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Assessment of Aliphatic Hydrocarbons in Soils from Selected Areas in Agbarho Communities, Delta State, Nigeria

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Abstract: *The occurrence of petroleum hydrocarbons in the environment has been remarkably discouraging in recent times due to the impeding toxicity of most hydrocarbons. In this study, the presence of aliphatic hydrocarbons was assessed in primary sources and in anthropogenic impacted soils within the Agbarho communities in Delta State, Nigeria. The petroleum hydrocarbons were quantified using gas chromatography equipped with flame ionization detector (GC-FID) after extraction and clean-up of the extracts with n-hexane/dichloromethane (1:1 v/v). The evaluated concentrations of the total aliphatic hydrocarbons in the primary sources ranged from 1,788,030 to 5,368,702 µg kg^{-1} while the concentrations of the total hydrocarbon were within the range, 813 to 11900 µg kg^{-1}. Source activities variation in the concentrations of the total aliphatic hydrocarbon in anthropogenic impacted soils was observed to followed the following trend, Mechanic Workshop Soil > Barbecue spot soil > Filling Station Soil > Motor Way Soil > Traffic point soil. On the average, the concentrations of the higher molecular weight n-alkanes (> C31 in the studied soils) were the highest. Evaluated molecular indices of the investigated aliphatic hydrocarbons showed that the aliphatic hydrocarbons in these soils might have originated from different anthropogenic sources such as petrogenic and terrestrial biogenic sources.*

***Keywords**: aliphatic hydrocarbons, molecular weight, molecular indices, Agbarho community*

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1.0 Introduction

The pollution of the environment by hydrocarbons has attracted significant worldwide environmental concern especially, concerning the increasing rate of hydrocarbon addition from diesel and petrol-powered equipment and vehicles, and spills of lubricants, oils and chemicals Also, their toxicity profile has been widely acknowledged because they are particularly mutagenic and carcinogenic (Gonul, and Kucuksezgin, 2012). Also, aliphatic (n-alkanes) hydrocarbons may find their way into the environments via: petrogenic, biogenic and pyrogenic/ pyrolitic processes (Volkman *et al.,* 1992). Regarding the presence of n-alkanes in the environment, anthropogenic and biogenic (algae, bacteria, etc) factors constitute the major sources (Ivwurie, 2004). The n-alkanes levels can be used to identify the sources of hydrocarbon pollution and to distinguish between biogenic and petrogenic sources of hydrocarbons (Ilechukwu *et al.,* 2016). Studies conducted by Udoinyang *et al*. (2020) indicated the presence of ethylbenzene and xylene (2.50 mg/kg), toluene (4.0 mg/kg), and other aromatics. The assessment result left a remark that shows that future contamination may be dangerous. Soil contamination by hydrocarbon can severely affect its quality by limiting the population and activity of important microorganisms (Adipah, 2019). They can be taken up by plants and consequently be transported to higher organisms via the food chain (Gennadiev *et al*., 2015). Among all the studies reported for various locations within Nigeria, literature is few on the levels of aliphatic hydrocarbons in soils within Ughelli North local government area of Delta state, yet anthropogenic activities have been confirmed to be major contributors in some areas, that are relatively close to the Agbarho communities. Therefore, the present study is aimed at analyzing soils to obtain information of the hydrocarbon contamination level in some selected areas of Agbarho communities and resultant health effect.

2.0 Materials and Methods

2.1 *Description of study area*

The Studied area is located at Agbarho community within the coordinates of latitude 05^{0} 31^{1}N and 05^{0} 37^{1}N and longitude 05^{0} 48^{1}E and 05^{0} 54^{1}E and is about 12 km from Warri city. It is situated in the south-south geographical zone of Nigeria with an elevation of about 111 m above sea level. It is made up of several agricultural/rural communities which include Oguname, Ohrerhe, Orhokpokpor, Uwiama, and Orho-Agbarho as the administrative headquarter, with a typical Sombreiro-Warri Deltaic Plain terrain which is lowland, generally flat and slopes gently southward towards the ocean. The coordinates of the sample location are MeWS-Mechanic workshop soil (5°35"N, 5°51"E), MoWs-Motorway soil (5°34"N, 5°52"E), TPS- Traffic Point soil (5°35'N, 5°51"E), BSS- Barbecue Spot soil-(5°34"N, 5°51"E), FSS- Filling Station soil (5°36"N, 5°52"E), FFCS- Farm field Control soil (5°35"N, 5°50"E) respectively.

