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Crude Oil Fractions in the Environment: A Comparative Study of Agbada Community in Rivers State and American University of Nigeria Community in Yola, Adamawa State of Nigeria.

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Abstract: *Crude oil has been found to contain various compounds, with corresponding properties and effect on the environment where they are found. This study seeks to investigate the crude oil fractions in the environments of Agbada community in Rivers State (an oil-rich state) and American University of Nigeria, Yola, Adamawa State both in Nigeria. The investigations were carried out using four samples namely: two soil and two water samples from the two study locations respectively. The soil and water samples from Agbada community were used as the test samples whereas those from American university Yola were used as the control. Infra-red spectroscopy, Gas chromatography-Mass spectrometry investigations were carried out on the samples, including elemental analysis of water quality. The result obtained showed the presence of particulates and heavy molecular weight hydrocarbons of various kind in the water and soil samples from Agbada community whereas water and soil samples from American university Yola were found to contain few and lower molecular weight hydrocarbons. It follows that the environment of Agbada community stands to be heavily polluted with these harmful heavy hydrocarbons with corresponding negative impact on the ecosystem, thus a need for routine clean-up of such environment for sustainability of its ecosystem.*

Keywords: *Crude oil, Environment, Hydrocarbons, Soil, water.*

I. Introduction

The historic discovery of crude oil in Nigeria by Shell British Petroleum at Oloibiri village in the present Bayelsa State in 1956 and its progressive exploration and exploitations has caused a lot of environmental issues especially in the entire sub-region of the explorations known as the Niger-Delta region comprising of several states namely, Imo, Akwa Ibom, Abia, Cross River, Bayelsa, Delta, Edo, Ondo and Rivers [1]. The environmental issues range from wild life destruction, farm land wasting, fish poisoning, water pollution and general disruption of the ecosystem. These issues arose due to the physicochemical interactions between the chemical components of crude oil and matter in the environment.

Crude oil is said to be a complex mixture of hydrocarbons ranging up to tens of thousands with significant amount of non-hydrocarbon and thus when discharged to the environment directly or indirectly mostly due to oil spillage will interact with the environment leading to its degradation [2]. Some of these hydrocarbons form a group called aromatics or BTEX group and they includes benzene, toluene, ethyl benzene and xylene derivatives amongst others; while other groups are known as poly nuclear aromatics or poly cyclic aromatic hydrocarbons which are found to be easily degraded by microbes [3]. On the other hand, there are the total petroleum hydrocarbons (TPH) which United States Environmental Protection Agency, EPA (2014) defined as a large family of several hundreds of chemical compounds that originates from crude oil. Crude oil is utilized intensively in the production of varieties of petroleum products and petrochemicals, which of course usually find their way directly or indirectly into our environmental media such as water and soil. More so, asserting to the fact that there are so many different chemicals found in crude oil and in other related petroleum products, it is then not empirical to measure each one separately. However, it is quite useful to measure the total amount of TPH in a media, mostly water and soil. It follows that the determination of total petroleum hydrocarbons depends on the analysis of the media in which they are found. TPH is therefore a mere mixture of chemicals, but they are all constituents of hydrogen and carbon, and thus are called hydrocarbons. In general, scientists divided TPH into groups of petroleum hydrocarbons that act alike in soil or water. These groups are known as petroleum hydrocarbon fractions with each fraction consisting of several individual chemicals. Examples of such chemicals includes hexane, mineral oils, toluene, jet fuels xylenes, naphthalene, benzene and fluorene, in addition to other petroleum products and gasoline components. However, it is most likely that samples of TPH will contain mainly some, or a mixture, of these chemicals [4].

Since the discovery of crude oil, its extraction, refinement, transportation and storage has been accompanied with a lot of occasional hazards leading to oil spillage. This spillage which could be as a result of natural disaster or man activities results in the accidental discharge of crude oil into the ecosystem directly or

indirectly [5]. Africa Network for Environmental and Economic Justice, ANEEJ (2004) reported that oil spillage exacts large effect on the totality of the ecosystem where it occurs. Furthermore, 5 to 10% Nigeria mangrove ecosystems have been wiped out either by settlement or as a result of oil spillage, in addition to the fact that rain forests which previously occupied some 7400km/sq. of land has recently disappeared courtesy of man activities including oil explorations, exploitations and spillage [6]. Oil spill affects the environment in about three ways; by poisoning consumers after ingestion of affected agricultural products, by direct contact and distorting the natural habitat [7]. Oil spillage has also led to the degradation of agricultural landmass, destruction of aquatic life, general reduction in the yield of agricultural production as a result of decrease in soil fertility [8].

In a study of socio-economic impact of oil pollution, Omofonmwan and Odia stated that crude oil explorations and exploitation has had an adverse environmental effect on the soil, forest and water bodies in host communities in the Niger Delta region. Many farmers have lost their farmlands, and consequently had no other choice than to relocate to other communities in search of livelihood thus exerting congestion on the natural resources in that geographical area. It is noteworthy that, the devastating consequences of oil spill in Niger Delta region with its eventual hazards on both aerial and terrestrial environments surmount to an irreversible chain effect on both the biodiversity and safety of the overall ecosystem [9].

This research study attempts to draw a distinct contrast between a community within the Niger delta region known as Agbada community and a community far away from the region geographically, thus supporting the much researched issue of environmental pollution of the Niger delta region through the processes of crude oil exploration and exploitation.

II. Materials and Methods

2.1 Sample collection and preparations: The samples were collected from both communities at random and convened to the Petroleum Chemistry Research Laboratory of American University of Nigeria Yola where the analyses were conducted. The solvent extraction method was used for the extraction of the crude oil fractions from the soil samples using methylene chloride as the solvent. 10g of both soil samples respectively were weighed and transferred into separating funnels containing 15ml methylene chloride and shaken vigorously to produce a thorough mixture and then allowed to settle for 5 minutes in fume hood at ambient temperature. The separating funnel taps were opened to drain off all the crude oil fractions from the two soil samples into two beakers and then stored properly for further instrumental analysis.

