclusion of infants in the human non-cancer and cancer risk evaluation from MAHs exposure. The values of the cancer risks and non-cancer arising from the exposure of infants and adults to MAHs compounds in soils around the petroleum product jetty in this study are presented in Table 3. The HQ for human exposure from MAHs in soils is in the order of HQING > HQDERM > HQINH. The HQ levels for both infants and adults for the individual exposure routes were < 1, while the HI values for all sites and depths were also < 1, depicting no adverse carcinogenic and non-carcinogenic health effects for human exposures from MAHs in soils from the vicinity of petroleum product jetty. The HI values for the infants' exposure were greater compared to that of the adults' exposure. The carcinogenic sensitivity of MAHs in infants is higher than adults; this is attributed to the exposure duration and smaller body weight of infants [34]. The risk value of soils around the petroleum product jetty through ingestion, inhalation, and dermal contacts ranged from 0.0 to 2.30×10^{-4}, 0.0 to 2.81×10^{-11} and 0.0 to 1.24×10^{-4} for infants and 0.0 to 2.88×10^{-5}, 0.0 to 3.10×10^{-11} and 0.0 to 5.07×10^{-6} for adults respectively. The observed inhalation cancer risks for MAHs were lower than the ingestion and dermal contact exposure routes. However, the total cancer risk ranged from 0.0 to 3.54×10^{-4} with a mean of 8.14×10^{-5} and 0.0 to 3.39×10^{-5} with a mean of 8.11×10^{-6} for infants and adults respectively. The cancer risk for infants through accidental ingestion and dermal contact were higher than that for adults. This raises concern due to possible adverse human health effects for infants' exposure to MAHs around the petroleum product jetty. According to the New York State Department of Health classifications, the obtained total cancer risk values for MAHs fall into the low-risk based factor [35]. These concentrations could promote human health hazards depending on the exposure concentrations and duration of exposed MAHS compounds [29,36].

