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Assay of Aliphatic Hydrocarbons in Soils from Selected Areas in Ughelli and its Environs, Delta State, Nigeria

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Abstract: *The distribution pattern of aliphatic hydrocarbons (AHCs) was determined in soils and pure hydrocarbon compounds from selected areas in Ughelli and its environs (Delta State, Nigeria) were investigated in this work. The AHCs were quantified with gas chromatography equipped with a flame ionization detector (GC-FID) after extraction and cleanup with n-hexane. Sample collection for soils was from the surface (0-10cm) at various vicinity suspected to be polluted (i.e mechanic workshop, compound with usage of so much generator, flow-station environment, motor-way and filling station), while a control sample was also collected from virgin farmland. The pure hydrocarbon compounds which included diesel, fuel, carbon soot and spent engine oil were used to compare the concentration of AHCs present in the soil. The evaluated concentration of AHCs (nC_8-nC_{40}) ranged from 321,515 to 5,368,702 mg L^{-1} and 27.42 to 16733 µg kg^{-1} for pure hydrocarbon compounds and soils respectively. The concentration of n-alkanes in the soil samples showed some variations with contamination sources for different locations and consequently defined the trend, mechanic workshop soil > generator compound soil > flow-station soil > motorway soil > filling station soil. The molecular indices for aliphatic hydrocarbons showed that the aliphatic hydrocarbons in the soils might have originated from different anthropogenic sources*

Keywords: *Aliphatic hydrocarbons, analysis of variance (ANOVA), Gas chromatography flame ionization detector (GC-FID), Soil.*

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1.0 Introduction

Potentially harmful chemicals, including aliphatic hydrocarbons, are present in petroleum hydrocarbons and their compositions and distribution vary from each other depending on the source, physical state, and primary activities within the zone under consideration, etc (Wang *et al*., 2004). For example, crude oil contains heavier hydrocarbon composition than its refined product fractions which contain fewer constituents compared to crude oil. Petroleum hydrocarbons are naturally occurring compounds formed from crude oil, natural gas, coal and other energy-related sources. They are highly combustible and give rise to water, heat and carbon dioxide when burned. This makes it an important substance for energy generation which is used to make living satisfiable. Petroleum hydrocarbons when released in large quantity to the environment have their environmental and health effect which is significant when compared to their usefulness. Environmental hydrocarbons released either by accident or by actions carried out by humans can interfere with soil properties since the land

and the aquatic environments are the major recipients of hydrocarbon contamination (Holliger *et al*., 1997). Hydrocarbons can adversely affect plants and animals and their entrance route to man includes direct penetration through the mouth, nose, or dermal contact or the consumption of contaminated plants or animals. These pose considerable health risks such as diverse respiratory illnesses, diminished lung function, and cardiovascular diseases (Turner and Hefzi, 2010) This poisonous substance gets to humans through a given area's food chain (Gibson and Parales, 2000).

Aliphatic hydrocarbons are separated into three types of structural hydrocarbons namely; alkanes/saturated hydrocarbon (C-C) bonds which could also be subdivided into; normal alkanes (n-alkanes), branched alkanes (isoalkanes), and cyclic alkanes. The cyclic alkanes mostly are often abundant alkanes in crude oil, alkenes/unsaturated hydrocarbons (C=C) bond and alkynes/unsaturated hydrocarbon (C≡C) bond. ACHs are commercially available in petroleum ether, benzine (not benzene), petroleum naphtha, gasoline and paint thinner. Its higher boiling point mixtures include jet fuels, kerosene and lubricating oils. Aromatic hydrocarbons however are present in these mixtures and more toxic than the dominant ACHs. Therefore, the daily handling of these pure hydrocarbons constituents if not properly checked will have far reaching effects on the environment and the health of lives. Studies on hydrocarbon contamination of soils have been reported by Edori and Wodi (2020) on high concentrations of aliphatic hydrocarbons in soils sample taken within the vicinity of heavy-duty stationary engines in some estates and universities in Port Harcourt using gas chromatography equipped with flame ionization detector (GC-FID). The results indicated that the level of contamination was dominantly contributed by anthropogenic sources while the contribution from terrestrial vascular plants and biogenic sources was minor. While, Ilechukwu *et al.* (2019) examined the AHCs in soils in the vicinity of mechanic workshops in Nnewi, Anambra State. The authors found the presence of an unresolved complex mixture, which indicated that AHCs in the soils had undergone degradation. Furthermore, Aly Salem *et al*. (2014) carried out a study on sediment in selected port stations of Egypt. He discovered that one of the stations El-Tour has a maximum concentration 553.48 mg/g, while a minimum of 33.97ng/g. This signals that n-alkane content material may conform to anthropogenic sources and natural inputs.

Considering the inadequacy of literature on the levels of aliphatic hydrocarbons in soils in Ughelli and its environs, with its attendant influx of mechanic workshops, generator compounds, oil flow-station, filling stations, and busy motor-way, which may affect soil quality, hence this research work arose to determine the concentration, distribution pattern, source identification of aliphatic hydrocarbons present in the soil about pure hydrocarbon compounds to obtain contamination levels and its resultant health implication.

1.1 The study area

The studied area was located at Ughelli metropolis and it lies within latitude 5.500187 and Longitude 5.992834. The city is placed categorically with GPS coordinate 5° 30’ 0.6732” N and 5° 59’ 37.8024” E it is bounded to the North by Ethiope East, Patani to the South, Ughelli South to the west, and Isoko North and South to the east. It houses a population of over 321,028 as published by the National population commission in a census conducted in 2006. Ughelli metropolis houses the headquarters of the Ughelli North local government area of Delta state and is one of the fastest growing cities in Delta state as well as an oil producing city with five flow and flare stations which is the highest in the Niger Delta region.

2.0 Materials and Methods

Five samples were pure hydrocarbon and six were soil samples collected from the topsoil (0-10cm) from the suspected pollution sites using a stainless-steel soil auger. Control samples were collected from virgin farmland that has not witnessed hydrocarbon contamination. Each soil sample was transferred into a clean amber-colored glass bottle and was transported in an ice chest at a temperature below 4°C to the laboratory for chemical analysis.