2.2 IR Spectroscopy: The instrument used for obtaining the IR spectra was Thermo Electron Corporation IR Spectrophotometer. Two drops of the samples were placed on one of the KBr plates and spread sensibly around the top of the plate into a thin capillary film and enclosed with a second plate. The plates were gently inserted into the plate holder and then introduced into the IR spectrometer machine.

2.3 Gas chromatography mass spectrometry: Gas chromatography is a method of analysis which is used to separate the components of oils based on their volatility. This is complemented by a mass spectrometric analysis, which gives the names and masses of possible compounds with a specific peak and their percentage composition in the samples. Agilent GC 7890-MS 5975C fitted with a column stationary phase DB-5MS (30m x 0.25µm) was used in the analyses of the control sample (AUN) and for the contaminated sample. Helium gas was used as the carrier gas at flow rate of 1ml/min with an oven temperature of 40^0 C and an inlet temperature of 270^0C. The major aim of this procedure is to carry out a gas chromatography analysis as well as to obtain a mass spectrometric analysis of the samples compared.

2.4 Water quality test: The water quality test was carried out by the use of Vernier lab Quest for water quality testing, which provides instant data on water quality, either in a laboratory or in the field. The Lab Quest was connected with the PH sensor, Turbidity sensor, Alkalinity sensor to collect the data's by dipping the sensors into the water sample.

III. Figures and Tables

Table 1: IR of the Control Sample (AUN)

Alkyl halides	850–550 (m)	C–Cl stretch
Aldehydes	2830–2695 (m)	H–C=O: C–H stretch
Alkanes	3000–2850 (m)	C–H stretch
Aromatic amines	1335–1250 (s)	C–N stretch
Alkanes	1470–1450 (m)	C–H bend
Aromatics	1500–1400 (m)	C–C stretch (in–ring)

Table 2: The IR ranges for Contaminated Sample (Agbada)

Functional Group	**Characteristic Absorption (s) (cm^{-1})**	**Bond**
Alkane	2950-2850 (m or s)	Alkyl C-H Stretch
Alkane	1600-1585	C-C stretch (in-ring)
Alkanes	1470–1450 (m)	C–H bend
Alkanes	725–720 (m)	C–H rock
Aromatic	860-680 (s)	C-H Bending
Aromatic	1700-1500 (m,m)	C=C Bending
aromatics	1600–1585 (m)	C–C stretch (in–ring)
Alkenyl	1680- 1620 (v)	C=C Stretch
Alkyl halides	1300-1150 (m)	C-H wag (-CH_2X)
Alkyl halides	850-550 (m)	C–Cl stretch
alkyl halides	690–515 (m)	C–Br stretch
Alkenes	1000–650 (s)	=C–H bend
1˚ amines	1650–1580 (m)	N–H bend
Alkynes	700–610 (b, s)	–C≡C–H: C–H bend

From table 1 & 2' while we observe few hydrocarbons (aromatics) presence in the soil samples of the control (AUN), the soil samples from Agbada contains multiple hydrocarbons, aromatics and alkyl halides. This signifies that there is a higher TPH contamination in the Agbada soil sample than that of the control sample from AUN.

Table 3: The Gas Chromatogram Data of Control Sample (AUN)

Serial No	Retention Time (s)	Compound	Molecular Weight	Quality time
1	4.772	p-xylene	106	94
2	2.517	1-Buten-3-yne, 1-chloro	86	64
3	2.447	1,2,3- Butatriene, 1-chloro-	86	72

Table 4: The Gas Chromatogram Data of Test Sample (Agbada)

Peaks Serial No	**Retention Time (s)**	**Compound**	**Molecular weight**	**Quality**
1	**10.0099**	Nondecane	**268**	**90**
2	**10.116**	Tricosane	**324**	**87**
3	**10.311**	2-piperidinone, N-(bromo-n-butyl)	**233**	**94**
4	**10.327**	17-pentatriacontene	**490**	**86**
5	**11.701**	1-Heptadecene	**238**	**84**
6	**11.701**	Oxirane, tridecyl	**248**	**81**
7	**10.122**	Benzene,(1-hexyltetradecyl)	**358**	**70**
8	**11.711**	N-(1-hydroxy-4-oxo-1-phenylperhydroquinolizin-3-yl) carbamic acid, benzyl ester	**394**	**91**
9	**11.805**	2-Methyl-cis-7,8epoxynonadecane	**300**	**85**
10	**11.810**	1-Heptadecene	**240**	**90**

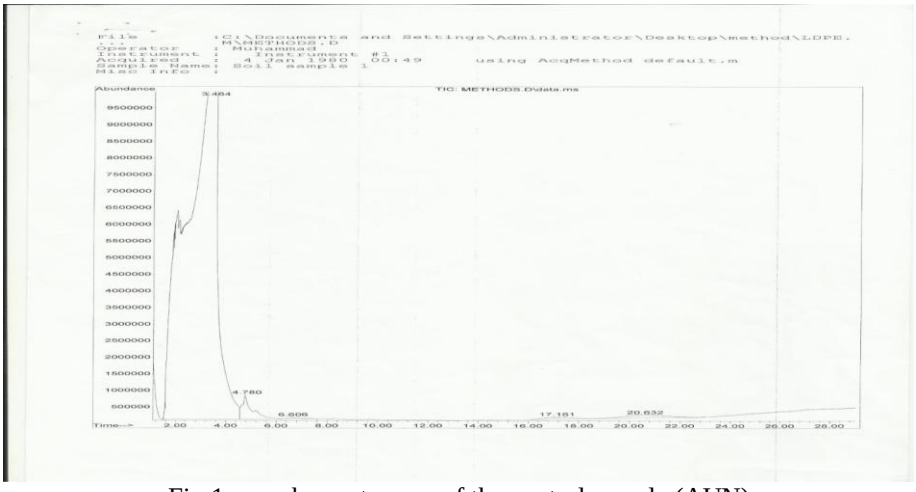

Fig 1: gas chromatogram of the control sample (AUN)

