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Profiling Organic Biomarkers in Petroleum Depot and Its Biogeochemical Relevance

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ABSTRACT

The occurrence of organic biomarkers in an ecosystem should be of great concern due to their effects on the environment and health of residents. The study profiled the organic biomarkers in soil and sediment samples towards identifying the various classes of organic biomarkers present and their biogeochemical relevance. Soil and sediment samples were collected from the petroleum depot at Mosinmi, Ogun State. The extraction of the samples (soil and sediments) were done with the aid of sonicator. Silica-alumina column chromatography was used for further clean-up of the extracts into polar, aromatic and saturate fractions. Gas chromatography-Mass spectrometer (GC-MS) was used for the analysis of the organic biomarkers from the concentrated fractions. The National Institute of Standards and Technology (NIST) library reference was used as basis of comparison of mass spectra for the identification of the organic biomarkers. Biogeochemical parameters including Pristane/Phytane (Pr/Ph), Odd-Even Carbon Prevalence (OEP), Pristane/Carbon-17 (Pr/nC17) were determined. The values obtained gave indication of the state of the environment and anthropogenic activities of the sampled area.

KEYWORDS: Organic biomarkers, Odd-Even carbon preference (OEP), Sonicator, Mass Spectra, petroleum depot.

1. INTRODUCTION

Biomarkers are organic matter whose identity can be traced back to biologically synthesized organic molecules. They occur in sediments, rock, and crude oils and show little or no change in structure from their parent organic molecules in living organisms. Their chemical fingerprint in petroleum provide unique clues to indicate source rocks and biological sources of organisms that generated the organic matter, environmental conditions, thermal maturation and level of microbial biodegradation. Biomarkers generally retain their source information after burial in soil and sediment regardless of any alteration (Derrien *et al*., 2017). Soil and sediment contain organic matter with very complex sources (Ortiz *et al*., 2013), hence, different tools such as stable isotopic, total organic carbon (TOC) and specific biomarker methods are used to identify their origin of organic carbon. Specifically, n-alkanes and geochemical parameters such as: carbon preference index (CPI), average chain length (ACL), pristine/phytane (Pr/Ph) ratio are widely used in identification and oil-source rock correlations, origin and environment of depositions determination (Cheng *et al.*, 2023). Only a few reports, including Olayinka *et al*., (2020) exists on organic biomarkers in the petroleum depots. However, to ensure a clean and safe environment, proper profiling of organic biomarkers in sediments and soils of petroleum depots is essential.

2. MATERIALS AND METHODS

The soil and sediment samples were collected at the identified locations at a depth of 0 – 30 cm each using hand shovel. 20 g of the freeze-dried composite soil and sediment samples were weighed into 100 ml beaker. 25 cm^3 of dichloromethane was added and sonicated for 15 minutes at 25 ^oC. The sonication was done three times, and all the extracts collected together into a beaker covered with perforated aluminum foil. The beaker was labeled and set for purification with column chromatography.

3. RESULTS AND DISCUSSION

3.1 Occurrence of saturated organic biomarkers in sediment samples of Mosinmi, Sagamu

Aliphatic compounds detected in the sediment sample of Mosinmi, Sagamu ranged from nC_8 to nC_{17} (table 1).Cetene and E-15- heptadecenal both have high similarity indices of 92% and 91% respectively. 1- Ethyl -2- methylcyclopentane which is an n- alkane nC_8 show the least similarity index of 59%, it is however the most predominant as it exhibited the highest area percentage of 33.26 (table 1). This is an indication of petrogenic input of hydrocarbons in the surface sediments, supported by Hassaan *et al.*, (2024). The high predominance of low molecular weight n-alkane indicates oil contamination in the sample while its petroleum source input is corroborated by Sojinu *et al.*, (2012).

