

Evaluation of n-Alkanes Hydrocarbon from two Communities in Udu Local Government Area, Delta State

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Received: 11 September 2021/Accepted 06 December 2021/Published online: 15 December 2021

Abstract: Hydrocarbon pollution is constantly contributing some threats to our environment. The key approach to solving environmental contamination problems starts with impact assessment. The present study was designed to investigate the concentration profiles and the distribution of n-alkanes in some soils within two communities in the Udu local government area of Delta State, Nigeria. Five soil samples suspected to have been contaminated with hydrocarbons were collected from the selected communities which are located within the Udu Local Government Area Delta State. They were analyzed for aliphatic hydrocarbons using gas chromatography equipped with a flame ionization detector (GC-FID). The results obtained from the hydrocarbon analysis gave concentrations of C₈–C₄₀ aliphatic hydrocarbons in soil samples within the range 3.0 to 325ppm with a mean value of 75ppm. The carbon preference index (CPI) of soil in the studies area ranged from 0.0-2.8 but with higher values for soils from the vicinity of some mechanic workshops (CPI = 1.1), busy traffic points (CPI = 2.8) than soil from other environments. A thorough analysis of the experimental data led to the conclusion that hydrocarbon inputs to the affected soil are majorly biogenic sources.

Keywords: Hydrocarbon contamination, soil, Udu communities, contamination indices

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1.0 Introduction

Aliphatic hydrocarbons consist of carbon chains. In acyclic compounds, the carbon chains are successive or branched. Key families included in this company are alkanes, alkenes and alkyne (homologous series) with member (homologous) case in point such as (methane and ethane), (ethane and propane), and (ethyne and propyne), respectively (Ahmed and Fakhruddin, 2018). Aliphatic hydrocarbons (n-alkanes) can enrich the environment through anthropogenic and industrial sources (Rushdi et al., 2010). Urbanization, shipping, fishing, and oil exploration activities have been indicted as major contributors to the levels of aliphatic hydrocarbons in our environment (Kingston, 2002). Other minor sources may include biological habitats or biogenic sources which involve, bacteria, insects, plankton, algal bacteria and come to rest plants (Sakaria et al., 2008a). Studies have shown that the odd number of aliphatic hydrocarbons are basically from anthropogenic source. For example, n-C₁₅, n-C₁₇ and n-C₁₉ are formed or created from aquatic nutrients, while nC₂₅-nC₃₃ hydrocarbons come from earthly vascular plants (Sakaria et al., 2008b). On the other hand, those below C₂₀ are associated with dwindling-ocean plankton such as bacteria and algae. Studies on hydrocarbon contaminations of some Nigerian soils have been reported. Edori and Wodi (2020) have reported

excessively high concentrations of some aliphatic hydrocarbons in soils taken within the vicinity of heavy-duty stationary engines in some estates and universities in Port Harcourt. 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. 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 results of the investigation left a remark that indicated that future contamination may be risky. Soil contamination by hydrocarbon can severely affect soil quality by limiting the population and activity of useful soil microorganisms (Adipah, 2019). They can be taken up by plants and consequently be transferred to higher organisms through the food chain (Gennadiev *et al.*, 2015). Among all the studies reported for various locations within Nigeria, literature is scanty on the levels of aliphatic hydrocarbons in soils within the Udu local government area of Delta state, yet anthropogenic activities have been confirmed

to be major contributors in some studied areas are significantly present in communities within Udu. Therefore, the present study is aimed at analyzing soils to obtain information of the level of hydrocarbon contamination in the two selected communities.

1.1 The study area

This research work was carried out in the Udu local government area of Delta State, Nigeria (the map of the study area is shown in Fig. 1). Udu is one of the Urhobo kingdoms, located close to Warri metropolis. This closeness with Udu has enhanced the developmental status of the Udu. The Udu land is interlocked (mesh) by rivers flowing across; it has tropical weather and rain forest with evergreen vegetation and plantation all year round. Its geographical attribute comprises many streams that interlink into a complex web of rivers, lagoons, swamps and wetlands. Udu has thirty-two Communities, but two of these Communities were chosen for this study amongst these are Egini (5° 27' 44"N and 5° 49' 56"E) and Ubogo (5° 27' 0"N and 5° 49' 60"E) as display in (Fig. 2)