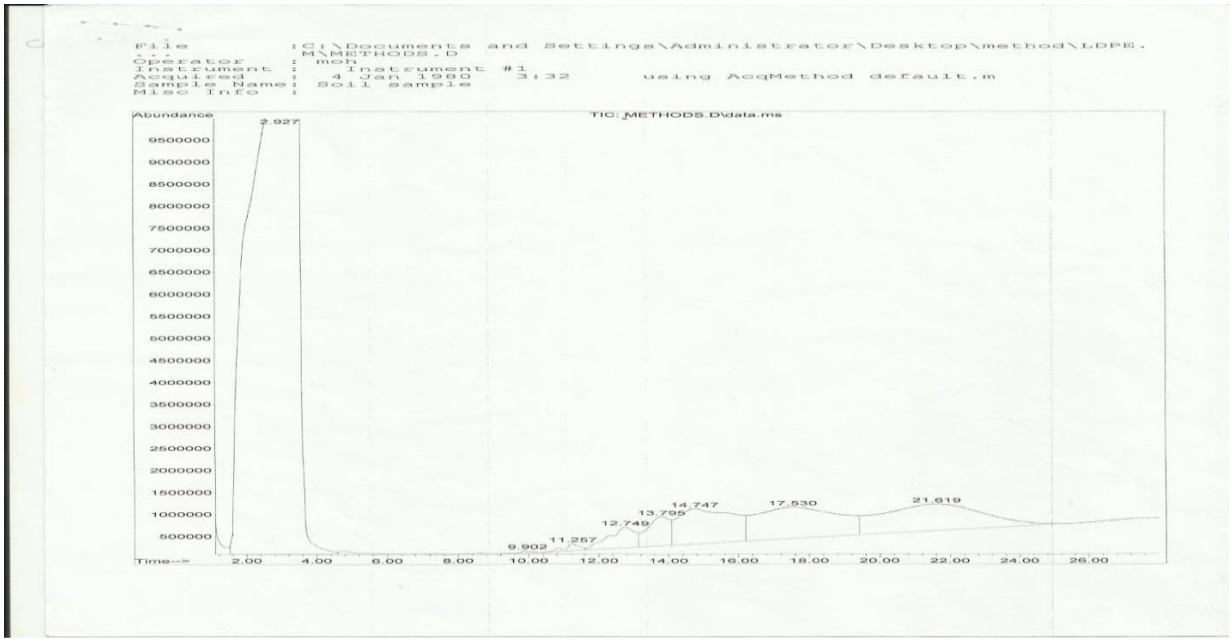

Fig 2: gas chromatogram of the contaminated sample (Agbada)

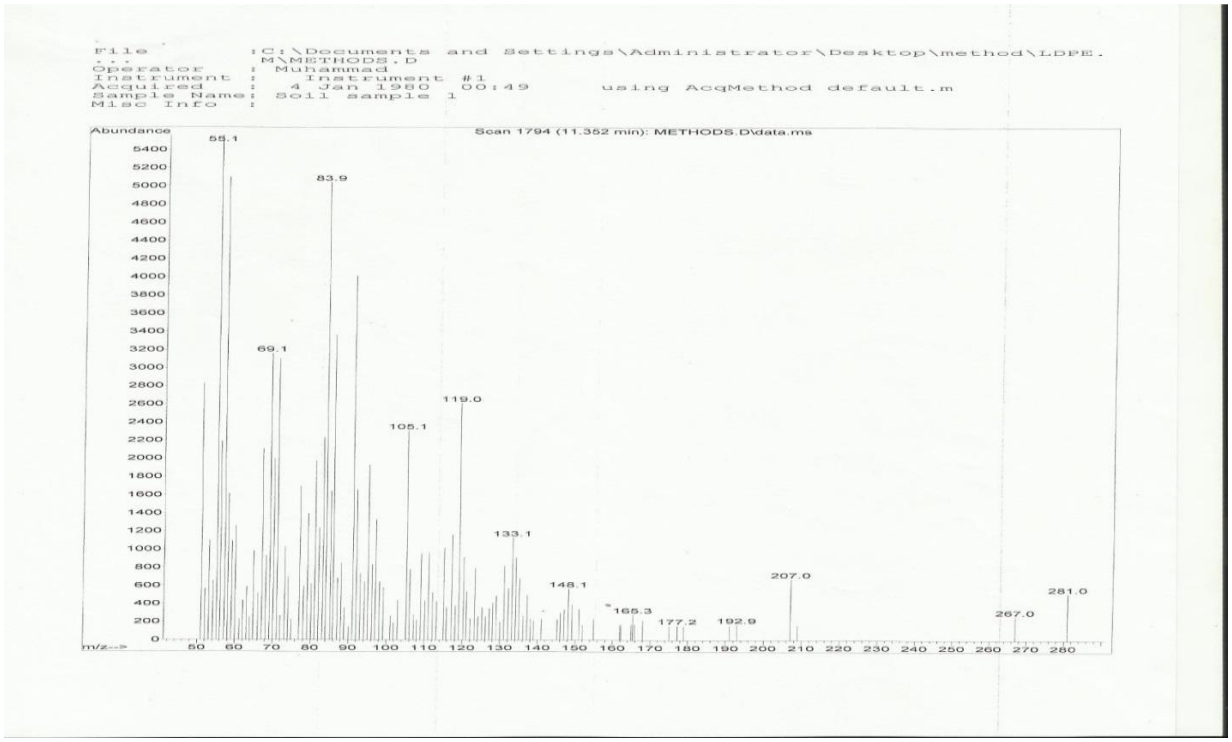

Fig 3: Mass Spectra of control sample (AUN)