Fig.1 Map showing selected sample sites in Agbarho community

.2.2 *Sample collection and preparation*

Five (5) soil samples were collected at 0-10 cm depth from areas suspected to be polluted by hydrocarbons in Agbarho communities. One (1) control sample was also obtained from a farmland with no proximity to hydrocarbon release. Samples were kept in aluminum foils and taken to the laboratory, where impurities were removed. Samples were then air-dried at room temperature, ground with mortar and pestle, then sieved using a 2 mm mesh and stored in clean amber coloured glass bottles that were previously washed before analyses.

All chemical analyses were carried out using the EPA (3550B methods (US EPA, 1996)

The sampling locations were spread within the following stations,

a) Vehicle Mechanic Workshop
b) Agbarho-Patani Motorway soil (Agbarho-patani expressway)
c) Traffic point soil (Agbarho five-junction)
d) Barbecue Spot (Agbarho princess junction)
e) Filling Station soil (Agbarho Vic&CC filling station Ekwerre Road)

2.3 Extraction of sample

The extraction of n-alkanes was carried out using ultrasonic extraction (EPA Method 3550B) (US EPA, 1996). 10 g of soil sample was weighed into a clean 100 ml glass beaker and homogenized with 10 g of anhydrous sodium sulphate until a completely dry homogenate was obtained. 20 ml of dichloromethane was added to the dry homogenate soil sample inside a 100 ml beaker. This was then shaken for 30 minutes in a mechanical shaker, after which the beaker was removed from the mechanical shaker and then placed in a sonicator and sonicated for 30 minutes at 70 °C. After sonication, 5 grams of anhydrous sodium sulphate was added to the samples again to eliminate any leftover water molecules. This was allowed to stand for 15 minutes. The extract was transferred to a rotary evaporator and concentrated to 2ml ready for the clean-up process (US EPA, 1996).

2.4 Clean-up procedure for aliphatic hydrocarbons and quantification

The column was eluted with 10 ml of hexane, the eluate was transferred into a round bottom flask and concentrated to 1ml using a rotary evaporator. The concentrate was transferred to a 2 ml Teflon screw-cap vial and labeled ready for GC-FID aliphatic analysis, (the rotary evaporator round bottom flask was rinsed with acetone before analysis).

The separation and detection of n-alkanes in the cleaned concentrated extract were carried out using Agilent 6890N Gas Chromatograph - Flame Ionization Detector (GC-FID) instrument. 1 µl of concentrated sample eluted from column was injected into GC vial pulsed splitless mode. Hydrogen gas with a flow rate velocity of 8°C/min was used as the carrier gas. The initial temperature of the column was programmed at 50°C for 5min, thenceforth, inclined to 300°C at 5-10min held on time. The infusion port and detector temperature were at 280 -300 °C respectively. The n-alkanes TPH was resolved at a particular chromatogram in ppm (US EPA 1996).

2.5 Quality control/assurance

Quality control and assurance were assessed by sequence analysis for all parameters accompanied with Gas Chromatography measures (such as blanks, duplicates and standards) for validation of analytical procedures used and to ascertain level of interference.

2.6 Data analysis

The statistical package for the social science (SPSS) was used for all statistical data examination. Descriptive statistics was used to establish the existence of significant variations in the aliphatic concentrations.