Table 2: MAHs concentrations (μg kg^{-1}) and physicochemical properties in soil

Site	Depth	TOC (%)	EC (μs/cm)	pH	Benzene	Toluene	Ethyl Benzene	o-xylene	p-xylene	∑MAHS
SS1	0-15	0.51	83.6	6.7	ND	ND	ND	ND	ND	0
	15-30	0.42	52.7	6.3	142	312	104	52	30	640
	30-45	0.39	43.5	5.2	12	52	166	280	114	624
SS 2	0-15	2.5	53.7	6.2	10	8	24	4	16	62
	15-30	1.96	50.2	6.3	ND	2	6	2	4	14
	30-45	1.8	39.6	4.6	26	78	42	360	18	524
SS 3	0-15	2.55	123	5.8	ND	2	2	2	2	8
	15-30	2.19	78.9	4.7	2	10	24	6	6	48
	30-45	1.66	53.1	4.3	2	2	14	12	10	40
SS 4	0-15	1.26	63.3	5.6	ND	4	4	10	4	22
	15-30	1.23	48.4	5.3	18	16	18	2	60	114
	30-45	1.04	47.6	4.9	16	52	2	10	28	108
SS 5	0-15	2.22	42.3	6.4	ND	2	14	20	4	40
	15-30	1.54	38.4	5.6	ND	2	2	2	2	8
	30-45	1.43	40.3	5.7	44	2	122	36	12	216
SS 6	0-15	4.55	39.8	4.7	ND	2	6	8	10	26
	15-30	3.84	39.6	4.4	16	2	6	4	16	44
	30-45	3.23	32.5	4.3	ND	4	10	8	6	28
SS 7	0-15	2.58	76.2	6.3	2	18	352	34	240	646
	15-30	2.24	59.6	6.5	48	12	164	36	12	272
	30-45	1.99	54.6	5.1	4	16	18	12	6	56
SS 8	0-15	1.8	66.7	4.9	22	64	196	266	134	682
	15-30	1.6	43.1	4.2	ND	30	24	30	16	100
	30-45	1.4	42.3	4.3	ND	ND	ND	ND	ND	ND
SS9	0-15	0.87	96.2	7.6	16	350	702	230	108	1406
	15-30	0.59	66.5	6.4	28	219	424	115	157	943
	30-45	0.48	49.8	6.3	31	264	314	272	261	1141
SS10	0-15	2.83	106	6.4	40	88	146	ND	206	480
	15-30	2.64	81.3	5.9	33	308	204	428	365	1338
	30-45	2.47	89.4	5.1	26	227	778	589	292	1911
SS11	0-15	3.56	48.9	5.8	38	156	102	266	6	568
	15-30	3.34	42.3	4.7	19	145	1351	749	219	2483
	30-45	3.09	28.6	4.3	18	206	881	433	141	1678
SS12	0-15	2.92	56.6	6.2	28	460	306	590	724	2108
	15-30	2.69	38.2	5.7	17	266	411	116	63	873
	30-45	2.64	33.3	5.3	26	270	319	206	264	1084
SS13	0-15	3.00	63.5	5.6	16	130	1174	952	240	2512
	15-30	2.53	58.9	5	34	274	226	295	465	1294
	30-45	2.19	50.3	4.5	31	209	432	452	294	1417
SS14	0-15	1.43	57.8	6.8	22	160	1528	546	198	2454
	15-30	1.15	39.7	6.4	27	143	638	609	123	1540
	30-45	0.98	31.2	6.2	22	150	643	543	126	1483
SS15	0-15	4.21	57.6	5.7	18	182	120	2	18	340
	15-30	3.79	44.7	5.3	17	156	647	477	129	1426
	30-45	3.39	46.4	5.1	23	188	536	296	143	1185