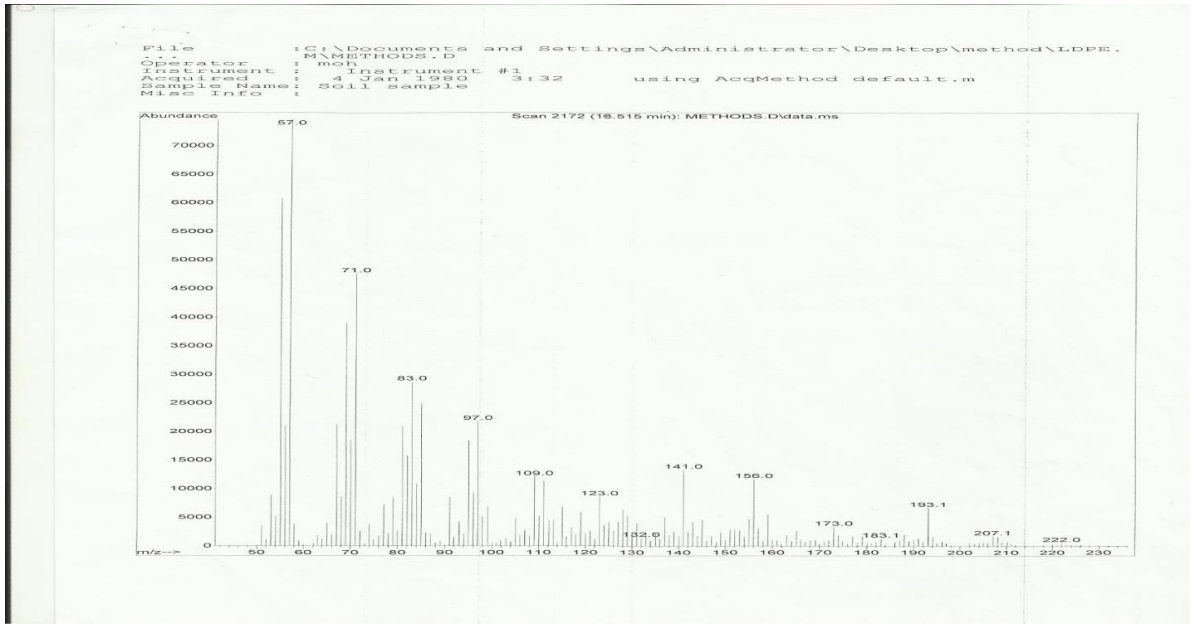

Fig 4: Mass Spectrum of Contaminated sample (Agbada)

The MS and structures for the individual component in the control sample (AUN)

