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Comparative Effect of Artisinal Crude Oil Products' Storage on the Soils of Ijalla and Okere-Urhobo Communities, Warri, Delta State, Nigeria

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Abstract- Illegal (Artisanal) refining of petroleum products in Niger Delta creeks has been a great concern over the years as it has debilitating effects on the environment. This study aimed at determining the effects of artisanal products on the geochemical status of the soil of Ijalla and Okere-Urhobo community. To achieve this, 10 soil samples each were collected from both communities. Back titration was used to determine the TOC in the samples while n-hexane was used to extract the oil and grease from measured samples. Biomarkers of AHCs were detected using GC-FID after the extracts were collected by the soxhlet extraction method using dichloromethane as the solvent for extraction and then fractionated into AHCs, Aromatics Hydrocarbon and NSOs using Column Chromatography. Elution of fractions in the column was achieved using n- hexane, Dichloromethane and chloroform of AHCs, Aromatics and NSOs respectively. Aliphatic Hydrocarbons in both sites shows that more AHCs were present in IJalla sites than Okere-Urhobo. A pristane/phytane ratio that is near to 1 in the context of the okere-urhobo assumed non-petroleum soil indicates that the organic matter contained in the soil is probably of mixed origin while some samples of Ijalla has a CPI close to 1 suggests minimal microbial degradation and a predominantly terrestrial source. The TOC results shows that all soil samples have POC greater than 0.2%, which indicates that both soil has other source carbon. In comparison, Ijalla site is much higher than that of Okere-Urhobo. On analysis of O%G, the samples from Ijalla have an average concentration of oil and grease of 5440mg/kg with soil JA having 7460mg/kg, which far exceeds the DPR, (Department of Pesticides Regulation), California, 2007 states the maximum permissible concentration of oil and grease is 1000mg/kg in an average of 30cm depths.

Keywords- Artisinal refinery, Artisinal crude oil, Aliphatic hydrocarbons

I. INTRODUCTION

Artisanal means products gotten from local ways. It is an alternative method of making crafts in a more traditional way. Or a craft requiring manual skill, an artisan is a skilled or craft person who makes or creates material objects partly or entirely by hand or with little minimum requirement of orthodox techniques. (Wikipedia 2023). The activities of artisanal refiners pose a lot of environmental threat to the environment (air, water and soil). During the refining process, a lot of spilling is done either accidentally or intentionally. During the refining process a lot of heating is carried out, thereby releasing gases and heavy metals into the atmosphere, these pollutants are washed down into the soil during rainfall or atmospheric condensation. These pollutants in the soil, have adverse effect on people around its operation including its users. As a result of deposition of heavy chemicals in sediments and soil which can affects humans, animals and plants within the environment. This research work is set to analyse the Total Organic Carbon (TOC) in the soil, the Oil and grease contents of both soils, Biomarkers' of aliphatic hydrocarbons the soil (AHC).The objectives of this study is to; Determine the amount of the Total Organic Carbon (TOC) of the soil, level of Oil and Grease (O&G) content of the soil, and the Biomarkers of Saturated hydrocarbon of the soil.

This study is carried out to ascertain health safety of the inhabitants of the people of Ijalla community; how healthy are their plants and animals, including the quality of their Agricultural Produce by comparing the soils of Okere-Urhobo with Ijalla, by checking for crude oil pollution parameters in both soils. This is because crude oil polluted soils leads to the production of plants and animals that becomes hazardous to health when consumed. The soil quality parameters were analyzed classically or instrumentally as the case may be. Oil and grease contents of both soils will be analysed using N-hexane direct extraction method on soils, the Total organic Carbon (TOC) will be analysed using walkey-blackey back titration method (wet chemistry), fractionation of extracts from samples will achieved using column chromatography separation methods, samples are to be fractionated into Aliphatic Hydrocarbons (AHC), Aromatic Hydrocarbons and Nitrogen Sulphur Oxygen Compounds (NSOs). The AHCs were further analysed using the Gas Chromatography – flame Ionization detector to check the level of Isoprenoids, pristine, and phytane biomarkers.

II. MATERIALS AND METHODS

1. Area of the Study

Between latitude 5o46'05"N and longitude 5o03'41"E is Ijala Creek. It can be found in the low-density Ijala, Ifie-kporo, and Aja-etan towns in Delta state, Nigeria's Warri South local government area, and it flows to the Tori Creek.

2. Sampling

Soil samples were collected from twenty Agricultural farmlands, ten each from Ijalla on and Okere-Urhobo community. The soil samples were collected from 20cm depth into plastics and glass bottle sampling containers.

3. Materials and Chemicals

The materials used for soil sampling in both communities are: Auger, Trowel, Cutlass, Acetone, Wash bottles, Distilled water, White clean pre-extracted Handkerchief, Sample bottles (glass and plastic), Latex Gloves.

4. Sample Preservation

Samples were refrigerated at a temperature of 40C for one week prior to analysis. This is due to arrangement and preparation of relevant apparatus needed for the of laboratory work.

Extraction and Determination of Oil and Grease from Soil

Oil and grease in the samples were extracted classically from samples of both communities. Oil is liquid mixture of different hydrocarbons present in the soil sample while grease is a thick oil substance. Oil and grease are usually present in suspected petroleum polluted media hence there is need to check for the average content in the samples.