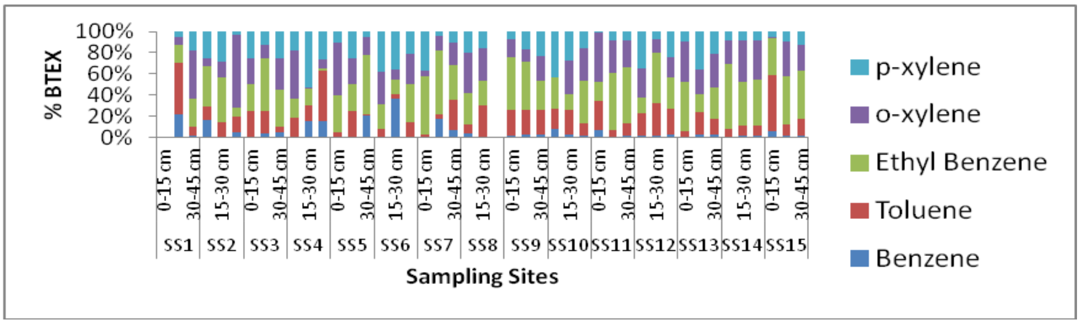

Figure 2: MAHs compositional patterns in soils.

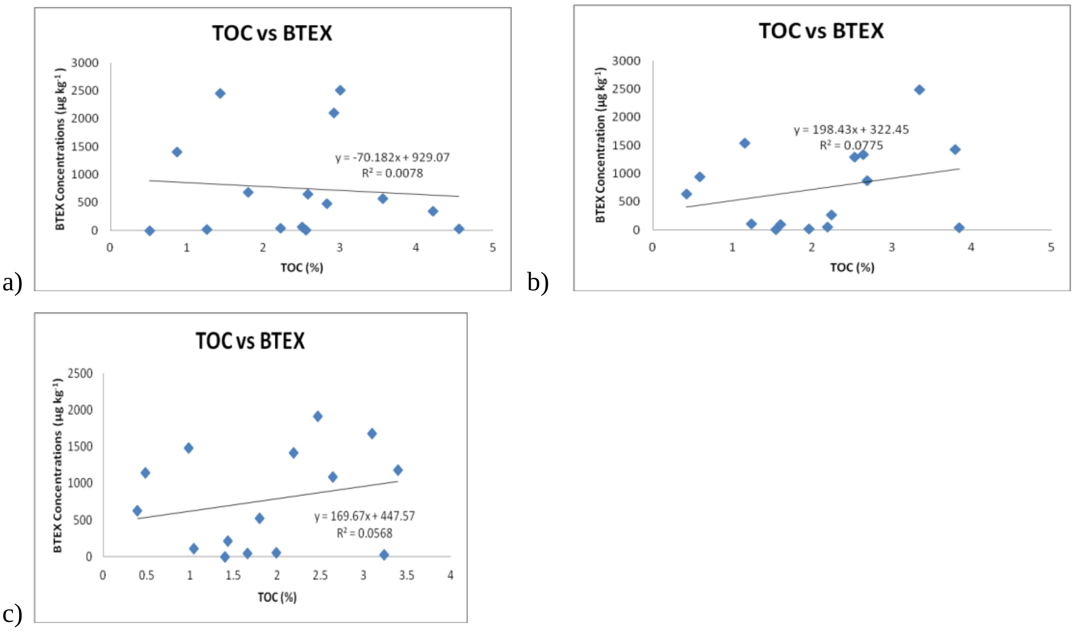

Figure 3a-c: Figure 3: Plot of TOC vs MAHs concentrations in soil for top soil (a) sub soil (b) and bottom soil (c).depth

Source identification

Several studies have established the use of MAHs ratios and multivariate statistics in the identification of MAHs sources in environmental compartments [37-42]. The principal component analysis, Pearson Correlation analysis, and the ratio of xylenes and ethylbenzene (X/E), toluene and benzene (T/B), xylenes and benzene (X/B) and ethylbenzene and benzene (E/B) were evaluated to identify the potential sources of MAHs occurrence in the petroleum jetty, Tables 4-6.

Principal component analysis (PCA)

In this study, five PCA components were extracted, explaining 100% of the variance as presented in Table 4. Component 1 explained 32.896% of the variance with positive high loading values of ethylbenzene and o-xylene. Components 2 and 3 explained 23.903% and 21.573% of the variance with positive high loading of p-xylene and benzene respectively, and components 4 and 5 explained 15.888% and 5.740% of the variance with positive high loading of toluene and o-xylene respectively. The MAHs in Factors 1-5 are components in gasoline and diesel petroleum fractions [23]. Therefore, the PCA revealed that the sources of MAHs in the petroleum product jetty are attributed to gasoline-diesel spills, solvent use, and other stationary sources.

Pearson correlation coefficients (PCC)

Pearson correlation coefficient was applied to identify the relationship between **MAHs** assuming that two or more **MAHs** compounds may correlate due to common physicochemical behavior and/or source [6]. The matrix showed the existence of a moderate correlation between benzene-toluene, ethylbenzene-toluene-toluene-o-xylene, and ethylbenzene-p-xylene, a good correlation between ethylbenzene-o-xylene, toluene-p-xylene and o-xylene-p-xylene, Table 5. The correlation between MAHs indicated similarity in their photochemical reactivity and physicochemical properties [43]. The correlation between the MAHs suggests a common origin attributed to gasoline-diesel evaporative spills, solvent and paint use, and particulate emission from gasoline/diesel combustion exhaust in the petroleum product jetty [37, 44].