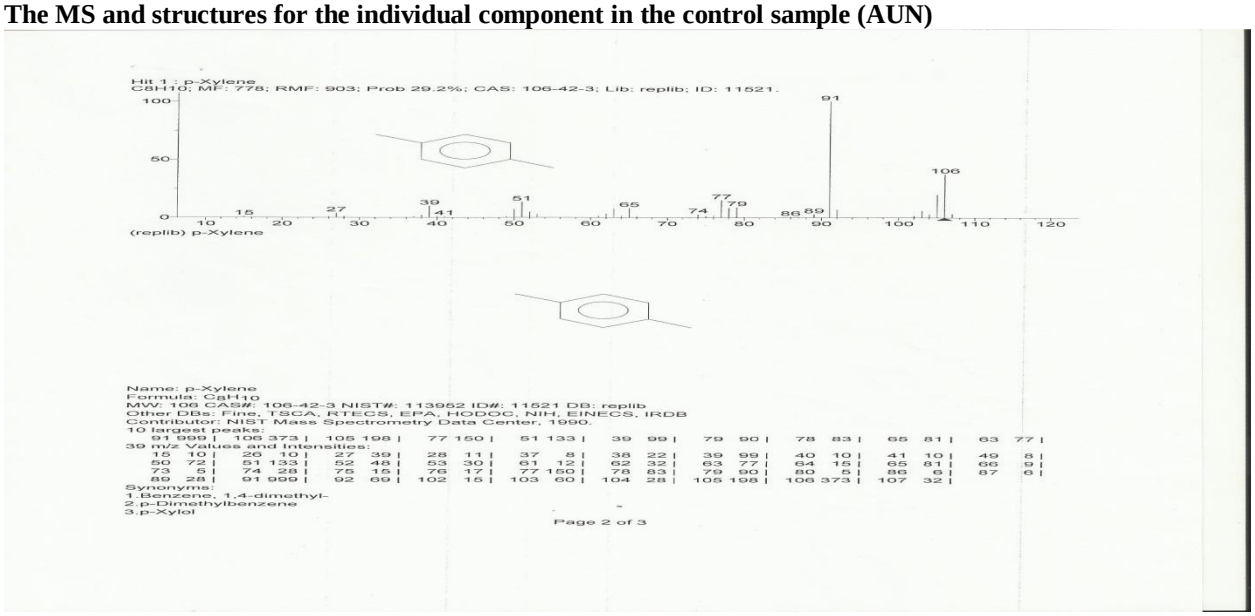

Fig 5: p-xylene

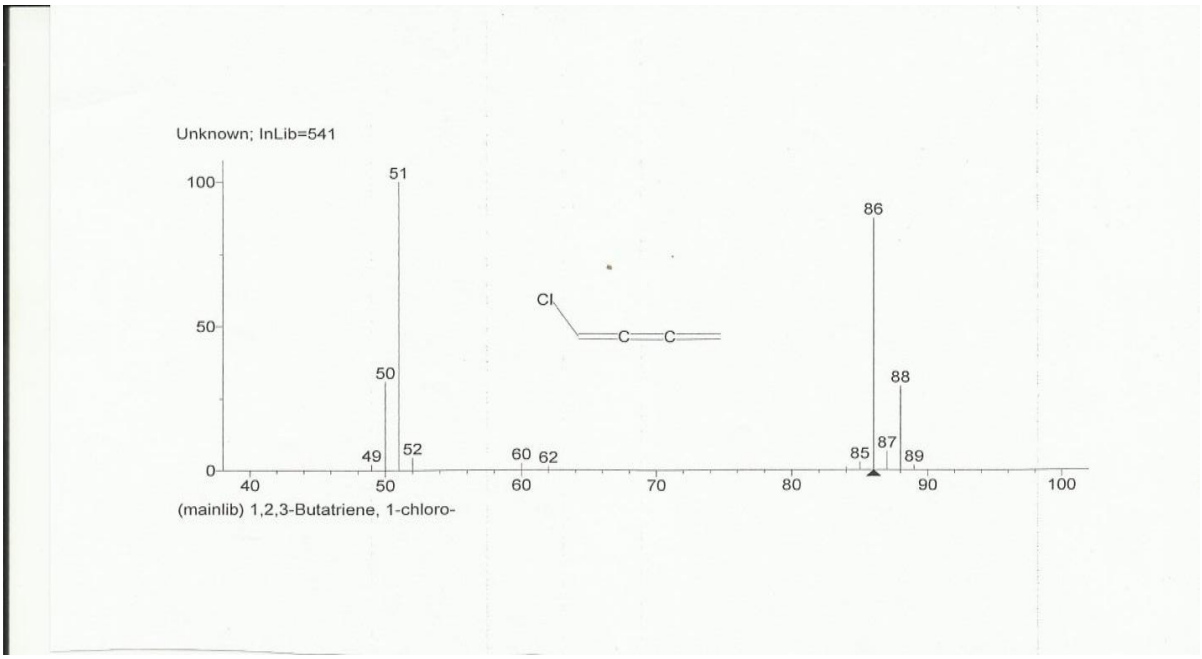

Fig 6: 1, 2, 3- Butatriene, 1-chloro-

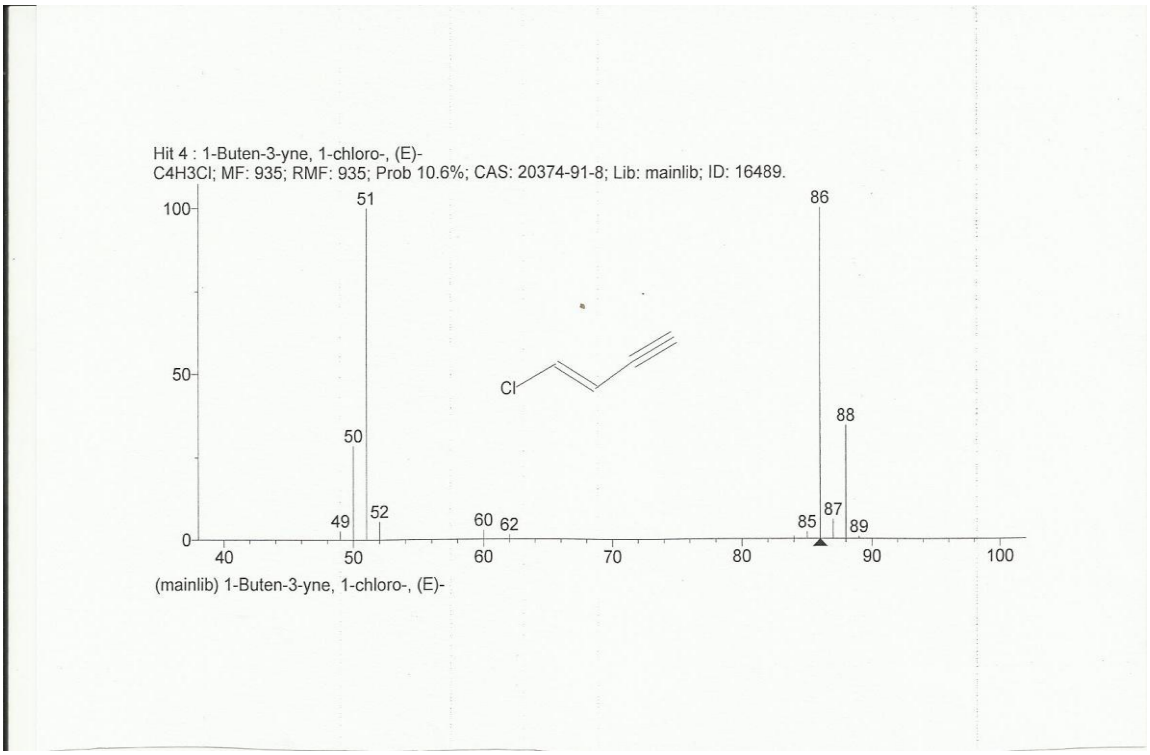

Fig 7: 1-Buten-3-yne, 1-chloro

The MS and structures for the individual component in the test sample (Agbada)