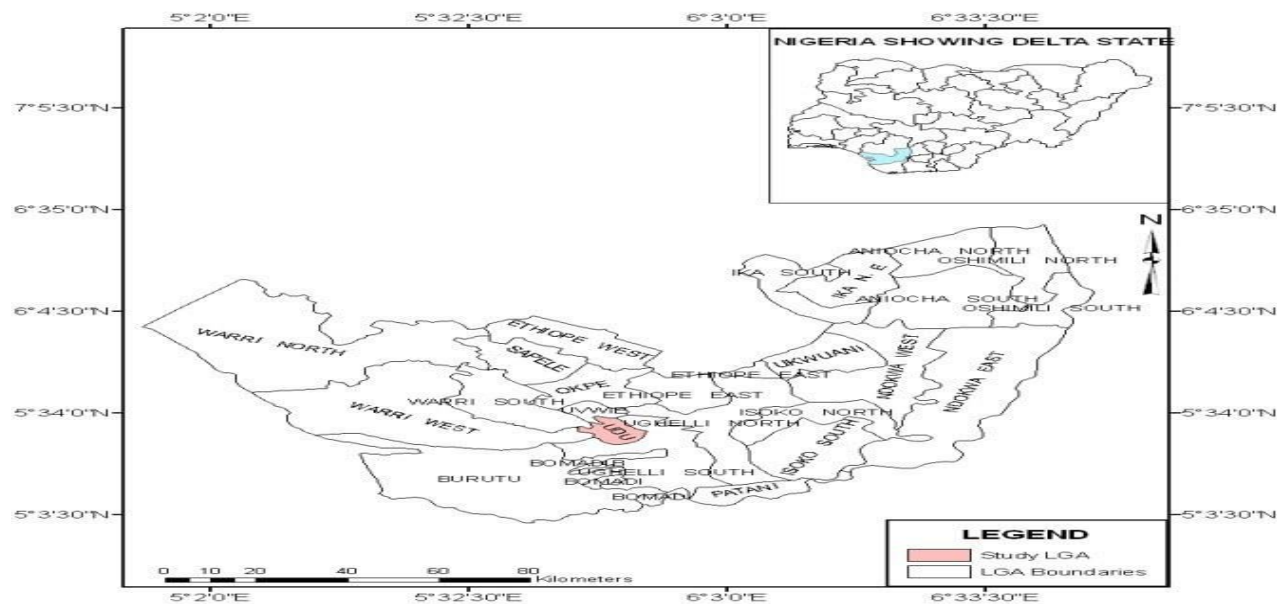


Fig 1: Map of Delta State showing Udu Local Government Area (Ijeomah and Pudie, 2015).





Fig. 2: The green dots indicate sampling area and core sites (Google maps 2020).

2.0 Materials and Methods

Soil samples were collected from the area suspected to have been contaminated with petroleum products in Egini/Ubogo communities. The sampling locations were spread within the following stations,

- a) Mechanic workshop soil (Egini junction, Udu Road);
- b) Drainage soil (Close to Egini Secondary School junction);
- c) Farm field soil (from Egini Community).
- d) Traffic point soil (Ubogo Market); and
- e) Petrol station soil (Udu road, close to Ubogo Market);

However, a control sample was collected from untouched or virgin land. Topsoil composite samples (including 3 to 4 composite samples from each site) were collected at a depth of 0-10 cm using a stainless steel auger. Samples were transferred to aluminum foil and transported to the laboratory for storage in a refrigerator with an ice pack. The samples were air-dried, in a dark at room temperature. Foreign matter such as leaves, stems, and stones was removed. The samples were ground with a mortar and pestle and sieved through a 2 mm sieve 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)

2.1 Extraction of sample

The extraction of n-alkanes extraction was carried out using ultrasonic extraction (EPA Method 3550B) (US EPA, 1996). 10g 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 100ml 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).

2.2 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 μ l 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).