Table 3: Hazard index (HI) and total cancer risk of MAHs in soils

		HAZARD INDEX								TOTAL CANCER RISK							
		CHILD				ADULT				CHILD				ADULT			
SITES		HQING	HQINH	HQDERM	HI	HQING	HQINH	HQDERM	HI	RISKING	RISKINH	RISKDERM	Total Cancer Risk	RISKING	RISKINH	RISKDERM	Total Cancer Risk
SS1	0-15	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	15-30	5.22E-01	2.69E-06	1.28E-01	6.50E-01	6.53E-02	1.34E-06	2.27E-02	8.80E-02	1.14E-04	9.64E-12	3.06E-05	1.45E-04	1.43E-05	1.06E-11	2.52E-06	1.68E-05
	30-45	9.31E-02	2.12E-06	3.17E-02	1.25E-01	1.16E-02	1.06E-06	5.65E-03	1.73E-02	3.18E-05	3.59E-12	1.50E-05	4.67E-05	3.97E-06	3.96E-12	6.99E-07	4.67E-06
SS2	0-15	3.76E-02	2.63E-07	9.74E-03	4.73E-02	4.70E-03	1.31E-07	1.73E-03	6.43E-03	1.04E-05	9.73E-13	3.47E-06	1.39E-05	1.30E-06	1.07E-12	2.29E-07	1.53E-06
	15-30	1.47E-03	3.12E-08	6.66E-04	2.14E-03	1.84E-04	1.56E-08	1.19E-04	3.02E-04	8.44E-07	1.06E-13	4.73E-07	1.32E-06	1.05E-07	1.17E-13	1.86E-08	1.24E-07
	30-45	1.25E-01	2.21E-06	3.39E-02	1.59E-01	1.56E-02	1.11E-06	6.04E-03	2.17E-02	2.42E-05	2.17E-12	7.40E-06	3.16E-05	3.02E-06	2.39E-12	5.32E-07	3.56E-06
SS3	0-15	8.31E-04	1.99E-08	3.37E-04	1.17E-03	1.04E-04	9.97E-09	5.99E-05	1.64E-04	2.81E-07	3.53E-14	1.58E-07	4.39E-07	3.52E-08	3.89E-14	6.19E-09	4.13E-08
	15-30	1.18E-02	1.00E-07	3.95E-03	1.58E-02	1.48E-03	5.00E-08	7.03E-04	2.18E-03	4.78E-06	5.33E-13	2.21E-06	6.99E-06	5.98E-07	5.88E-13	1.05E-07	7.03E-07
	30-45	9.91E-03	1.42E-07	3.01E-03	1.29E-02	1.24E-03	7.08E-08	5.37E-04	1.78E-03	3.38E-06	3.57E-13	1.42E-06	4.79E-06	4.22E-07	3.93E-13	7.43E-08	4.96E-07
SS4	0-15	2.05E-03	6.81E-08	8.02E-04	2.85E-03	2.56E-04	3.40E-08	1.43E-04	3.99E-04	5.63E-07	7.05E-14	3.15E-07	8.78E-07	7.03E-08	7.78E-14	1.24E-08	8.27E-08
	15-30	6.64E-02	5.83E-07	1.64E-02	8.27E-02	8.29E-03	2.92E-07	2.92E-03	1.12E-02	1.52E-05	1.31E-12	4.25E-06	1.94E-05	1.90E-06	1.44E-12	3.34E-07	2.23E-06
	30-45	6.21E-02	4.35E-07	1.52E-02	7.73E-02	7.77E-03	2.18E-07	2.71E-03	1.05E-02	1.15E-05	9.15E-13	2.68E-06	1.42E-05	1.44E-06	1.01E-12	2.54E-07	1.70E-06
SS5	0-15	3.64E-03	1.20E-07	1.63E-03	5.27E-03	4.55E-04	5.98E-08	2.90E-04	7.45E-04	1.97E-06	2.47E-13	1.10E-06	3.07E-06	2.46E-07	2.72E-13	4.33E-08	2.89E-07
	15-30	8.31E-04	1.99E-08	3.37E-04	1.17E-03	1.04E-04	9.97E-09	5.99E-05	1.64E-04	2.81E-07	3.53E-14	1.58E-07	4.39E-07	3.52E-08	3.89E-14	6.19E-09	4.13E-08
	30-45	1.60E-01	9.73E-07	4.14E-02	2.01E-01	2.00E-02	4.86E-07	7.37E-03	2.73E-02	4.81E-05	4.57E-12	1.65E-05	6.46E-05	6.01E-06	5.04E-12	1.06E-06	7.07E-06