Table 1: Sampling codes, sites and coordinates of the study area

S/N	Field Sampling Code	Name of Site	Latitude	Longitude
1	FSS	Filling station soil	5°29'45" N	5° 59'40" E
2	MOWs	Motorway soil	5°28'57" N	6°1'6" E
3	FS	Flow- station.	5°31'33" N	6°3'4" E
4	GCS	Generator compound soil.	5°28'48" N	6°1'5" E
5	MeWS	Mechanic workshop soil	5°29'18" N	6°1'4" E
6	CTR	Control	5°36'19"N	5°52'25"E

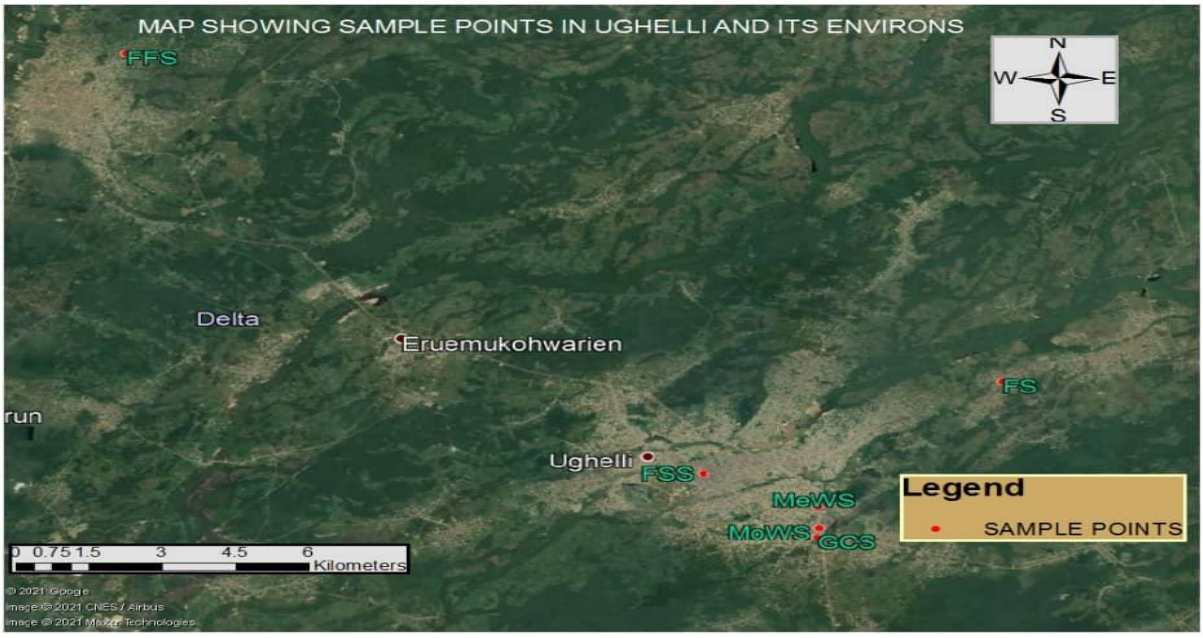

Fig. 1: The red dots indicate the sampling area and core sites for soil samples (Google maps 2020).

2.1 Extraction and analysis

The samples were extracted using the US-EPA method 3550B (US EPA, 1996). Thus, 10g of the soil samples and 10 grams of anhydrous sodium sulphate, Na_2SO_4 (BDH grade) were mixed in an 100 mL glass beaker until a dry homogenate was obtained. For carbon soot, 1.0gram was used, while gasoline and diesel required no extraction. 20mL of dichloromethane, DCM (99% reagent grade) Fischer Scientific (Loughborough, UK) was added to the dry homogenate and was shaken in a mechanical shaker (Searchtech instrument, HZ-300 model, USA) for 30mins, it was then transferred to a sonicator (Omegasonic quantum series model) and was sonicated for

30 minutes at 70°C; after sonication 5g of Na_2SO_4 was added to the sample again to remove any residual water molecule. The extracts were then filtered into a 100ml beaker, and the process was repeated thrice with a fresh mixture of DCM each time with the same sample. A rotary evaporator (Searchtech instrument, RE52-2 model, USA) was then used to concentrate the extracts to 2 mL. The resulting extract was fractionated using a glass column packed with glass wool, then silica gel (60-120 mesh) which was preconditioned at 105°C and mixed with DCM and Na_2SO_4. The extract was then eluted with 10 mL of n-hexane (HPLC grade) for aliphatic and concentrated to 1mL in a rotary evaporator (Searchtech instrument, RE52-2 model, USA) before the concentration the round bottom flask of the rotary evaporator was rinsed with acetone (US EPA, 1996). The obtained concentrate was pipetted into a clean 2mL Teflon screw-cap vial and cap tightly and labelled ready for gas chromatography-flame ionization detector (GC-FID) analysis.

The extracts were analyzed using Agilent 6890 gas chromatography coupled with a flame ionization detector. Chemstation software was used to quantify normal alkanes ranging from n-C_8 to n-C_{40} pristane/phytane. The carrier gas was helium, in the split-less mode, the injection volume and injector temperatures were 1.0 µl and 250 °C respectively. While the oven temperature is set at 300 °C and the final temperature (i.e outlet) is 320 °C.

2.2 Quality control/assurance

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

2.3 Data analysis

The statistical package for social science (SPSS) was used for all statistical analyses. Descriptive statistics were used to establish the existence of significant variations in normal alkanes ranging from n-C_8 to n-C_{40} pristane/phytane concentrations.

2.4 Source apportionment of aliphatic hydrocarbons (AHCs)

Since AHCs are nonpolar and photo-catalytically stable hydrocarbon compounds, they are employed as indices for molecular identification of hydrocarbon contaminants and their respective sources (Duan *et al*., 2010). The sources of AHCs in environmental media were evaluated by employing different isomeric ratios highlighted below

2.4.1 Carbon Preference Index (CPI)

This ratio represents the sum of odd-number hydrocarbons relating to even numbers (Charriau *et al;* 2009). The equation below was used to calculate the CPI (equation 1) for the entire carbon range (Aboul-Kassim and Simoneit, 1995):

$$CPI_{25\text{-}33} = 0.5 \times \left[\frac{C25+C27+C29+C31+C33}{C24+C26+C28+C30+C32}\right] + \left[\frac{C25+C27+C29+C31+C33}{C26+C28+C30+C32+C34}\right] \quad (1)$$

Petroleum-derived n-alkanes have no predominance of odd over even numbers. They show an extensive range, and thus CPI values are closer to 1. CPI higher than 1.0 stipulates the influence of odd-numbered hydrocarbons of biogenic origin.