3.0 Results and Discussion

3.1 Concentration and distribution of n-alkanes in secondary sources

The concentrations of n-alkanes and distribution in the studied soils are recorded in Table 1 and shown in Figs. 1 and 2 as bar charts. The concentrations are seen to vary with sampling locations and tend to reflect the nature of human activities in the studied areas. The concentrations of n-alkanes in soils ranged from: 0.25 to 94.5 ppm for samples from mechanic; 0.4 to 1.6ppm in farm field soil, 0.3 -14.4 ppm in rad traffic soil, 0.7-19.3 ppm in petrol station soil; 0.6-2.4ppm in drainage soil; and from 0.3 to 0.8 ppm in soil from the control station. This defines an average range of 3.0 ppm (in drainage soil) to 325 ppm (soils from the vicinity of some mechanic workshops) and the mean concentration was 75.86 ppm. The analysis of variance (ANOVA) for the n-alkanes and relative composition at secondary sources at the studied area displayed significant variation (p -value >0.05 ; $F_{cal} > F_{crit}$) as shown in Table 2, and seems to reflect differences in patterns of input sources, circulation, rainfall and degradation (Frena *et al.*, 2017). The distribution of the n-alkane carbon ranged from C₁₀-C₃₉ with a maximum concentration

recorded for C₃₆. The carbon number distribution of n-alkanes in the soil sample ranged between C₃₅ and C₃₆ in drainage soil, C₂₆ and C₃₅ in Petrol station soil, C₁₀, phytane, C₁₉, C₂₀, C₂₆, C₃₁, C₃₃-C₃₅ in road traffic soil, C₁₀, C₁₃, C₁₄ C₁₇ and C₃₂ in farm field soil and C₁₂-C₃₉ in mechanic workshop soil. However, in the control soil, the carbon number distribution was between C₁₉ and C₂₆.

The hopane biomarker was found mainly in soils from some mechanic workshops and ranged from C₂₇-C₃₅ with a maximum concentration recorded for C₃₃. Also, the C₂₇-C₂₉ sterane biomarker was found only in soil samples from the vicinity of some mechanic workshops. This can be attributed to the fact that lubricating oils are mainly used in such environments and the presence of these biomarkers implies extensive contamination by oils and greases. However, these biomarkers are not found in secondary sources of Farm field soil, Road traffic soil, Drainage soil, and Control soil, because hopane and sterane are not normally found in gasoline and diesel but include a higher temperature fraction and are not expected to be present in such soils (Rushdi *et al.*, 2013).

3.2 Sources identification of n-alkanes in soils from secondary sources

The source identification of n-alkanes in this study are shown in Table 1 and Fig. 3. The major hydrocarbon (MH) in three (3) of the studied sites Road traffic soil, Petrol station soil, and Drainage soil were nC₃₅; nC₃₂ was the major hydrocarbon in farm field soil while nC₃₆ was the major hydrocarbon in Mechanic workshop soil, but the high molecular weight of n-alkanes was in higher proportion.

3.3 Carbon preference index (CPI)

CPI measures the comparative load of odd to even carbon n-alkanes for identification (Ahmed *et al.*, 2006). If there is an odd to even carbon number, this indicates a biogenic alkane. Organics of recent biological origin usually have a CPI value of 6-9 or higher. Generally, values of CPI above 3 are indices for



the dominance of n-alkanes associated with biological substances. Though, the values for CPI in oil, car emissions, and coal consumption are nearer to units (Ivwurie, 2004; Oro and Simoneit 2000).

Table 1 The mean concentrations and distribution of n-alkanes in secondary sources