SS6	0-15	2.24E-03	8.76E-08	9.24E-04	3.16E-03	2.80E-04	4.38E-08	1.65E-04	4.44E-04	8.44E-07	1.06E-13	4.73E-07	1.32E-06	1.05E-07	1.17E-13	1.86E-08	1.24E-07
	15-30	5.35E-02	3.48E-07	1.24E-02	6.59E-02	6.69E-03	1.74E-07	2.21E-03	8.90E-03	1.21E-05	9.86E-13	2.99E-06	1.51E-05	1.51E-06	1.09E-12	2.66E-07	1.78E-06
	30-45	2.81E-03	7.09E-08	1.23E-03	4.04E-03	3.52E-04	3.54E-08	2.19E-04	5.71E-04	1.41E-06	1.76E-13	7.88E-07	2.19E-06	1.76E-07	1.94E-13	3.09E-08	2.07E-07
SS7	0-15	7.18E-02	1.49E-06	3.35E-02	1.05E-01	8.97E-03	7.43E-07	5.96E-03	1.49E-02	5.09E-05	6.31E-12	2.80E-05	7.89E-05	6.36E-06	6.96E-12	1.12E-06	7.48E-06
	15-30	1.79E-01	1.06E-06	4.78E-02	2.27E-01	2.24E-02	5.28E-07	8.51E-03	3.09E-02	5.68E-05	5.53E-12	2.05E-05	7.73E-05	7.10E-06	6.10E-12	1.25E-06	8.35E-06
	30-45	1.88E-02	1.57E-07	5.40E-03	2.42E-02	2.35E-03	7.86E-08	9.62E-04	3.31E-03	5.34E-06	5.37E-13	2.05E-06	7.39E-06	6.68E-07	5.93E-13	1.18E-07	7.86E-07
SS8	0-15	1.31E-01	2.32E-06	4.18E-02	1.73E-01	1.64E-02	1.16E-06	7.45E-03	2.38E-02	4.30E-05	4.66E-12	1.89E-05	6.19E-05	5.38E-06	5.14E-12	9.47E-07	6.33E-06
	15-30	1.08E-02	2.30E-07	4.32E-03	1.51E-02	1.35E-03	1.15E-07	7.69E-04	2.12E-03	3.38E-06	4.23E-13	1.89E-06	5.27E-06	4.22E-07	4.67E-13	7.43E-08	4.96E-07
	30-45	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SS9	0-15	2.18E-01	2.20E-06	8.78E-02	3.06E-01	2.73E-02	1.10E-06	1.56E-02	4.29E-02	1.10E-04	1.33E-11	5.78E-05	1.68E-04	1.37E-05	1.46E-11	2.42E-06	1.62E-05
	15-30	1.96E-01	1.94E-06	6.80E-02	2.64E-01	2.45E-02	9.69E-07	1.21E-02	3.66E-02	7.93E-05	9.01E-12	3.78E-05	1.17E-04	9.92E-06	9.94E-12	1.75E-06	1.17E-05
	30-45	2.14E-01	3.15E-06	6.99E-02	2.84E-01	2.67E-02	1.58E-06	1.25E-02	3.92E-02	6.56E-05	7.21E-12	2.95E-05	9.51E-05	8.20E-06	7.95E-12	1.44E-06	9.64E-06
SS10	0-15	1.74E-01	1.67E-06	4.82E-02	2.22E-01	2.17E-02	8.36E-07	8.59E-03	3.03E-02	4.87E-05	4.77E-12	1.78E-05	6.65E-05	6.08E-06	5.26E-12	1.07E-06	7.15E-06
	15-30	2.31E-01	4.37E-06	7.18E-02	3.03E-01	2.89E-02	2.18E-06	1.28E-02	4.17E-02	5.19E-05	5.41E-12	2.13E-05	7.32E-05	6.49E-06	5.97E-12	1.14E-06	7.63E-06
	30-45	2.75E-01	4.93E-06	1.05E-01	3.80E-01	3.44E-02	2.47E-06	1.88E-02	5.31E-02	1.28E-04	1.51E-11	6.53E-05	1.93E-04	1.60E-05	1.67E-11	2.81E-06	1.88E-05
SS11	0-15	1.77E-01	1.94E-06	4.87E-02	2.26E-01	2.21E-02	9.68E-07	8.68E-03	3.08E-02	4.11E-05	3.89E-12	1.40E-05	5.51E-05	5.13E-06	4.29E-12	9.04E-07	6.04E-06