3.0 Results and discussions

3.1 Concentration and distribution of n-alkanes in secondary sources

Measured concentrations of the total AHCs in the studied soils ranged from 813 µg kg^{-1} (at traffic points) to 11900 µg kg^{-1} (at a mechanic workshop). Recorded concentrations of total PAHs in the studied soils were higher than the total AHCs concentration (498 µg kg^{-1}) obtained in the control sample. Results obtained from the analysis of variance (ANOVA) showed that there was no significant variation in the concentrations of the total AHCs in these soils (p-value > 0.05; Fcal < Fcrit) as shown in Table 1. The insignificant spatial variation in the concentrations of the studied soils may be linked to the similarity in source inputs. The United Nations Environment Programme recommended limit for AHCs in soil is 10,000 μg kg^{-1} (UNEP, 1995). Total AHCs concentrations in the studied soils were below the recommended limit except for soils from the mechanic workshop which exceeded the UNEP guideline. The total AHCs concentrations in these soils were also lower than those reported by Emoyan *et al.* (2020) for soils in the vicinity of petroleum tank farms in the Niger Delta.

Table 1: AHCs (μg kg^{-1}) concentrations in soil samples

	MeWS	**MoWS**	**TPS**	**BSS**	**FSS**	**CTR**
C8	ND	ND	ND	ND	ND	ND
C9	ND	ND	ND	ND	ND	ND
C10	ND	ND	240	ND	ND	ND
C11	ND	53.2	ND	80.9	ND	ND
C12	ND	ND	ND	ND	ND	ND
C13	51.7	ND	ND	247	ND	88.2
C14	ND	ND	ND	ND	ND	ND
C15	62.8	ND	ND	289	ND	98.7
C16	ND	ND	ND	ND	ND	ND
C17	ND	ND	ND	ND	ND	ND
Pr	ND	ND	ND	ND	ND	ND
C18	ND	ND	ND	ND	ND	ND
Ph	ND	57.7	ND	95.6	52.8	ND
C19	ND	ND	ND	148	ND	70.7
C20	ND	ND	ND	63.8	ND	ND
C21	ND	ND	ND	ND	ND	ND
C22	ND	ND	ND	ND	ND	ND
C23	ND	ND	ND	ND	ND	ND
C24	ND	ND	ND	ND	ND	ND
C25	ND	ND	ND	ND	ND	ND
C26	162	45.7	57.4	142	86.5	88.8
C27	ND	ND	ND	ND	ND	ND
C28	ND	ND	ND	ND	ND	ND
C29	60.2	ND	ND	ND	ND	ND
C30	132	ND	ND	ND	ND	ND
C31	309	ND	ND	72.5	ND	151
C32	586	ND	516	ND	ND	ND
C33	1659	ND	ND	1341	ND	ND
C34	400	1676	ND	ND	ND	ND
C35	8476	593	ND	5579	2143	ND
C36	ND	ND	ND	ND	ND	ND
C37	ND	ND	ND	ND	ND	ND
C38	ND	ND	ND	ND	ND	ND
C39	ND	ND	ND	ND	ND	ND
C40	ND	ND	ND	ND	ND	ND
TOTAL	**11900**	**2426**	**813**	**8058**	**2282**	**498**

MeWS = Mechanic Workshop Soil, MoWS = Motor Way Soil, TPS = Traffic Point Soil, BSS = Barbecue Spot Soil, FSS = Filling Station Soil, CTR =Control

Table 2: ANOVA results of AHCs in soil

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2527393	4	631848.2	0.974292	0.423086	2.424815
Within Groups	1.1E+08	170	648520.3			
Total	1.13E+08	174				