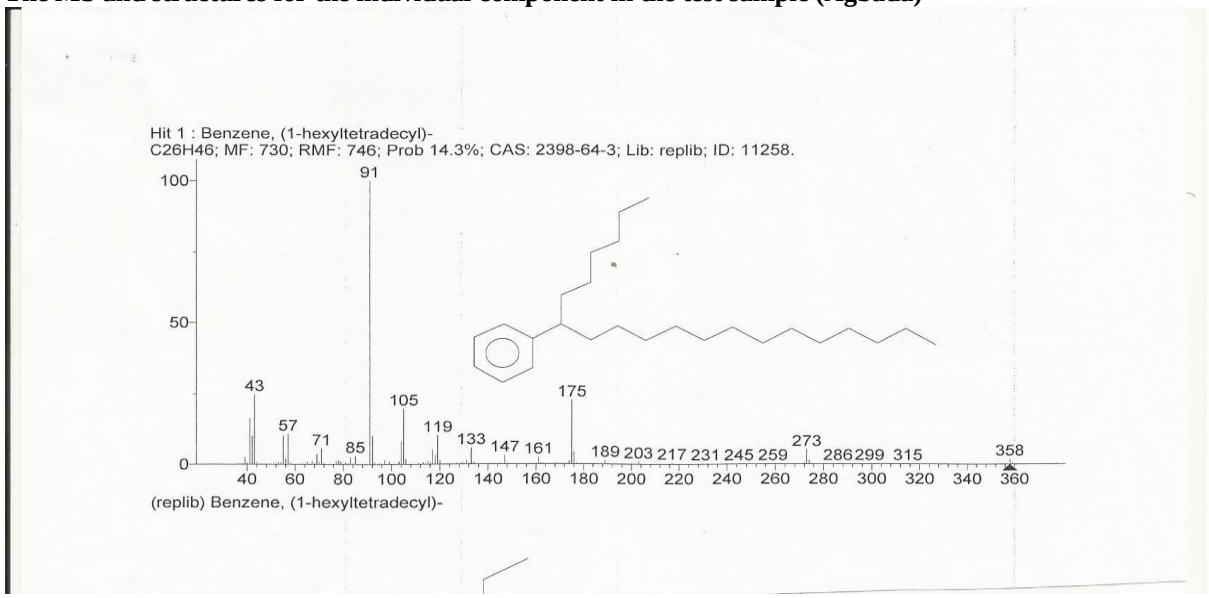

Fig 8: Benzene, (1-hexyltetradecyl)