	15-30	3.19E-01	5.50E-06	1.39E-01	4.57E-01	3.98E-02	2.75E-06	2.47E-02	6.46E-02	2.03E-04	2.49E-11	1.09E-04	3.13E-04	2.54E-05	2.74E-11	4.47E-06	2.99E-05
	30-45	2.40E-01	3.41E-06	9.93E-02	3.39E-01	3.00E-02	1.71E-06	1.77E-02	4.77E-02	1.37E-04	1.65E-11	7.22E-05	2.09E-04	1.71E-05	1.82E-11	3.00E-06	2.01E-05
SS12	0-15	2.86E-01	6.80E-06	9.49E-02	3.81E-01	3.58E-02	3.40E-06	1.69E-02	5.27E-02	6.27E-05	6.93E-12	2.85E-05	9.12E-05	7.84E-06	7.65E-12	1.38E-06	9.22E-06
	15-30	1.61E-01	1.33E-06	5.97E-02	2.21E-01	2.01E-02	6.63E-07	1.06E-02	3.07E-02	6.98E-05	8.18E-12	3.50E-05	1.05E-04	8.72E-06	9.02E-12	1.53E-06	1.03E-05
	30-45	1.95E-01	2.78E-06	6.56E-02	2.61E-01	2.44E-02	1.39E-06	1.17E-02	3.61E-02	6.27E-05	7.02E-12	2.91E-05	9.18E-05	7.84E-06	7.74E-12	1.38E-06	9.22E-06
TF13	0-15	2.98E-01	6.42E-06	1.28E-01	4.26E-01	3.73E-02	3.21E-06	2.28E-02	6.01E-02	1.76E-04	2.16E-11	9.50E-05	2.71E-04	2.20E-05	2.38E-11	3.88E-06	2.59E-05
	15-30	2.30E-01	4.24E-06	7.16E-02	3.02E-01	2.87E-02	2.12E-06	1.27E-02	4.15E-02	5.57E-05	5.85E-12	2.32E-05	7.88E-05	6.96E-06	6.46E-12	1.23E-06	8.19E-06
	30-45	2.34E-01	4.21E-06	8.00E-02	3.14E-01	2.92E-02	2.10E-06	1.42E-02	4.35E-02	8.22E-05	9.29E-12	3.88E-05	1.21E-04	1.03E-05	1.02E-11	1.81E-06	1.21E-05
SS14	0-15	3.39E-01	4.58E-06	1.50E-01	4.89E-01	4.24E-02	2.29E-06	2.67E-02	6.90E-02	2.30E-04	2.81E-11	1.24E-04	3.54E-04	2.88E-05	3.10E-11	5.07E-06	3.39E-05
	15-30	2.38E-01	4.18E-06	8.84E-02	3.26E-01	2.97E-02	2.09E-06	1.57E-02	4.54E-02	1.09E-04	1.27E-11	5.45E-05	1.63E-04	1.36E-05	1.40E-11	2.39E-06	1.60E-05
	30-45	2.19E-01	3.81E-06	8.42E-02	3.03E-01	2.74E-02	1.90E-06	1.50E-02	4.24E-02	1.06E-04	1.25E-11	5.41E-05	1.60E-04	1.32E-05	1.38E-11	2.33E-06	1.56E-05
SS15	0-15	1.03E-01	4.50E-07	3.17E-02	1.35E-01	1.29E-02	2.25E-07	5.64E-03	1.85E-02	2.95E-05	3.11E-12	1.23E-05	4.18E-05	3.69E-06	3.42E-12	6.50E-07	4.34E-06
	15-30	2.01E-01	3.43E-06	7.99E-02	2.81E-01	2.51E-02	1.72E-06	1.42E-02	3.93E-02	1.03E-04	1.23E-11	5.36E-05	1.57E-04	1.29E-05	1.36E-11	2.27E-06	1.51E-05
	30-45	1.98E-01	2.69E-06	7.39E-02	2.72E-01	2.48E-02	1.34E-06	1.32E-02	3.80E-02	9.11E-05	1.07E-11	4.57E-05	1.37E-04	1.14E-05	1.18E-11	2.01E-06	1.34E-05
	MIN	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	MAX	5.22E-01	6.80E-06	1.50E-01	6.50E-01	6.53E-02	3.40E-06	2.67E-02	8.80E-02	2.30E-04	2.81E-11	1.24E-04	3.54E-04	2.88E-05	3.10E-11	5.07E-06	3.39E-05
	MEAN	1.40E-01	1.99E-06	4.84E-02	1.89E-01	1.75E-02	9.95E-07	8.63E-03	2.62E-02	5.52E-05	6.26E-12	2.62E-05	8.14E-05	6.90E-06	6.91E-12	1.21E-06	8.11E-06