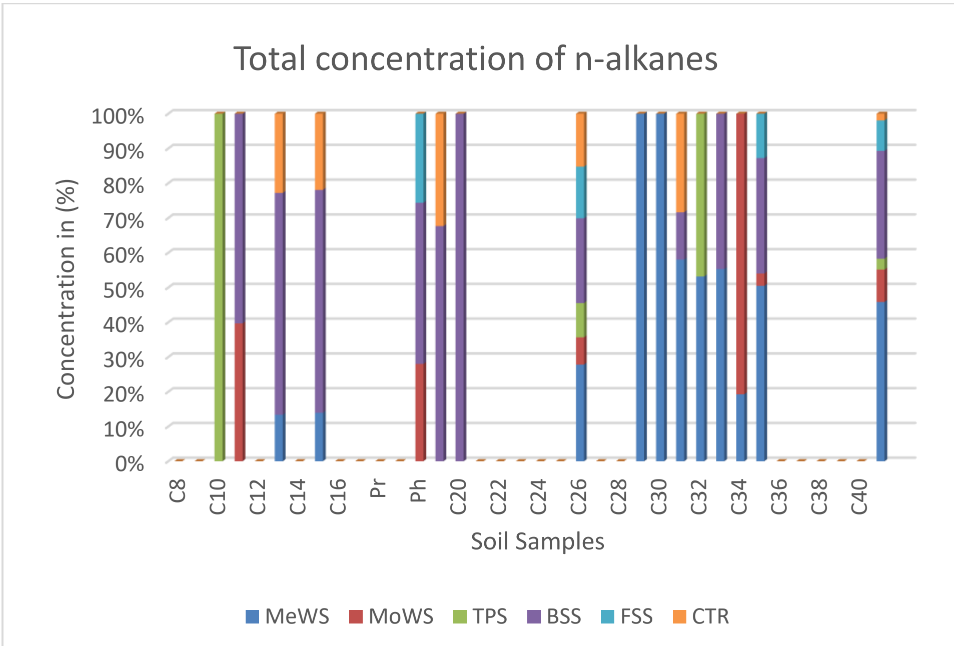

Fig. 2: Total concentration (%) of n-alkanes in all soils.

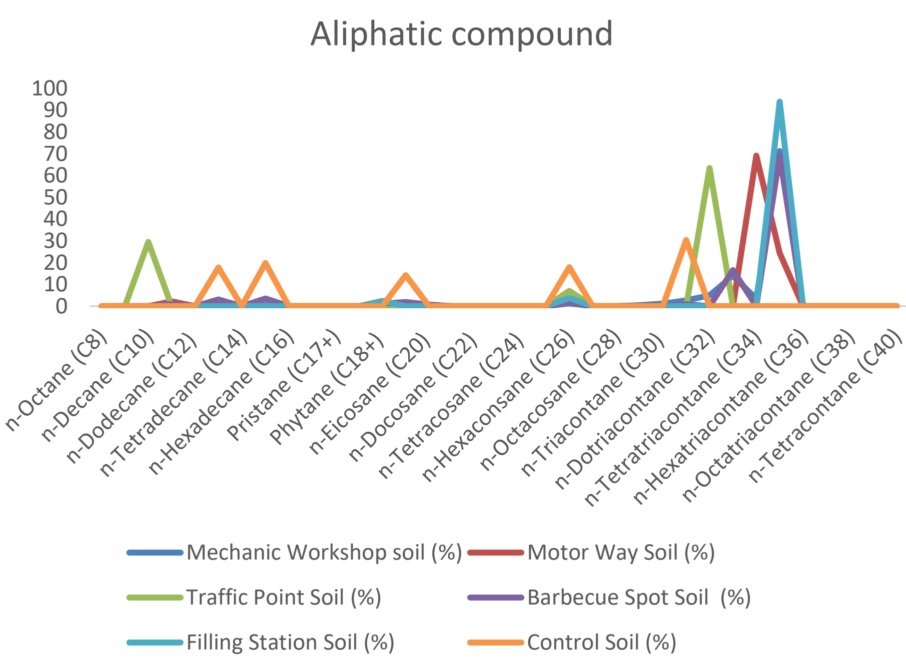

Fig. 3: Total concentration percentage and carbon number distribution of n-alkanes in all soils.