2.4.2 Natural n-alkane ratio (NAR)

The NAR was evaluated using equation 2

$$NAR = \sum n-alkanes\ (C19-C32) - \left[2 \times \frac{\sum n-alkanes\ (C20-C32)}{\sum n-alkanes\ (C19-C32)}\right] \quad (2)$$

NAR close to 1 designates input by higher terrestrial or marine plants (Aly Salem *et al*., 2014).

2.4.3 Terrigenous/aquatic n-alkane ratio (TAR)

The ratio of terrigenous to aquatic n-alkanes was used to evaluate the contributions of terrigenous and aquatic sources of hydrocarbons. It was evaluated using equation 3

$$TAR = \frac{C27+C29+C31}{C15+C17+C19} \quad (3)$$

TAR > 1 represents terrestrial input, while TAR <1 represents aquatic input (El Nemr *et al*., 2016).

2.4.4 Average carbon chain length (ACL)

ACL is useful for identifying environmental changes in a given ecosystem. An unchanging value of ACL shows that the changes occurring in an environment are minimal (El Nemr *et al*., 2013). It was evaluated using the ratio shown in equation 4

$$ACL = \frac{25\,(C25) + 27\,(C27) + 29\,(C29) + 31\,(C31) + 33\,(C33)}{C25 + C27 + C29 + 31 + C33} \quad (4)$$

2.4.5 Low molecular weight/high molecular weight (LMW/HMW)

In distinguishing between macrophytes and terrestrial plants ratio of LMW to HMW n-alkanes is used. Sum of aliphatic hydrocarbons concentration ranging C_{16} -C_{26} and are related to the marine biogenic source is regarded as LMW, whereas HMW ranging C_{27}-C_{36} are related to terrestrial vascular plants (Fagbote and Olanipekun, 2013). The ratio of LMW to HMW < 1 shows natural input from terrestrial biogenic sources, while >1 stipulates natural input from marine biogenic sources. When it nears 1 it stipulates petroleum and plankton sources. LMW/HMW ratio >2 depicts contamination from fresh oil sources (Gao *et al.*, 2008; Emoyan *et al.*, 2021; Iwegbue *et al.*, 2021).

2.4.6 Major Hydrocarbon (MH)

Major hydrocarbon present in long chain n-alkanes can show soil source of emission. It can show whether the source comes from an anthropogenic or natural source.

2.4.7 n-C_{29}/n-C_{17} ratio

n-C_{29} and n-C_{17} ratio is greatly present in land plants and marine organisms respectively. It provides information on the comparative contributions of allochthonous and autochthonous hydrocarbon input to the sediment (Rouidi *et al;* 2013).

3.0 Results and Discussions

Measured concentrations of n-alkanes in pure hydrocarbon compounds are recorded in Table 2 while Fig. 2 shows the total concentration and distribution of n-alkanes in pure hydrocarbon.

The concentrations of n-alkanes in diesel exhaust ranged from 27,102 to 369,126 µg kg^{-1} with a total concentration of 1,788,030 µg kg^{-1}. The most abundant hydrocarbon (MH) was C_{37}. Hydrocarbons of C_8 to C_{18} and C_{36} to C_{40} were not detected in diesel exhaust (Fig. 3). Similar results were reported for diesel particulate matter (Liang *et al*., 2005) and diesel particulate exhaust (Williams *et al*., 2016).

The concentrations of the detected n-alkanes ranged from 490 to 583,859 mg L^{-1} with a total concentration of 4,257,796 mg L^{-1}. Pristane is the most abundant hydrocarbon in diesel. However, C_8, C_9, C_{32}, C_{36} to C_{40} were not detected in diesel (Fig.4). The total aliphatic hydrocarbons obtained in this study for diesel were higher than those reported by Liang *et al*. (2005).

The concentrations of the individual n-alkanes in car exhaust ranged from 3,641 – 86,223 µg kg^{-1} with a total concentration of 321,515 µg kg^{-1}. Only n-alkanes C_9, C_{19} and C_{30}-C_{36} were detected in car exhaust and C_{33} recorded the highest concentrations (Fig. 5). The heavier n-alkanes dominated car exhaust even as hopane and sterane biomarkers were not detected. This may be a consequence of combustion since shorter-chained alkanes are likely to undergo complete combustion than the heavier ones (Liang *et al.*, 2005).

The concentrations of individual n-alkanes detected in spent oil ranged from 24,065 – 683,666 mg L^{-1} with a total concentration of 5,368,702 mg L^{-1}. All the n-alkanes were detected in spent oil except C_8, C_9, C_{14}, C_{17}, Pr, C_{38}, C_{39} and C_{40} (Fig. 6). A similar result has been reported previously in literature for lubricating oil (Liang *et al.*, 2018).

The concentrations of individual n-alkanes detected in petrol ranged from 5,230 to 3,183,100 mg L^{-1} with a total concentration of 4,799,658 µg L^{-1}. Only C_8 to C_{15} and C_{19} were detected in the petrol samples with C_8 having

the highest concentrations (Fig. 7). In this study, hopane and sterane biomarkers were absent in petrol and this is because petrol is a lower boiling point petroleum product, and these biomarkers are not expected to be present in it (Maricq, 2007).