Table 4: PCA of MAHs **in soils around jetties**

	Component				
	1	**2**	**3**	**4**	**5**
Benzene	.034	.069	**.981**	.179	.022
Toluene	.252	.445	.326	**.791**	.076
Ethyl Benzene	**.976**	.150	.034	.154	-.002
o-xylene	**.755**	.357	.065	.168	**.520**
p-xylene	.240	**.918**	.073	.291	.101
% Variance	**32.896**	**23.903**	**21.573**	**15.888**	**5.740**
Cumm %	**32.896**	**56.799**	**78.372**	**94.260**	**100.000**

Table 5: Pearson's correlation coefficient of MAHs in soils around jetties

	Benzene	**Toluene**	**Ethyl Benzene**	**o-xylene**	**p-xylene**
Benzene	1.00	0.50**	0.10	0.16	0.20
Toluene		1.00	0.45*	0.54**	0.73*
Ethyl benzene			1.00	0.82*	0.42**
o-xylene				1.00	0.61**
p-xylene					1.00

*Pearson's correlation significant at 0.01 level of significance

**Pearson's correlation significant at 0.05 level of significance

MAHS ratio

Toluene/Benzene

Benzene and toluene are volatile MAHs with an atmospheric half-life of 226 and 46 hours respectively [45]. The T/B ratio greater and less than 1 indicates the presence of MAHs from stationary sources and emission from petroleum-combustion exhaust respectively. The T/B ratio ranged from 0.13 to 21.9 with an average ratio of 5.12. The lowest and highest T/B ratios were observed at SS6 and SS9 respectively, in Table 6. The T/B ratio indicated that 36% of the samples had ratios less than 1; depicting typical values of combustion emissions and other stationary sources. The T/B ratios suggest that the MAHs were derived from a mixture of stationary sources such as gasoline-diesel spills and particulates deposits from gasoline/diesel combustion exhausts [37,38].

Xylene/Ethylbenzene

The atmospheric lifetime of xylene and ethylbenzene are 14-31 and 41 hours respectively. The principal environmental sources of ethylbenzene and xylene are particulate emission from fuel service stations, gasoline/diesel combustions exhaust, and solvent use respectively [37, 47]. Several studies have shown that the X/E ratio range from 2.4 to 5.3 with a mean value of 3.5 is characterized as emission from gasoline/diesel combustion exhaust sources [48-51]. In this study, the X/E ratio ranged from 0.29 to 19 with an average ratio of 2.05. The lowest and highest X/E ratios were observed at SS7 and SS4 respectively, in Table 6. The observed X/E ratio in this study indicated that 91% of the sites had a ratio of less than 3.5, depicting that the sources of MAHs in the petroleum product jetty are from stationary sources [52-53].

Ethyl Benzene/benzene

The E/B ratio ranged from 0.13 to 176 with a mean ratio of 17.7. The lowest and highest E/B ratios were observed at SS4 and SS7 respectively, in Table 6. The E/B ratio observed in this study shows that 97% of the sites had ratios greater than 1, suggesting that benzene concentration is lower than the more reactive and unstable ethylbenzene congener. The E/B ratios indicate that the origins of MAHs in this study are from stationary sources such as paint and solvents and gasoline-diesel spills ([53-54].

Xylenes/Benzene

The X/B ratio ranged from 0.58 to 137 with an average ratio of 17.3. The lowest and highest X/B ratios were observed at SS1 and SS7 respectively, in Table 6. The X/B ratio observed in this study shows that 99% of the sites had ratios greater than 1, depicting significant amount of MAHs are from stationary sources such as gasoline-diesel spills and particulate deposits from gasoline/diesel combustion exhaust ([52-53, 55].