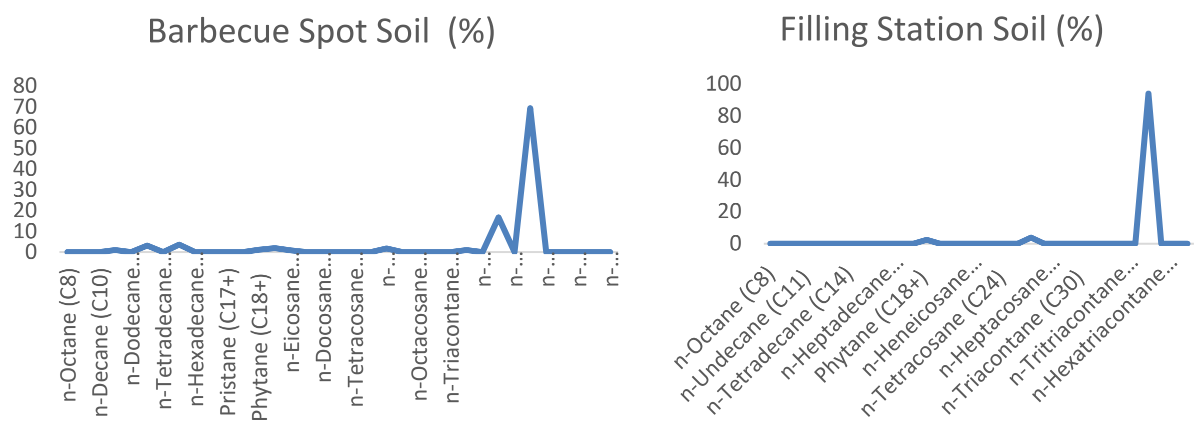

Fig. 4: Total concentration percentage and carbon number distribution of n-alkanes in Barbecue Spot Soil and Filling Station Soils.

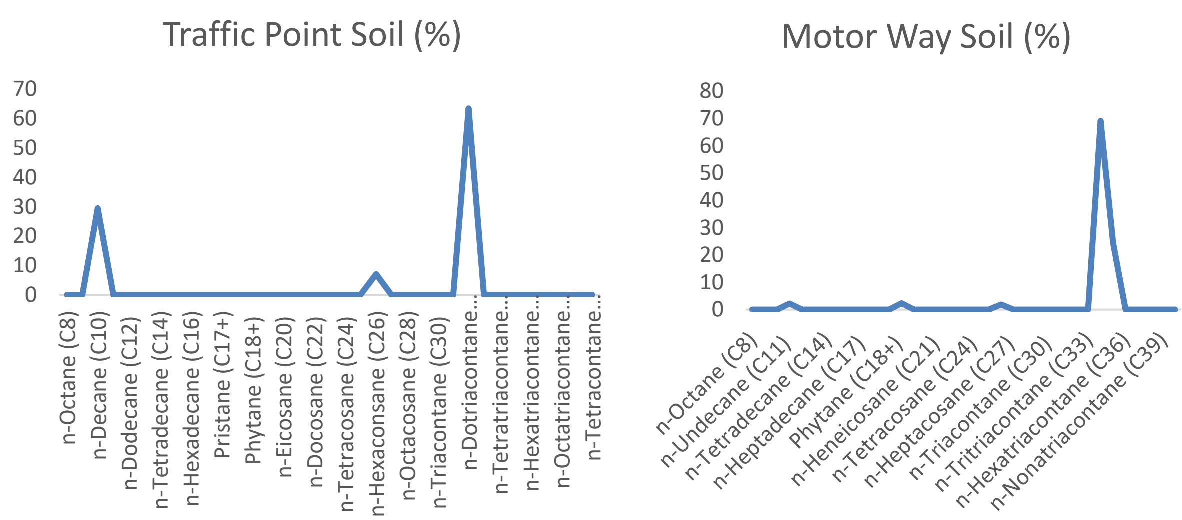

Fig 5: Total concentration percentage and carbon number distribution of n-alkanes in Traffic Point Soil and Motor Way Soils.