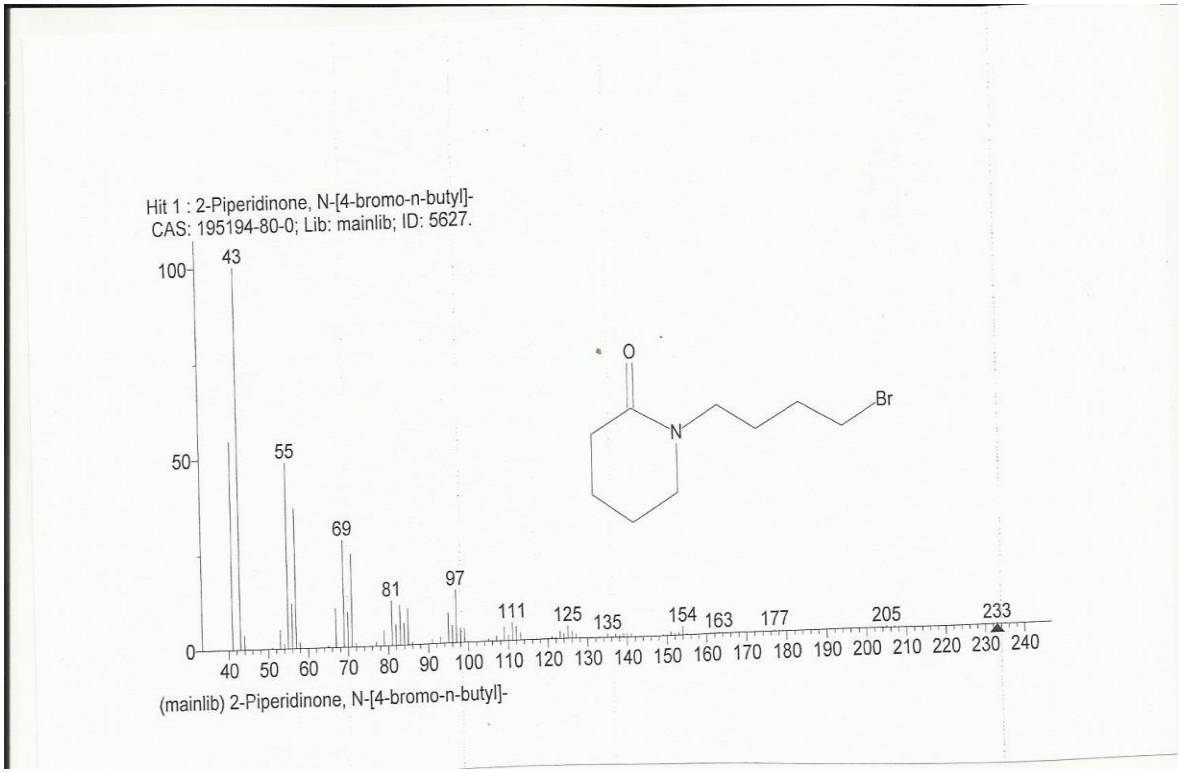

Fig 9: 1,2,3- Butatriene, 1-chloro-

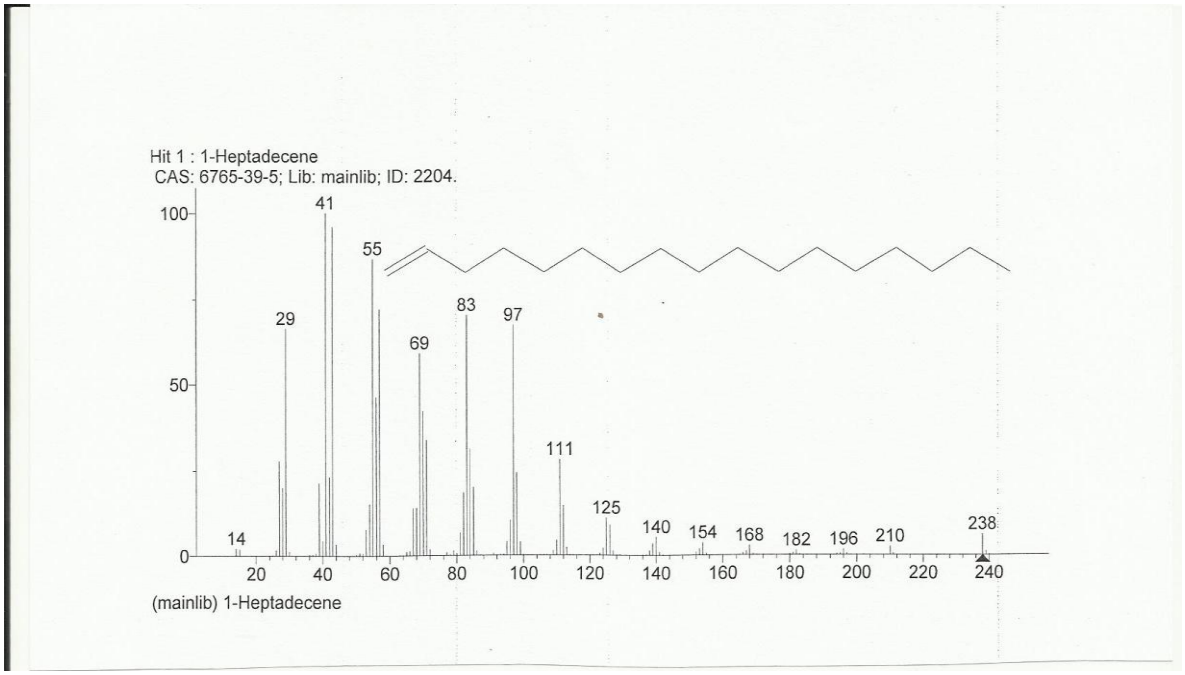

Fig 10: 1-Heptadecene

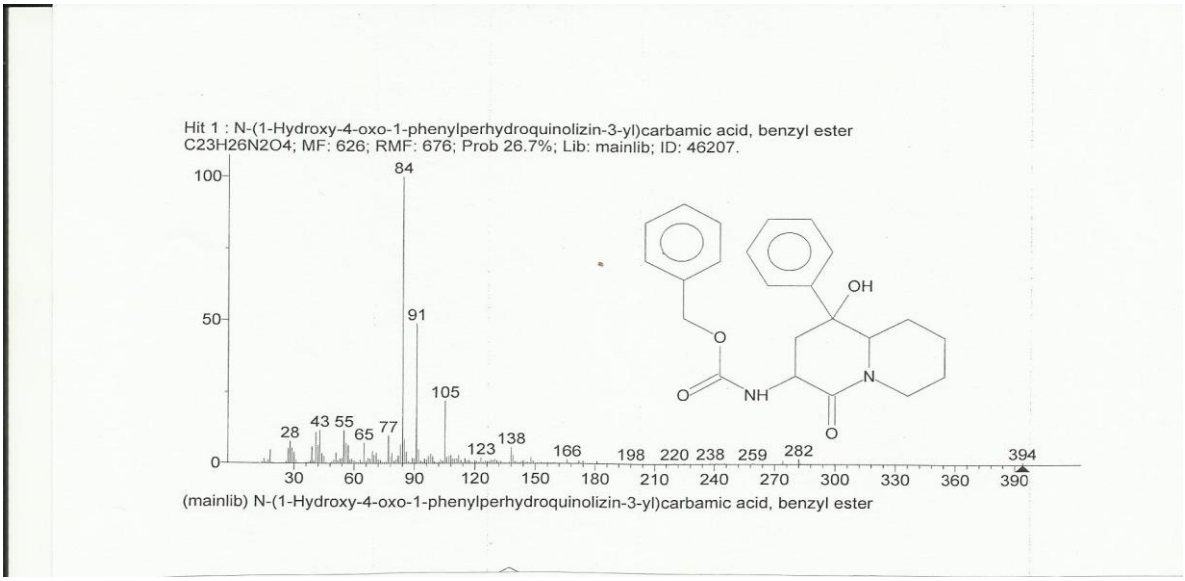

Fig 11: N-(1-hydroxy-4-oxo-1-phenylperhydroquinolizin-3-yl) carbamic acid, benzyl ester