	MWS (ppm)	FFS (ppm)	RTS (ppm)	PSS (ppm)	DS (ppm)	CS (ppm)
C8	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0
C9	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0
C10	<0.0	0.46	0.69	<0.0	<0.0	<0.0
C11	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0
C12	0.25	<0.0	<0.0	<0.0	<0.0	<0.0
C13	0.78	0.89	<0.0	<0.0	<0.0	<0.0
C14	0.36	<0.0	<0.0	<0.0	<0.0	<0.0
C15	0.39	0.9	<0.0	<0.0	<0.0	<0.0
C16	0.44	<0.0	<0.0	<0.0	<0.0	<0.0
C17	0.28	0.4	<0.0	<0.0	<0.0	<0.0
Pr	0.54	<0.0	<0.0	<0.0	<0.0	<0.0
C18	0.56	<0.0	<0.0	<0.0	<0.0	<0.0
Ph	0.56	<0.0	0.39	<0.0	<0.0	<0.0
C19	0.64	<0.0	0.6	<0.0	<0.0	0.3
C20	0.33	<0.0	0.3	<0.0	<0.0	<0.0
C21	1.2	<0.0	<0.0	<0.0	<0.0	<0.0
C22	1.3	<0.0	<0.0	<0.0	<0.0	<0.0
C23	2.3	<0.0	<0.0	<0.0	<0.0	<0.0
C24	3.9	<0.0	<0.0	<0.0	<0.0	<0.0
C25	3.2	<0.0	<0.0	<0.0	<0.0	<0.0
C26	12.7	<0.0	1.3	0.7	<0.0	0.8
C27	7.5	<0.0	<0.0	<0.0	<0.0	<0.0
C28	13	<0.0	<0.0	<0.0	<0.0	<0.0
C29	14.6	<0.0	<0.0	<0.0	<0.0	<0.0
C30	23.8	<0.0	<0.0	<0.0	<0.0	<0.0
C31	29.1	<0.0	0.3	<0.0	<0.0	<0.0
C32	16.4	1.6	<0.0	<0.0	<0.0	<0.0
C33	41.4	<0.0	6.5	<0.0	<0.0	<0.0
C34	13.7	<0.0	2.4	<0.0	<0.0	<0.0
C35	25.2	<0.0	14.4	19.3	2.4	<0.0
C36	94.5	<0.0	<0.0	<0.0	0.6	<0.0
C37	9.2	<0.0	<0.0	<0.0	<0.0	<0.0
C38	6	<0.0	<0.0	<0.0	<0.0	<0.0
C39	0.6	<0.0	<0.0	<0.0	<0.0	<0.0
C40	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0
TOTAL	325.1	4.3	26.9	20	3	1.1

MWS = Mechanic workshop soil; FFS = Farm field soil RTS = Road traffic soil PSS = Petrol station soil DS = Drainage soil CS = Control soil; PPM= Part per million



Table 2: ANOVA results of aliphatic hydrocarbons in soil

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2225.491	4	556.3728	8.222816	4.37E-06	2.424815
Within Groups	11502.55	170	67.66208			
Total	13728.04	174				