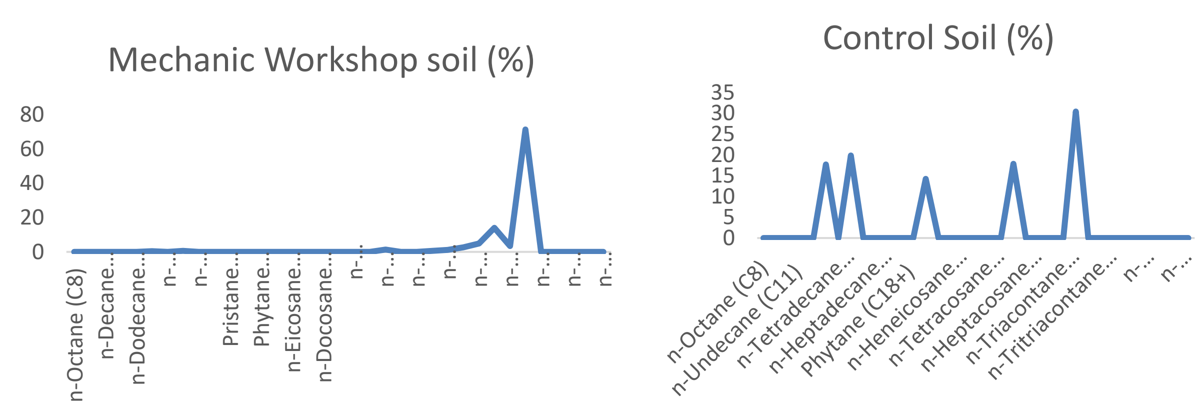

Fig. 6: Total concentration percentage and carbon number distribution of n-alkanes in Mechanic Workshop Soil and Control Soil.

3.2 Source Apportionment of AHCs using molecular indices

3.2.1 Major Hydrocarbon (MH)

The major hydrocarbon (MH) in the mechanic workshop, barbecue spot and filling station was the C35 streams while the MH for solid from the motor-way and traffic point were C34 and C32 respectively. The C32, C34 and C35 are long-chain n-alkanes that are products of anthropogenic sources such as petroleum contribution by urban run-off, soil erosion, industrial emission (Bourbonniere and Meyer 1996). Therefore the dominance of these n-alkanes in these soils reflects inputs from anthropogenic mediated sources. The molecular indices of AHCs used for source apportionment in this study are shown below in Table 3.

3.2.2 Carbon preference index (CP1)

Carbon preference index (CP1) refers to the ratio of odd to even number alkanes. It is an important tool for the distinction of biogenic sources from the anthropogenic input to the environmental loads of *n*-alkanes. The CP1 value near unity suggests a contribution from microorganisms, recycled organic matter and/or petroleum. CP1 values lower than 3 is associated with oiled soil/sediments while CP1 values in the range of 5 to 10 are consistent with inputs from higher terrestrial plant waxes (Iwegbue *et al.*, 2021; Ivwurie, 2014)..

Table 3: Molecular indices of source apportionment

Indices	MeWS	MoWS	TPS	BSS	FSS
MH	C35	C34	C32	C35	C35
LMW/HMW	0.01	0.05	0.11	0.06	0.07
CPI	1.94	0.00	0.00	9.93	0.00
C31/C19	0.00	0.00	0.00	0.49	0.00
TAR	4.91	0.00	0.00	0.50	0.00
NAR	-0.41	-1.00	-1.00	0.03	-1.00
ACL	32.58	0.00	0.00	32.90	0.00

MeWS = Mechanic Workshop Soil; MoWS = Motor Way Soil; TPS = Traffic Point Soil; BSS = Barbecue Spot Soil; FSS = Filling Station Soil; MH = major hydrocarbons; LMW = lower molecular weight; HMW = higher molecular weight; CPI = carbon preference index; TAR = terrigenous/aquatic n-alkanes ratio; NAR = natural n-alkanes ratio; ACL = average carbon chain length

The CP1 values of the soil from the mechanic workshop indicated an oiled rich soil while the CPI for solid from barbecue spot indicated inputs from terrestrial higher plant waxes as contamination source

3.2.3 Ratio of low molecular weight/high molecular weight (LMW/HMW)

The ratio of low molecular weight/high molecular weight (LMW/HMW) alkanes is a useful index for delineating the possible origins of *n*-alkanes. The LMW/HMW alkanes ratio that is less than unity suggests *n*-alkanes associated with higher plants, marine animals and sedimentary bacteria, while the ratio of LMW/HMW alkanes close to 1 relates to *n*-alkanes from petroleum and plankton sources, and LMW/HMW value greater than 2 are consequences of contamination from fresh oil input (Gao *et al.*, 2007; Emoyan *et al.*, 2021; Iwegbue *et al.*, 2021). The ratios of alkanes in the studies soils ranged from 0.01 to 0.11 which are indicative that the soils are likely contaminated with *n*-alkanes associated with higher plants, marine animals and sedimentary bacteria.