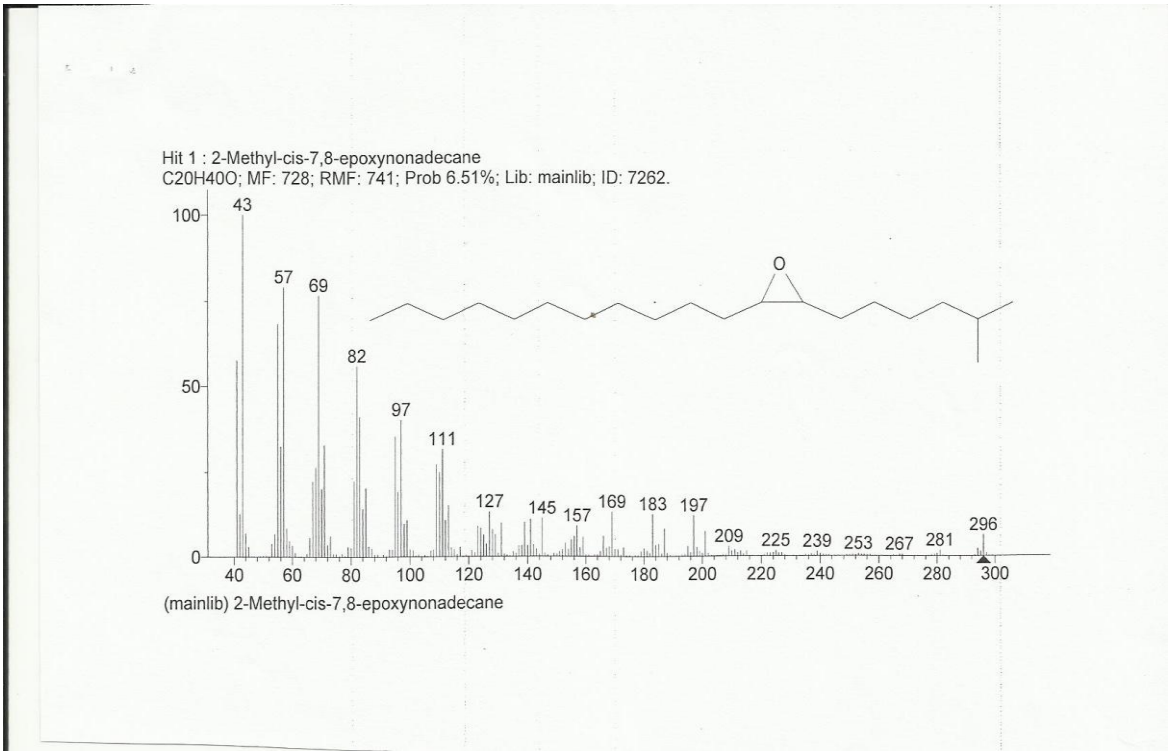

Fig 12: 2-Methyl-cis-7, 8-epoxynonadecane

From the GC-MS data of tables 3 & 4, as well as figures 1 & 2, there were fewer hydrocarbons presence in control sample as compared with the Agbada samples, signifying that the TPH value in the Agbada soil is predominantly higher than in the control sample.

The MS results as shown in figures 3-12, reveals higher presence of aromatic compounds and long chain hydrocarbons in the Agbada samples than in the control samples.

3.4 Water quality test

Table 5: The Water Quality Tests and Results.

Test	**Agbada (contaminant)**	**AUN (control sample)**
PH	6.03 (Unlikely to be directly harmful to fish unless free CO_2 is high).	5.93
Turbidity (NTU)	40.1	1.8
TDS (µs/cm)	214	90
Alkalinity	8.27	6.27

From the results of table 5, the high level of turbidity and total solids present in the Agbada water sample could have been as a result of the dissolution of particulates evolved from long contamination of the water source by hydrocarbons.

3.5 Soil elemental Analysis and heat value

Table 6: The elemental analysis and heat value of both samples.

	Contaminant (Agbada)	**Control sample**
Nitrogen	0.0653446	0.008298319
Carbon	5.524679661	2.06659554
Hydrogen	5.53779125213623	5.33153247833251
Sulfur	0	0
GHV	453.0237427	194.4058228
NHV	453.0237427	190.6851044
CO_2	106.7620468	94.8788681
Weight	74.95	51.05

The higher heating value of the Agbada sample (table 6 & figure 14), confirms the higher amount of contaminants in the sample compared with the control sample from AUN. Table 6 and figure 13 results also reveals higher carbon content in the Agbada sample.

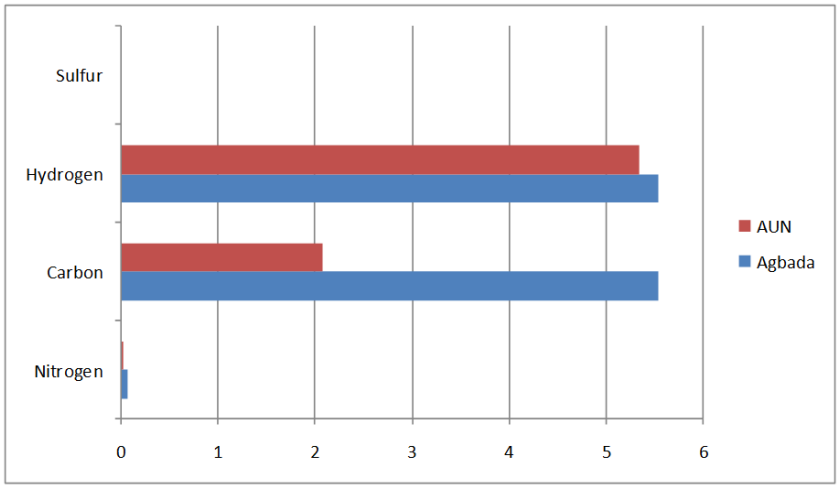

Fig 13: Bar chart comparing elements present in Agbada and AUN soil samples

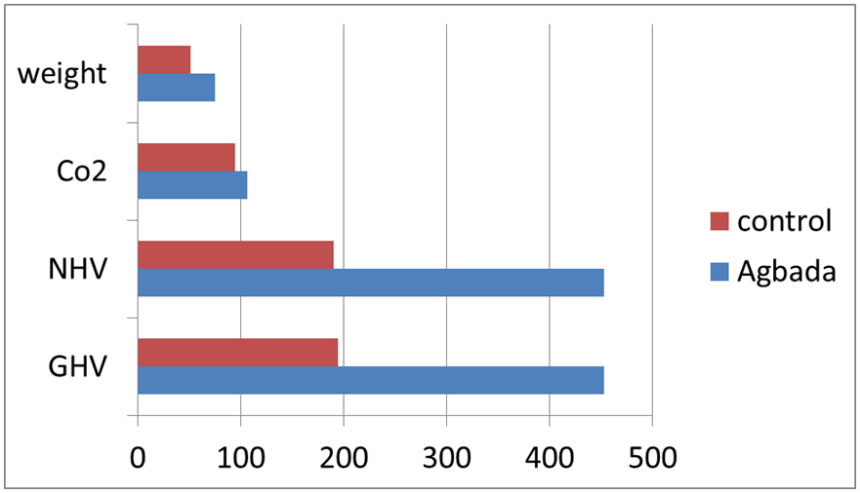

Fig 14: Bar chart of heat content

IV. Conclusion

We have observed high presence of long chain hydrocarbons, aromatic compounds and alkyl halides in the soil and water samples from Agbada community in Rivers State. The impact of crude oil fractions on the degradation of the environment of Agbada community as well as other communities in Niger delta region of Nigeria is quite obvious and this has raised a lot of concern from the generality of the communities who have suffered polluted air, water resources, degraded farm lands, and very high atmospheric temperature. This study has thus generated an empirical confirmation of this fact.

We therefore recommend immediate commencement of proper clean-up of the contaminated soil and water in the Agbada community in order to avert impending health crises in that community and the Niger delta region of Nigeria.

Acknowledgements

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