Table 2: n-alkanes concentrations in pure hydrocarbon compounds

	Diesel exhaust (µg/kg)	**Diesel (mg/L)**	**Car exhaust (µg/kg)**	**Spent oil (µg/kg)**	**Petrol (mg/L)**
C_8	ND	ND	ND	ND	3183100
C_9	ND	ND	5641	ND	1041520
C_{10}	ND	13234	ND	30761	168556
C_{11}	ND	58540	ND	112010	308810
C_{12}	ND	58155	ND	28124	69792
C_{13}	ND	66263	ND	28360	10065
C_{14}	ND	207631	ND	ND	4248
C_{15}	ND	103620	ND	37058	5230
C_{16}	ND	166730	ND	37058	ND
C_{17}	ND	532026	ND	ND	ND
Pr	ND	583859	ND	ND	ND
C_{18}	ND	107597	ND	38272	ND
Ph	27154	459320	ND	27806	ND
C_{19}	27272	431924	31114	31158	8336
C_{20}	42468	264760	ND	26125	ND
C_{21}	51092	540778	ND	25654	ND
C_{22}	68104	147911	ND	39803	ND
C_{23}	88024	138611	ND	37894	ND
C_{24}	152828	56658	ND	46969	ND
C_{25}	179408	41878	ND	250308	ND
C_{26}	193370	76935	ND	146589	ND
C_{27}	168126	47830	ND	164303	ND
C_{28}	165796	18694	ND	403796	ND
C_{29}	27102	22683	ND	314332	ND
C_{30}	47230	11555	11255	540944	ND
C_{31}	28858	10105	7806	512544	ND
C_{32}	31570	ND	48906	590176	ND
C_{33}	42698	490	86223	582184	ND
C_{34}	77804	31950	57752	572444	ND
C_{35}	369126	58052	62019	683666	ND
C_{36}	ND	ND	10799	36299	ND
C_{37}	ND	ND	ND	24065	ND
C_{38}	ND	ND	ND	ND	ND
C_{39}	ND	ND	ND	ND	ND
C_{40}	ND	ND	ND	ND	ND
TOTAL	**1788030**	**4257796**	**321515**	**5368702**	**4799658**

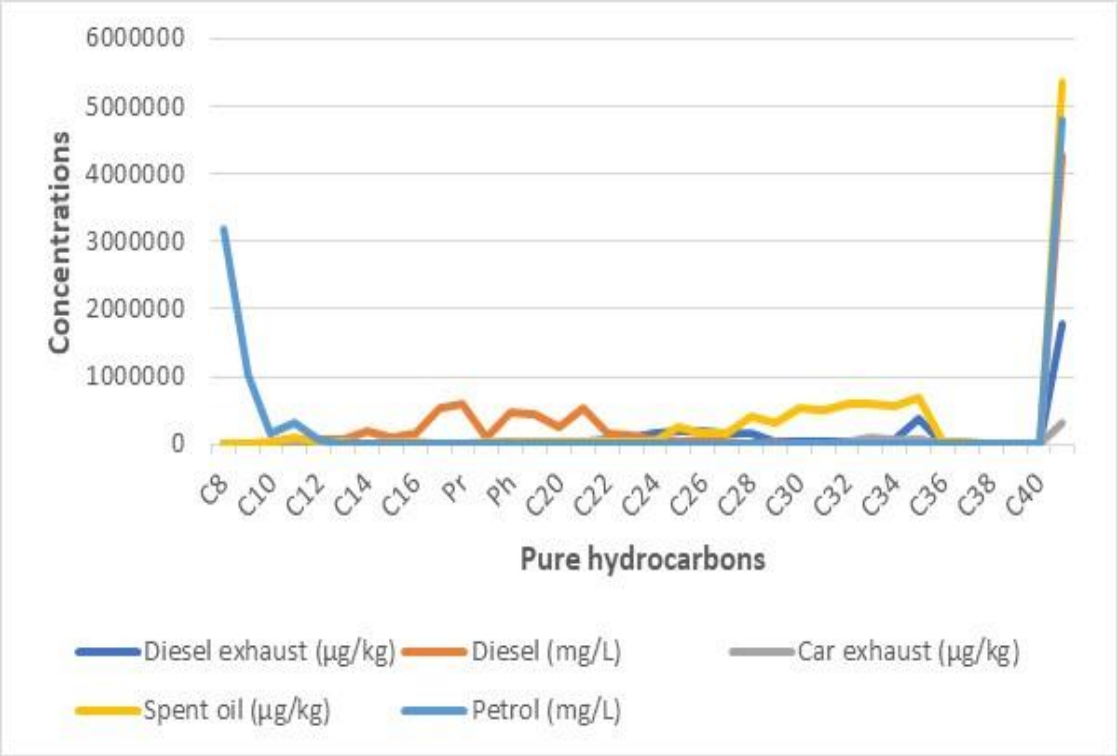

Fig. 2: Total concentration and distribution of n-alkanes in pure hydrocarbon sources.