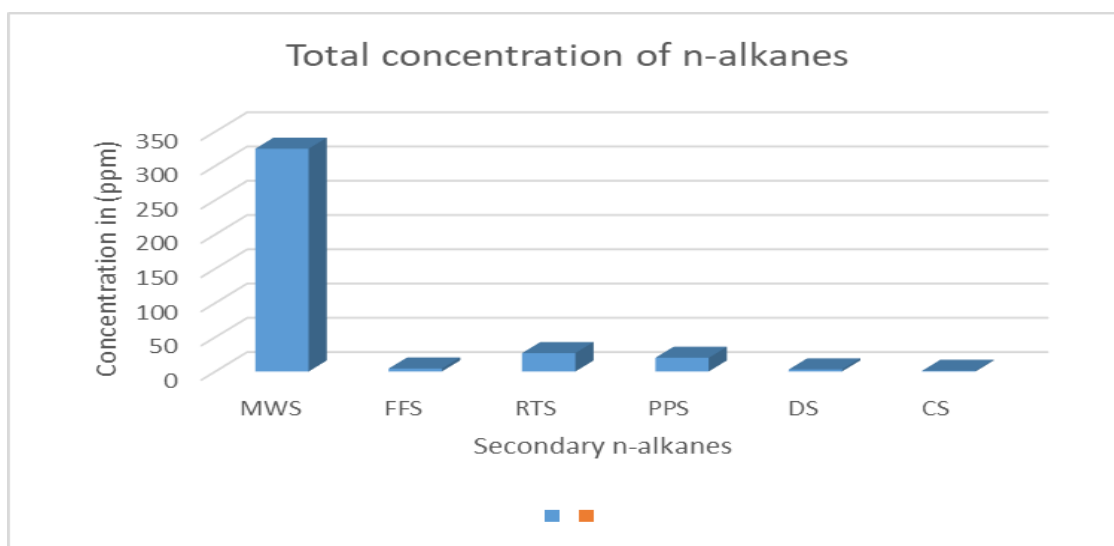


Fig. 3 Total concentration (ppm) of n-alkanes in soil from secondary sources

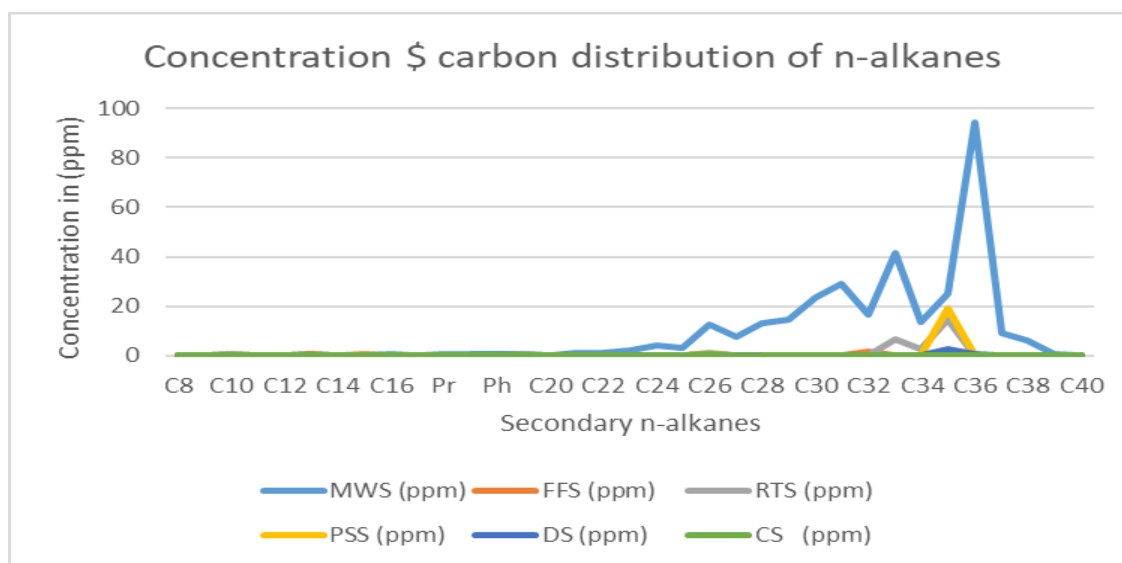


Fig. 4: Concentration (ppm) and carbon number distribution of n-alkanes in all soils



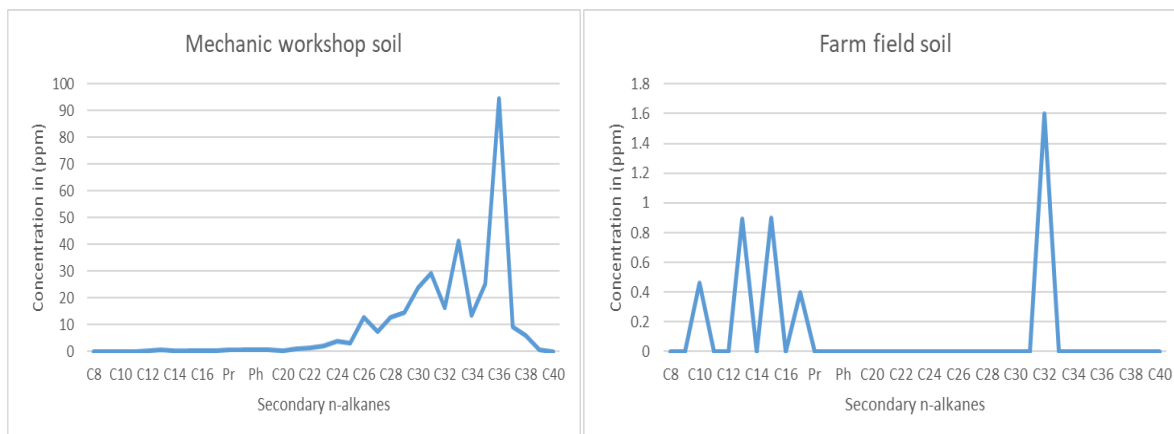


Fig. 5 Concentration (ppm) and carbon number distribution of n-alkanes in MWS and FFS in soil or secondary source