Table 1: Occurrence of compounds in sediment sample of Mosinmi, Sagamu

S/N	RT (mins)	Name	CAS Number	%Quality	%Area
1.	2.26	1-ethyl-2-methylcyclopentane	019781-68-1	59	33.26
2.	14.16	Cetene	000629-73-2	92	0.63
3.	16.03	E-15-Heptadecenal	100130-97-9	91	1.74

3.2 Occurrence of aliphatic Compounds in sediment sample of Mosinmi (outside depot), Sagamu

The n-alkanes in the sample ranged from nC_6 to nC_{26} (table 2). Hexacosene, 2, 6, 11-trimethyldodecane, nonadecene, hexadecane and tetradecane have similarity indices of 97%, 96%, 95%, 93% and 94% respectively. 1, 2- dimethylaziridine, 3methylene heptane and (E)- 2- octane show moderate similarity indices of 59%, 59% and 58% respectively. (Z)- 2- hexane is the saturate with the least similarity index of 53%.,indicating sensitive response to anthropogenic interactions and petroleum hydrocarbon pollution (Zhan *et al.*, 2022).The predominantly low to medium molecular weight nC_8 to nC_{19} n- alkanes reveals the abundant algal organic matter biomakers with terrigenous inputs (Egbeola *et al.*, 2024).

Table 2: Occurrence of compounds in sediment sample of Mosinmi (outside) depot, Sagamu

S/N	RT (mins)	Name	CAS Number	%Quality	%Area
1.	2.27	1,2-Dimethylaziridine	030757-96-1	59	2.68
2.	3.09	(Z)- 2-Hexene	007688-21-3	53	0.89
3.	4.33	3-methyleneheptane	001632-16-2	59	1.79
4.	4.46	(E)- 2- octane	013389-42-9	58	0.60
5.	12.15	Tetradecane	000629-59-4	94	0.63
6.	14.22	Hexadecane	000544-76-3	93	0.88
7.	16.06	1-Nonadecene	018435-45-5	95	8.80
8.	16.10	2,6,11-trimethyldo decane	031295-56-4	96	0.61

9.	22.06	1-Hexacosene	018835-33-1	97	0.84

3.3 Occurrence of aliphatic compounds in soil sample, Mosinmi (inside) depot, Sagamu

The n-alkanes ranged from nC_6 to nC_{35} (table 3), most of the compounds have similarity index above 70% while 1-bromo–4-bromomethylpetane and 1- methylpentane have similarity indices of 64% and 56% respectively. 2- Cyclopropylpentane and 1- docosene have relatively high area percentage of 13.39 and 11.64 respectively.

Table 3: Occurrence of compounds in soil sample of Mosinmi (inside) depot, Sagamu

S/N	RT (mins)	Name	CAS Number	%Quality	%Area
1.	2.21	2- methyl -Pentane	000107-83-5	56	5.34
2.	2.97	2-cyclopropyl-Pentane	005458-16-2	78	13.39
3.	12.08	(E)-5-Tetradecene	041446-66-6	96	1.04
4.	12.17	Tetradecane	000629-59-4	94	1.91
5.	13.21	Nonadecane	000629-92-5	83	0.38
6.	14.18	1-Octadecene	000112-88-9	94	5.32
7.	14.26	Hexadecane	000544-76-3	97	3.94
8.	15.18	Heptadecane	000629-78-7	90	0.24
9.	15.25	1-bromo-Octadecane	000112-89-0	83	0.42
10.	16.13	Hentriacontane	000630-04-6	91	2.39
11.	17.79	1-Docosene	001599-67-3	99	11.64
12.	20.11	1-Bromo-4-bromo-Methyldecane	061639-11-0	64	0.34
13.	26.40	17-Pentatriacontene	006971-40-0	87	0.44

3.4 Occurrence of aliphatic compounds in soil sample, Mosinmi (outside) depot, Sagamu

The compounds present in the soil sample of Mosinmi (outside depot) are n-alkanes ranging from nC_8 to nC_{19} (table 4). The number of saturated compounds detected was relatively small but with considerably high similarity index with octadecane having the highest index of 94% and 2-hexyloctylcyclopentane with the least similarity index of 70%. This is an indication of sensitive response to anthropogenic interactions and petroleum hydrocarbon pollution (Zhan *et al.*, 2022).