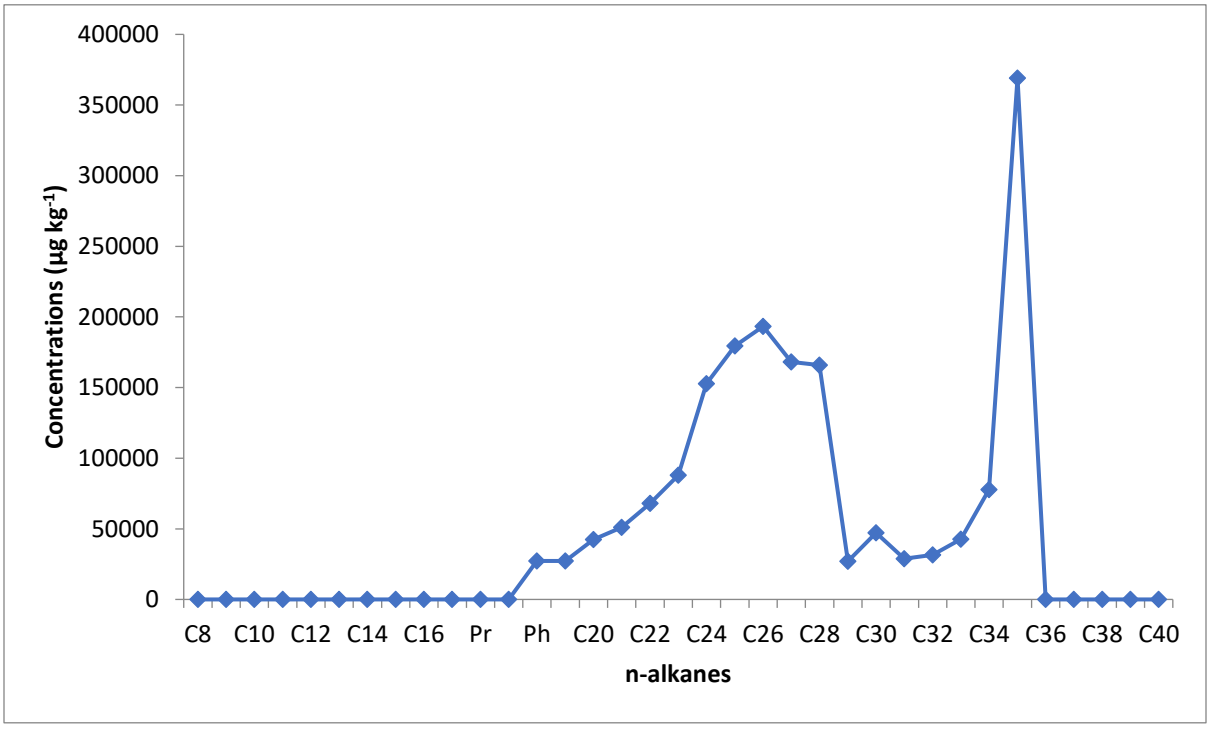

Fig. 3: Concentration and distribution of n-alkanes in diesel exhaust

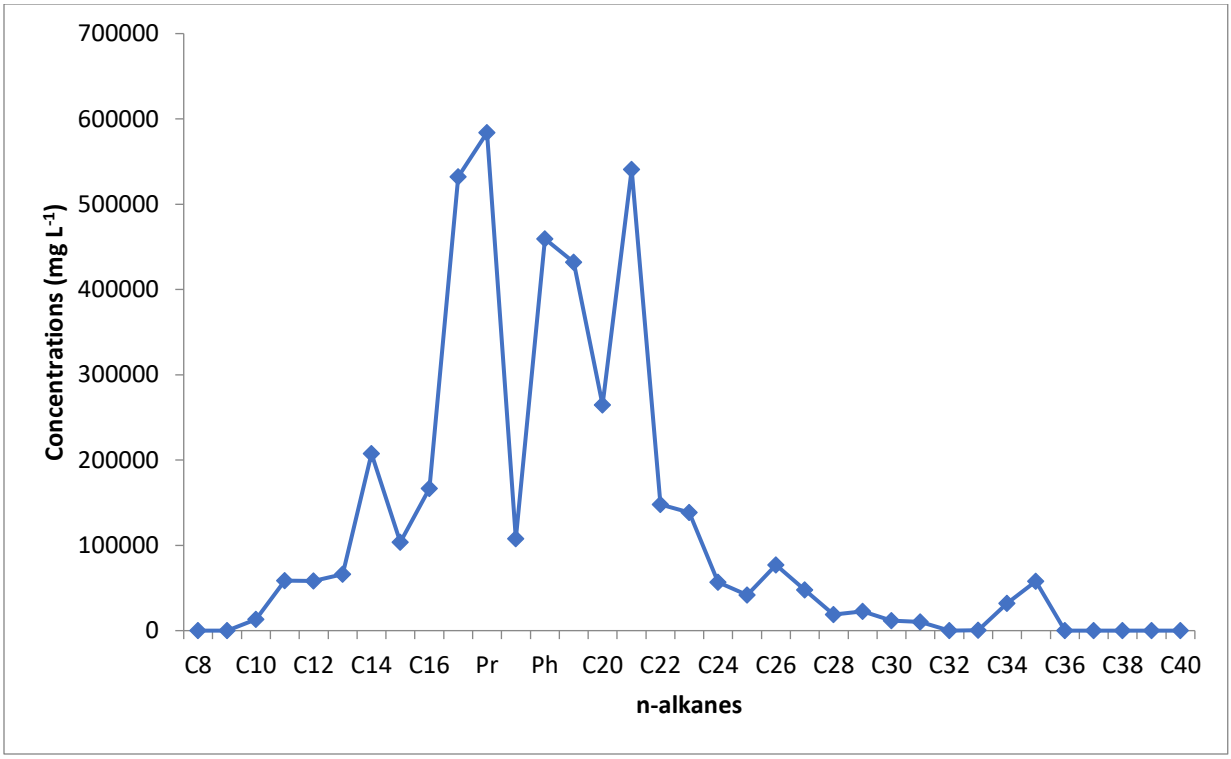

Fig. 4: Concentration and distribution of n-alkanes in diesel

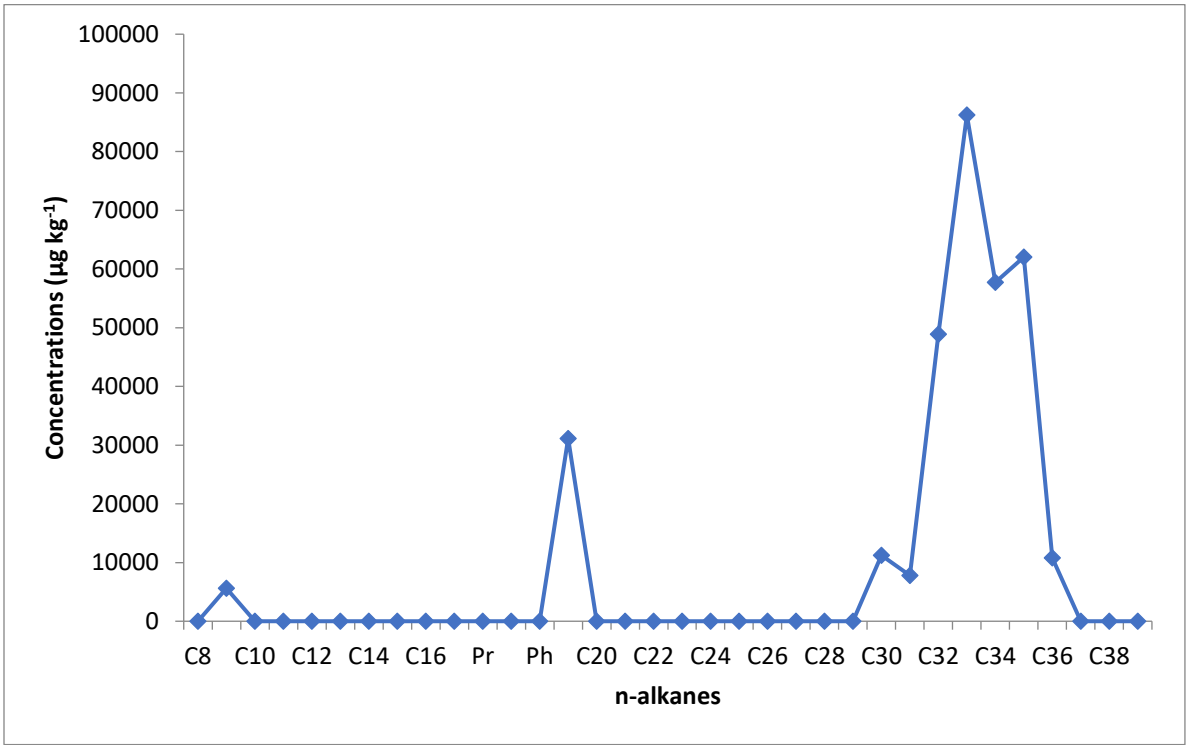

Fig. 5: Concentration and distribution of n-alkanes in car exhaust

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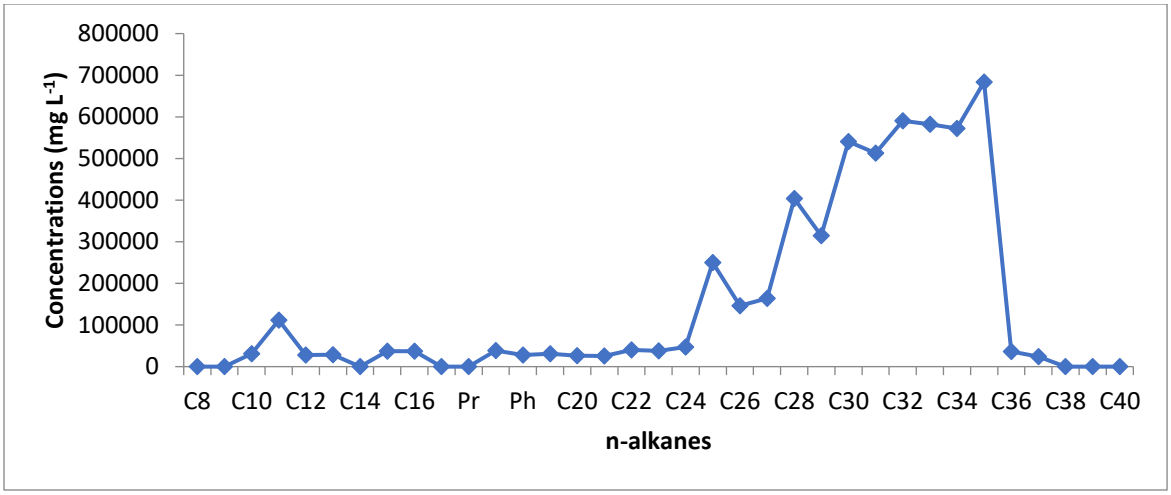

Fig. 6: Concentration and distribution of n-alkanes in spent oil

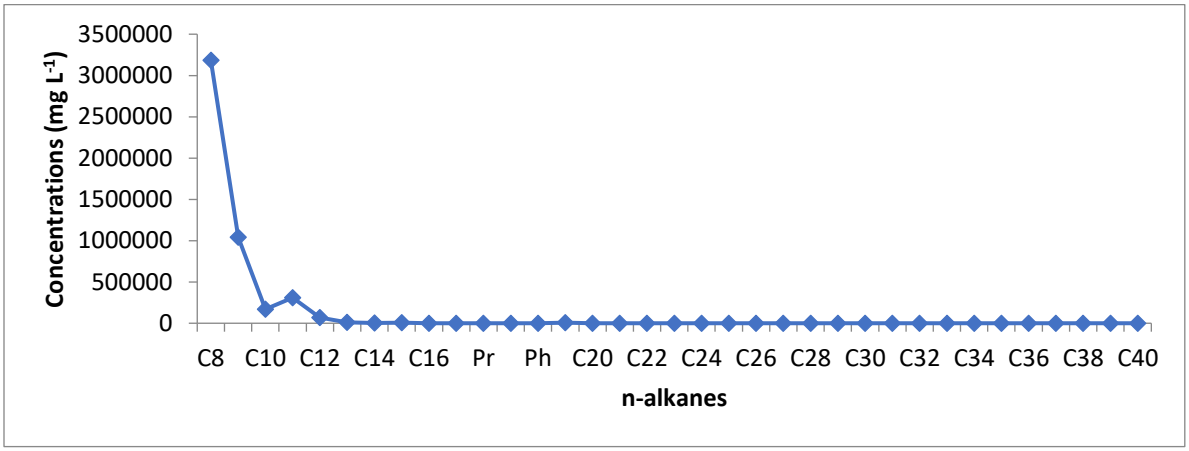

Fig. 7: Concentration and distribution of n-alkanes in petrol

The results of aliphatic n-alkanes concentration in the studied soil samples are shown in Table 3 which reveals the concentration (µg kg^{-1}) a range of 1,571 (for samples from soil at the filling station) to 16,733 (for samples from soils around the mechanic workshops). The control site similarly had a total concentration of 27.4 µg kg^{-1}. The observed total concentration of n-alkanes was within the United Nation Environment Program (UNEP) recommended limit of 10,000 ug/kg in soils from filling stations, motorways and flow-station; but the limit was exceeded in soils from generator compounds and mechanic workshops.

The carbon number distribution of n-alkanes across the five sites ranged from phytane, C_{19} – C_{20} and C_{26} in filling station soil, phytane, C_{20}, C_{26}, C_{35} – C_{36} in motorway soil, phytane, C_{19} – C_{20} and C_{26} in generator compound soil, C_{11}, C_{15}, - C_{17}, phytane, C_{20} – C_{22}, C_{24}, C_{26}, C_{29} – C_{31} in mechanic workshop soil and C_{18}, phytane, C_{19}, C_{26}, C_{33} – C_{36} in flow-station. For the control sample, the carbon number distribution was C_{19}, C_{26} and C_{35}. Hopane biomarkers, ranging from C_{27} – C_{35} and sterane biomarkers, ranging from C_{27} – C_{29} were detected only in soils from mechanic workshop soil. Although hopanes are not recognized as environmental pollutants, their persistent natures make it possible for them to be used as geochemical biomarkers in oil pollution (Boehm *et al.*, 2001). Hopanes are reportedly present in higher boiling petroleum products

such as lubricating oils and asphalt (Maricq., 2007). This could be the reason for their presence in lubricating oils, and the presence of these biomarkers suggests wide-scale contamination from oil and grease (Rushdi *et al*., 2013).