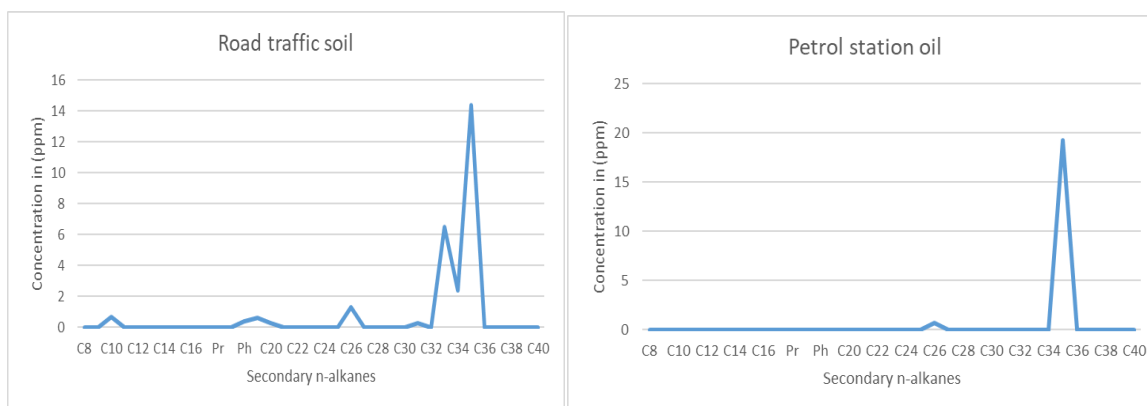


Fig. 6: Concentration (ppm) and carbon number distribution of n-alkanes in RTS and PSS in soil or secondary source

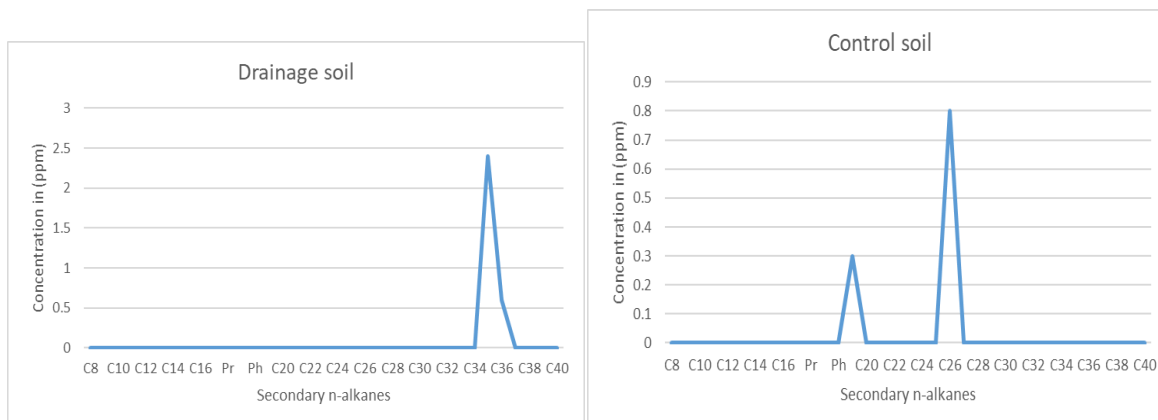


Fig. 7: Concentration (ppm) and carbon number distribution of n-alkanes in DS and CS in soil or secondary source

3.4 nC_{31}/nC_{19} ratio

According to Eguvbe *et al.*(2015), nC_{31} carbon number is established to be a signal of earthly



The values of CPI in the studied area ranged between 0.0–2.8. Apart from soils from some mechanic workshops environments and those from road traffic congestion environments, other CPI values were 0.0. A CPI value of 1.1 at mechanic workshop soil and 2.8 at road traffic soil indicates inputs from biogenic sources of oiled sediment (Ahmed *et al.*, 2006). biogenic hydrocarbons, where, nC_{19} presents maritime biogenic sources. The nC_{31}/nC_{19} ratio can be used for the detection of the prevalence of hydrocarbon input from both land and sea bases. Values lesser than 0.4 established the prevalence of maritime biogenic sources

whereas values greater than 0.4 are indicative of land-derived hydrocarbon. In this research work, the nC_{31}/nC_{19} ratio ranged between 0.0 and 45.2. Apart from Mechanic workshop soil and Road traffic soil other nC_{31}/nC_{19} ratio values were 0.0.

An nC_{31}/nC_{19} ratio value of 0.5 at Road traffic soil and 45.2 at Mechanic workshop soil indicates input from land-derived hydrocarbon sources. This could be attributed to the fact that lubricating oil is majorly used in such environments and the constant emission of carbon dioxide at traffic points.