Table 4: Occurrence of compounds in soil sample of Mosinmi (outside) depot, Sagamu

S/N	RT (mins)	Name	CAS Number	% Quality	% Area
1.	2.99	2-cyclopropyl- pentane	005458-16-2	72	30.34
2.	16.01	1-Nonadecene	018435-45-5	91	2.13
3.	16.06	Octadecane	000593-45-3	94	0.42
4.	17.55	(2-hexyloctyl)-Cyclopentane	055044-77-4	70	0.78

3.5 Biogeochemical significance of organic biomarkers in selected ecosystems

The biogeochemical parameters determined were carbon Preference Index 1 (CPI_1), Natural alkane Ratio (NAR), Carbon Preference Index 2 (CPI_2), Odd-Even Carbon Prevalence (OEP), Pristane/Phytane (Pr/Ph), Pristane/Carbon-17 (Pr/nC_{17}), Phytane/Carbon-18 (Ph/nC_{18}), Average Chain Length (ACL), Low Molecular Weight/ High Molecular Weight (LMW/HMW) and Carbon- 31/ Carbon-29 ($n\text{-}C_{31}/C_{29}$) (table5).

The CPI_1 values of less than 1 are for n-alkanes derived from petroleum and other anthropogenic activities such as combustion of fuel, wood and agricultural debris and values greater than 1 is source indicator of n-alkanes in marine sediments (Nascimeto *et al.*, 2023), CPI_2 values greater than 1 is an indication of input from terrestrial higher plant wax.

The LMW/HMW values of less than 1 is an indication of n-alkanes in marine sediments, contribution from higher plants, marine animals and sedimentary bacteria and values greater than 1 showed contribution from petroleum and plankton sources. The n-alkane ratio (nC_{31}/nC_{19}) differentiates sources inputs of n-alkanes in marine sediments, serving a measure of relative proportions of allochthonous and autochthonous hydrocarbon inputs, values greater than 0.4 is associated with non-marine sources. The values of OEP less than 1 suggested an input from petroleum, strong bacteria activities or low flux of terrestrial vascular plant debris and NAR values less than 1 indicated an input from petroleum hydrocarbons, values greater than 1, origin from terrestrial higher plants or marine plants. The environment of deposition is inferred from the Pr/Ph values with values less 1 indicating anoxic, aquatic environment and greater than 1, oxic, terrestrial with contribution from terrigenous plants.

Table 5: Geochemical parameters in samples

Indices	Mosinmi(1)	Mosinmi(2)	Mosinmi (in)	Mosinmi (out)
CPI_1	6.73	3.27	1.12	1.21
CPI_2	0.05	1.28	2.37	4.26
NAR	0.74	0.72	0.21	-0.10
OEP	0.08	3.46	0.31	0.00
Pr/Ph	0.00	2.18	0.00	2.35
Pr/C_{17}	1.32	0.00	0.06	0.81
Ph/C_{18}	0.00	2.86	0.00	3.00
ACL	0.04	1.13	0.05	3.85
LMW/HMW	1.31	3.49	0.30	4.08

C_{31}/C_{19}	0.00	0.00	0.00	0.00

The samples depositional environments ranged from oxic, sub-oxic to anoxic in the terrestrial and aquatic environment while the anthropogenuc activities and possible pollution indication have been established.

4. CONCLUSION

Aliphatic compounds including Cetene, E-15- heptadecenal and. 1- ethyl -2- methylcyclopentane, nonadecene, hexadecane, tetradecane, 2- cyclopropyl- pentane, and 1- methylpentane were identified in the petroleum depot. The anthropogenic and petrogenic sources indications established while the origin of the biomarkers such as terrestrial, aquatic, lacustrine and environment of depositions including oxic, sub-oxic and anoxic determined.

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