Table 3: Aliphatic hydrocarbons (µg kg^{-1}) concentrations in soil samples

	Filling station soil	Motor way soil	Generator compound soil	Mechanic workshop soil	Flow station	Control
C8	0	0	0	0	0	0
C9	0	0	0	0	0	0
C10	0	0	0	0	0	0
C11	0	0	0	19	0	0
C12	0	0	0	0	0	0
C13	0	0	0	0	0	0
C14	0	0	0	0	0	0
C15	0	0	0	19	0	0
C16	0	0	0	9	0	0
C17	0	0	0	7	0	0
Pr	0	0	0	0	0	0
C18	0	0	0	0	0	0
Ph	34	22	30	80	106	0
C19	20	0	12	0	392	15.4
C20	18	17	16	61	75	0
C21	0	0	0	10	0	0
C22	0	0	0	26	0	0
C23	0	0	0	0	0	0
C24	0	0	0	10	0	0
C25	0	0	0	0	0	0
C26	18	58	15	74	151	12.02
C27	0	0	0	0	0	0
C28	0	0	0	0	0	0
C29	0	0	0	96	0	0
C30	0	0	0	246	0	0
C31	0	0	0	454	0	0
C32	0	0	0	0	0	0
C33	0	0	0	0	910	0
C34	0	0	0	0	799	0
C35	0	3322	356	10285	1175	0
C36	0	85	2194	309	0	0
C37	0	0	4687	2842	0	0
C38	1481	0	3963	811	0	0
C39	0	0	403	582	0	0
C40	0	0	769	791	0	0
TOTAL	**1571**	**3504**	**12445**	**16731**	**3609**	**27.42**