3.2.4 Ratio of C31/C19

The C31/C19 index is suitable for the evaluation of hydrocarbons input from land or sea. The C31 is related to hydrocarbons with terrestrial biogenic origins, while C19 represents hydrocarbons from marine biogenic sources (Yusoff *et al.*, 2012; Iwegbue *et al.*, 2016b). Generally, C31/C19 value less than 0.4 depicts the prevalence of marine biogenic derived hydrocarbons, while C31/C19 value > 0.4 suggests the prevalence of land derived hydrocarbons (Yusoff *et al.*, 2012; Iwegbue *et al.*, 2021). The C31/C19 ratio for soil from barbecue spots indicates the prevalence of land-derived hydrocarbons.

3.2.5 Terrigenous/aquatic n-alkanes ratio (TAR)

The terrigenous/aquatic *n*-alkanes ratio (TAR) is an index for the evaluation of changes in the relative inputs of hydrocarbons with terrigenous or aquatic origins. TAR > 1 indicates terrestrial inputs while TAR < 1 indicates aquatic inputs (Emoyan *et al.,* 2020; Iwegbue *et al.,* 2021). The TAR value soils from the mechanic workshops indicate terrestrial input while the calculated index for soils around the barbecue spots reflects aquatic input.

3.2.6 Natural n-alkanes ratio (NAR)

Natural *n*-alkanes ratio (NAR) given by Mille *et al.* (2007) is applicable on the bases that NAR value close to zero are consistent with contaminations from crude oil and its derivatives, while values close to 1 depicts hydrocarbons from higher terrestrial or marine plants such as *Posidona* (Aly Salem *et al*. 2014; Iwegbue *et al*., 2016b). NAR values of soils in this study ranged from -1.0 to 0.03 which suggests inputs from crude oil and other petroleum hydrocarbons.

3.2.7 Average carbon-chain length (ACL)

Average carbon chain length (ACL) is an important tool to measure the impact of anthropogenic hydrocarbon inputs on the environment (Sakari *et al.,* 2012). The ACL is a measure of the average of carbons per molecules based on the prominence of odd carbon number in higher plants (C25-C33) *n*-alkanes (Sakari *et al*., 2008; Iwegbue *et al*. 2016b), and is presumed to be constant in a specific environment with same hydrocarbon input sources (Iwegbue et al., 2021). The ACL for mechanic workshop and barbecue soils in this study were approximately 33 which is constant and indicates the same hydrocarbon input sources in these two locations.

4.0 Conclusion

The ranges for the variation in the concentrations of aliphatic hydrocarbons in the studied anthropogenic impacted soils depend on the activities within the communities. The observed trend in variation of concentrations of aliphatic hydrocarbon in the various studied soils was Mechanic Workshop Soil > Barbecue spot soil > Filling Station Soil > Motor Way Soil > Traffic point soil. The higher molecular weight n-alkanes (> C31) were the dominant aliphatic hydrocarbons in these soils. The molecular indices of source apportionment showed that the aliphatic hydrocarbons in these soils came from different anthropogenic sources such as petrogenic and terrestrial biogenic sources. The study has shown that occurrence of aliphatic and polycyclic aromatic hydrocarbons in the soil falls within the DPR-EGASPIN not contaminated category. This study has contributed to knowledge by showing the source and concentration rates in the land-use sites of hydrocarbons in Agbarho communities of Delta state, Nigeria.

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Consent for publication

Not Applicable

Availability of data and materials

The publisher has the right to make the data public

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