Table 3: Molecular indices of aliphatic hydrocarbons in soil

	MWS	FFS	RTS	PSS	DS	CS
MH	C_{36}	C_{32}	C_{35}	C_{35}	C_{35}	C_{26}
LMW/HMW	0.1	0.2	0.1	0.0	0.0	1.1
CPI	1.1	0.0	2.8	0.0	0.0	0.0
C_{31}/C_{19}	45.2	0.0	0.5	0.0	0.0	0.0
Pr/Ph	1.0	0.0	0.0	0.0	0.0	0.0
$n-C_{17}/Pr$	0.5	0.0	0.0	0.0	0.0	0.0
C_{18}/Ph	1.0	0.0	0.0	0.0	0.0	0.0
nC_{29}/nC_{17}	51.7	0.0	0.0	0.0	0.0	0.0
TAR	38.9	0.0	0.5	0.0	0.0	0.0
NAR	-1	-1	-1	-1	-1	-1
Paq	0.1	0.0	0.0	0.0	0.0	0.0
ACL	29.8	0.0	31.0	0.0	0.0	0.0

****MWS =Mechanic workshop soil; FFS=Farm field soil; RTS= Road traffic soil; PSS= Petrol station soil; DS= Drainage soil; CS =Control soil; DECS= Diesel exhaust carbon soot; AGO= Diesel; MECS= Motor exhaust carbon soot; MWO= Motor waste oil P= Petrol; 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.**

3.5 Average carbon length (ACL)

Average carbon length (ACL) is a notable tool for evaluating the effect of anthropogenic hydrocarbon inputs on the environment (Sakaria *et al.*, 2012). It is presumed to be persistent in an explicit environment with the equal hydrocarbon put in sources. The interference by other hydrocarbon sources having distinct ACL values remains nearly frequent for a clear environment with

consistent input, while changes in ACL profile with time show changes in the ecological unit as a consequence of the environmental disorder. The ACL value in this study ranged between 0.0–31.0 with 3 of the locations having ACL values of 0.0, it, suggests minimal disturbance arising from any intense anthropogenic activities in these 3 sites. However, the occurrence of aliphatic hydrocarbons of various carbon lengths in Mechanic workshop soil and Road traffic soil



established that sources of aliphatic hydrocarbons in those sites are numerous (Fagbote and Olanipekun 2013).

3.6 The natural n-alkanes ratio (NAR)

The natural n-alkanes ratio (NAR) physically estimates the proportion of ecological and fuel n-alkanes (Mille *et al.*, 2007). NAR values between zero and unity indicate crude oil contamination while 1 indicates higher terrestrial plants hydrocarbon (Aly Salem *et al.*, 2014; Iwegbue *et al.*, 2016). The NAR values obtained in this study site were all -1.0 which indicated inputs from crude oil contamination and its derivatives.

3.7 Paq (n-alkanes proxy)

A proxy ratio (Paq) is useful for the quantification of diverse kinds of plants (e.g underwater versus growing deposit types (Fricken *et al.*, 2000). Generally, values of Paq ranging from 0.01–0.23 are connected to terrestrial plant waxes, whereas those in the range 0.48–0.98 are linked with underwater/growing species of macrophytes. Values between the two ranges are mixtures of the two sources (Fricken *et al.*, 2000). The values obtained in this study area ranged from 0.0–0.1 with 4 of the location having Paq values of 0.0. However, Paq n-alkanes proxy value of 0.1 at Mechanic workshop soil indicated input from terrestrial plant waxes.

4.0 Conclusion

The results of this study provide firsthand information on the presence and sources of hydrocarbons in the soil within the Udu local government area of Delta State. The total n-alkanes concentration in this soil ranged from 3-325.1 ppm and is included in the uncontaminated category. There was a predominance of low molecular weight and non-carcinogenic PAHs. The isometric ratios used for source apportionment suggest that the PAHs in these soils originate from biomass/diesel, combustion of fossil fuels or wood, coal and high-temperature combustion processes. The soils of the Udu metropolis, had

Benzo(a)pyrene total potency equivalent below the Canadian council of ministers of environment (CCME) threshold value, suggesting negative human health impact. The aliphatic hydrocarbons molecular index shows that the aliphatic hydrocarbons in these soils come from various anthropogenic sources.

5.0 References

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Conflict of Interest

The authors declared no conflict of interest