Table 6: Ratios of MAHs soils

	SS1			**SS2**			**SS3**			**SS4**			**SS5**		
	0-15 cm	**15-30 cm**	**30-45 cm**	**0-15 cm**	**15-30 cm**	**30-45 cm**	**0-15 cm**	**15-30 cm**	**30-45 cm**	**0-15 cm**	**15-30 cm**	**30-45 cm**	**0-15 cm**	**15-30 cm**	**30-45 cm**
T/B	0.00	2.20	4.33	0.80	0.00	3.00	0.00	5.00	1.00	0.00	0.89	3.25	0.00	0.00	0.05
X/E	0.00	0.79	2.37	0.83	1.00	9.00	2.00	0.50	1.57	3.50	3.44	19.0	1.71	2.00	0.39
E/B	0.00	0.73	13.8	2.40	0.00	1.62	0.00	12.0	7.00	0.00	1.00	0.13	0.00	0.00	2.77
X/B	0.00	0.58	32.8	2.00	0.00	14.5	0.00	6.00	11.0	0.00	3.44	2.38	0.00	0.00	1.09

	SS6			**SS 7**			**SS 8**			**SS9**			**SS10**		
	0-15 cm	**15-30 cm**	**30-45 cm**	**0-15 cm**	**15-30 cm**	**30-45 cm**	**0-15 cm**	**15-30 cm**	**30-45 cm**	**0-15 cm**	**15-30 cm**	**30-45 cm**	**0-15 cm**	**15-30 cm**	**30-45 cm**
T/B	0.00	0.13	0.00	9.00	0.25	4.00	2.91	0.00	0.00	21.9	7.82	8.52	2.2	9.33	8.73
X/E	3.00	3.33	1.40	0.78	0.29	1.00	2.04	1.92	0.00	0.48	0.64	1.70	1.41	3.89	1.13
E/B	0.00	0.38	0.00	176	3.42	4.50	8.91	0.00	0.00	43.9	15.1	10.1	3.65	6.18	29.9
X/B	0.00	1.25	0.00	137	1.00	4.50	18.2	0.00	0.00	21.1	9.71	17.2	5.15	24	33.9

	SS11			**SS12**			**SS13**			**SS14**			**SS15**		
	0-15 cm	**15-30 cm**	**30-45 cm**	**0-15 cm**	**15-30 cm**	**30-45 cm**	**0-15 cm**	**15-30 cm**	**30-45 cm**	**0-15 cm**	**15-30 cm**	**30-45 cm**	**0-15 cm**	**15-30 cm**	**30-45 cm**
T/B	4.11	7.63	11.4	16.4	15.6	10.4	8.13	8.06	6.74	7.27	5.30	6.82	10.1	9.18	8.17
X/E	2.67	0.72	0.65	4.29	0.44	1.47	1.02	3.36	1.73	0.49	1.15	1.04	0.17	0.94	0.82
E/B	2.68	71.1	48.9	10.9	24.2	12.3	73.4	6.65	13.9	69.5	23.6	29.2	6.67	38.1	23.3
X/B	7.16	50.9	31.9	46.9	10.5	18.1	74.5	22.4	24.1	33.8	27.1	30.4	1.11	35.6	19.1

Conclusions and recommendations

The occurrence of MAHs in this study showed significant and spatial distribution in all sites and depths. The ANOVA and linear regression showed that there is no significant variation in MAHs levels between soil depths, and no significant positive correlation between TOC and ΣMAHs concentrations respectively. **The source identification indicated that** MAHs **species are from a common source attributed to solvent, paints, and gasoline/diesel spills and particulate emission from gasoline-diesel combustion exhaust in the** vicinity of the petroleum product jetty. The individual and ΣMAHs concentrations were below the DPR-EGASPIN intervention values. However, continual deposition of MAHs and persistent human occupational exposures to the ΣMAHs in soils from the jetty could increase the risk of cancer and noncancerous associated ailments in terrestrial and aquatic organisms within the sites. The HI values from infant exposure were higher than that of the adult's exposure values. The soils from the petroleum product jetty should be subjected to appropriate clean-up actions to reduce the potential ecological and human exposure risks of observed ΣMAHs in the environment. Further study should be carried out to investigate the variation in the occurrence of total petroleum hydrocarbons and heavy metals across petroleum product jetties in Nigeria.

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