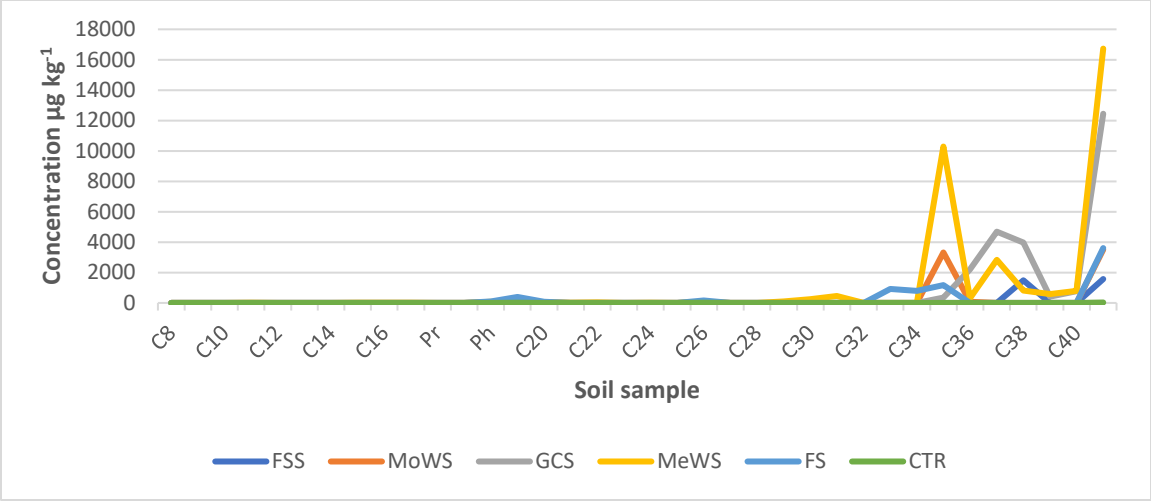

Fig. 8: Total concentration and distribution of n-alkanes in soil samples

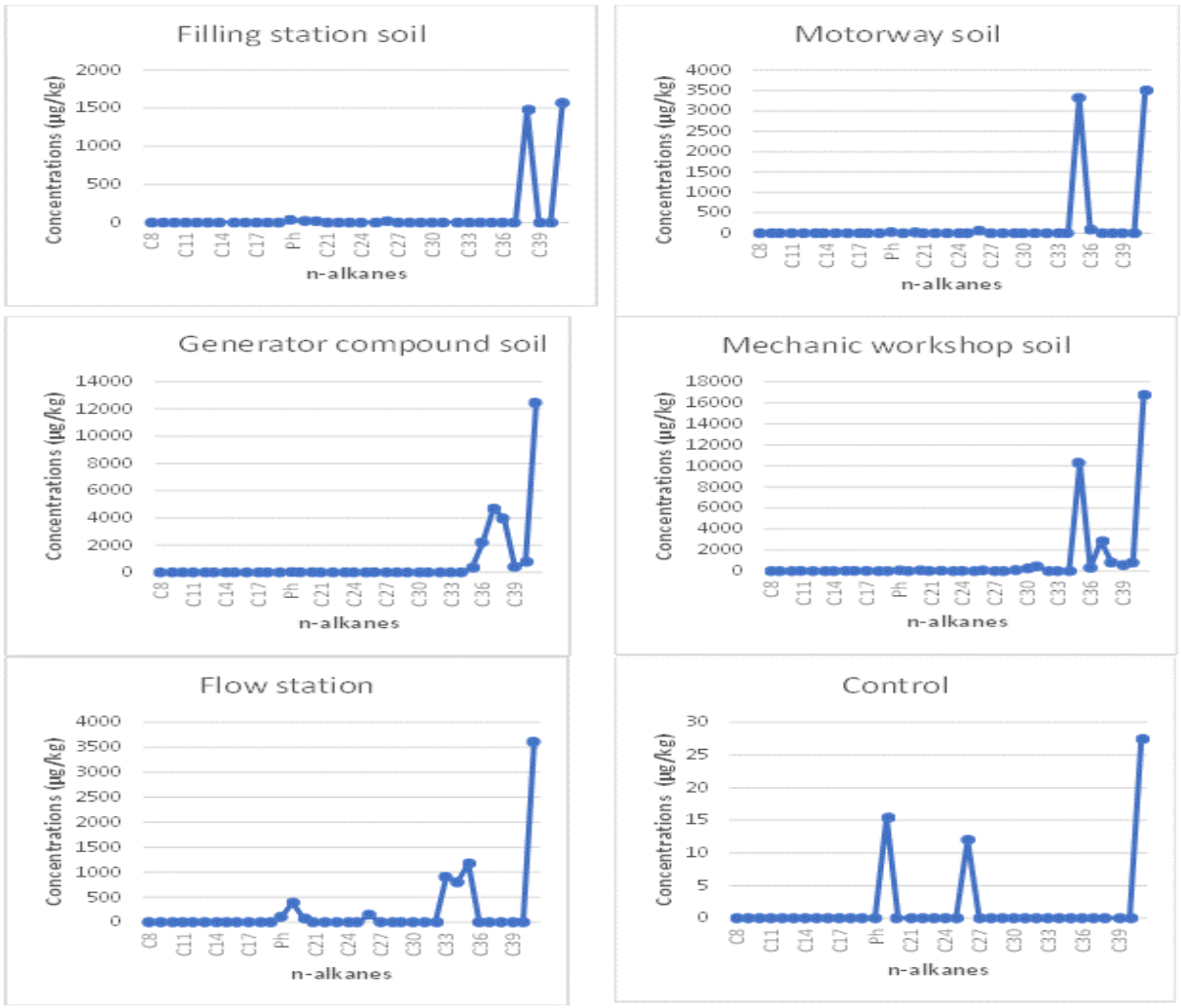

Fig. 9: Individual concentration and carbon number distribution of n-alkanes in soil samples

The analysis of variance (ANOVA) based on the result obtained indicated that there was no significant variation in the concentrations of the total aliphatic hydrocarbons in these soils (p-value > 0.05; Fcal < Fcrit) as shown in Table 4

Table 4: ANOVA results of aliphatic hydrocarbons in soil

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	5024868	4	1256217	1.315727	0.266093	2.424815
Within Groups	1.62E+08	170	954769.9			
Total	1.67E+08	174				

3.2 Source apportionment of aliphatic hydrocarbons using molecular indices

The molecular indices of aliphatic hydrocarbons used for source apportionment are shown in Table 5.

The major hydrocarbon (MH) in soils around the motorway, mechanic workshop and flow station were C_{35} while for filling station, C_{38} was the MH and C_{37} for generator compound. The C_{32}, C_{34} and C_{35} are long chain n-alkanes that are anthropogenic sources such as petroleum contribution by urban run-off, soil erosion, and industrial emission (Chapman, 1996). Therefore, the dominance of these n-alkanes in these soils reveals contributions from anthropogenic mediated sources.

Table 5: Molecular indices of source apportionment

	Primary sources					Secondary sources					
	Diesel exhaust	**Diesel**	**Car exhaust**	**Spent oil**	**Petrol**	**FSS**	**MoWS**	**GCS**	**MeWS**	**FS**	**CTR**
MH	C35	Pr	C33	C35	C8	C38	C35	C37	C35	C35	C19
LMW/HMW	0.9	17.6	0.1	0.2	0	0	0.03	0.03	0.02	0.25	2.28
CPI	0.8	0.8	1.2	0.9	0	0	0	0	1.69	3.49	0
$n\text{-}C_{29}/n\text{-}C_{17}$	0	0	0	0	0	0	0	0	13.7	0	0
TAR	8.2	0.5	1.3	10.4	0.6	0	0	0	21.2	0	0
NAR	0	0.4	-0.2	-0.1	1	-0.3	-1	0.43	0.14	0.34	0
ACL	27.2	27	32.8	30.1	0	0	0	0	30.65	33	0

FSS = Filling Station Soil; MoWS = Motor Way Soil; GCS = Generator Compound Soil; MeWS = Mechanic Workshop Soil; FS = Flowstation 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 CPI values of the soils ranged from 0.00 to 3.49 with mechanic workshop indicating soil contaminated with lubricating oil, while the CPI for flow-station indicates inputs from terrestrial higher plant waxes.

The ratio of the low to the high molecular weight (LMW/HMW) alkanes in soil samples were found to range from 0.00 to 0.03, which indicates that the soils were contaminated with n-alkanes associated with higher plants, marine animals and sedimentary bacteria.

The terrigenous/aquatic *n*-alkanes ratio (TAR) is an index that can be used 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 of soil from the mechanic workshop indicates terrestrial input.

The natural *n*-alkanes ratio (NAR) as given by Mille *et al.* (2007) indicates that the NAR value close to zero depicts contamination by crude oil and its derivatives, while values close to 1 depict hydrocarbons from higher terrestrial or marine plants such as *Posidona* (Aly Salem *et al*; 2014; Iwegbue *et al*; 2016b). The NAR values of soils in this study ranged from -0.3 to 0.14 which suggests inputs from crude oil and other petroleum hydrocarbons.

This is an important tool used 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 molecule based on the prominence of odd carbon numbers in higher plants (C_{25}-C_{33}) *n*-alkanes (Sakari *et al*., 2008; Iwegbue *et al*. 2016b), and is presumed to be constant in a specific environment with the same hydrocarbon input sources (Iwegbue *et al.*, 2021). The ACL for mechanic workshop and flow-station soils were between 30 and 33, which indicates similar hydrocarbon inputs from different sources in these two locations.

4.0 Conclusion

The result of this study has provided information on the occurrence and sources of n-alkanes in soil samples in comparison with pure hydrocarbons. The total aliphatic hydrocarbon concentrations based on source location were consistent with the following order, mechanic workshop soil > generator compound soil > flow-station soil > motorway soil > filling station. The measured concentrations are however below the United Nations Environment Program (UNEP) guideline value of 10000 µg kg^{-1} except for soils from the vicinity of the generator and mechanic workshop which exceeded the UNEP guideline value. The concentration of n-alkanes in these soils where higher when compared with the control sample. There was a shift of heavier aliphatic hydrocarbons to car exhaust emissions due to combustion. Hopane and sterane biomarkers were absent in petrol because of their lower boiling point. The n-alkanes distribution in diesel and diesel exhaust emissions were similar. The molecular indices of aliphatic hydrocarbons showed that the aliphatic hydrocarbons in these soils came from different anthropogenic sources. This study has contributed to knowledge by showing the distribution and source of aliphatic hydrocarbons concentration load in the land-use sites of Ughelli and its environs area of Delta state Nigeria.

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