Materials and Chemicals

Conical flask(250ml), Anhydrous Sodium Sulphate , Whatman 0.4mm Filter paper, Funnel, 250mlBeakers, N-Hexane (analytical grade), Separating Funnel, Distilled water.

Sample Preparation

After being air dried for five days, each sample was weighed at 50g using an electronic analytical weighing scale (S-Metter FA210A model, USA). The samples were then ground in a ceramic mortar and sieved using a 30mm screen.

Oil and Grease Extraction Procedure

50g of each sample was weighed into a 250 ml beaker, 20 ml of N-hexane was added, and the soil was gently mixed. The hexane extract was then decanted into a conical flask that had been previously been weighed. To enable the greatest possible extraction of oil and grease from the soil sample, 20ml more hexane was added. The extract was added to a separating funnel, 1g of anhydrous sodium sulphate was added, and the funnel was lightly shaken. A check was made to see if any water layer would form, and that layer was first run off before the hexane layer was collected in a pre-weighed 250ml conical flask using filter paper. The weight of the oil and grease was then calculated when the extract had finished evaporating, to be sure there is a weight constituency, weight was measured three days in a row.

Extraction of Soil Samples Using Soxhlet Extraction

Each soil sample was sieved with a 30mm mesh sieve before being weighed at 40g. The soil samples are sieved and then properly combined in a plastic container. Crude oil products were extracted using the Soxhlet extraction method from each sample in a series of extractions. Also added to the soil was 10g of sodium sulphate powder, which was metered out into a thimble. The soxhlet extractor jar was cautiously lowered with the thimble within. Six anti-bumping granules put to a dry, clean 250 ml round flask the six soxhlet extractor units were put up and linked correctly. There was refluxing of 12 hours spent on each sample, following which the water bath was turned off. After that, the solvent was separated from the extract and collected into a beaker, leaving roughly 50ml of solvent behind. The extract was washed into a second, already weighed 100 ml round bottom flask. To remove any residual extract from the 500ml bottom flask, it was rinsed twice with 10ml of distilled solvent. The washing was then added to the 100ml circular bottom flask. Once the solvent has been distilled off, the 250 ml round bottom flask was connected to the distillation system. A 100ml round bottom flask was weighed and recorded using an analytical balance after being weighed and dried in a desiccator.

Fractionation of Extracts

In order to determine the concentration of Aliphatic Hydrocarbons (saturated) in the samples, there is need to separate to chromatographically elute various fractions from the extract. The fractions eluted in this work are AHCs, Aromatic Hydrocarbons and Nitrogen, Sulphur Oxygen containing compounds (NSOs).

Materials and Chemicals

1mx1m3 Column Chromatography, N-Hexane (analytical grade), Dichloromethane (analytical grade), Chloroform (analytical grade), Silica gel (60-120mesh), conical flask (250ml), Glass dropper, beaker (250ml).

Fractionation Procedure

The silica gel was first activated at a temperature of 1200 c for two hours before being developed in N-hexane. The column was carefully packed using slurry method. The sample was introduced into the packed column measuring 1ml of the extracts using a glass dropper to drop the sample extract into the column. The extracts is covered with silica gel and then n- hexane is used to elute the aliphatic hydrocarbon (Saturated hydrocarbon). Aromatic hydrocarbon is then eluted with Dichloromethane, after ensure all the hexane in the column has dried out. Lastly is the elution of NSO (Nitrogen, Sulphur and Oxygen compounds) using Chloroform. (Ibe et. Al., 2006).

Determination of Aliphatic Hydrocarbon Biomarkers in Analytical Test Method: USEPA 8015b Soil Sample.

Instruments, Materials and Chemicals

Agilent Technology, Palo Alto, California, USA, is the manufacturer of the Agilent 7890 Gas Chromatography-Flame Ionization Detector (GC-FID). Rotary evaporator (Searchtech instrument; RE52-2 type; USA), 2 ml Teflon Screw-cap vial, glass wool, glass fractionating column, and 2 ml glass pipette. Electronic analytical weighing balance (S-

Mettle; FA210A model; USA), 250 ml Erlenmeyer flask, 250 ml extraction glass flask, 100 ml conical flask, a 100 ml beaker, soxhlet extractor, 100 ml measuring cylinder, hand gloves, and organic nasal mask.

GC-FID analysis Procedure

The saturated Hydrocarbon extracts was transfer to a round bottom flask and concentrated to 1ml final volume using a rotary evaporator. The concentrate was pipetted into a clean 2ml Teflon screw-cap vial and cap tightly, labelled and preserved to avoid oxidation prior to aliphatic hydrocarbon biomarker analysis with GC-FID.

GC-FID Working Condition

Using an Agilent 7890B, the analyte in the sample was separated and found. In order to analyze the aliphatic hydrocarbon fractions, a Gas Chromatograph-Flame Ionization Detector (GC-FID) fitted with an auto sampler was employed. A 30m x 0.32mm HP-5 5% Phenyl Methyl Siloxane coated fused capillary column with a film thickness of 0.25 m received an injection of 1 l of sample solution in the spilt mode. The column head pressure was kept at 12.6 psi while helium was employed as the carrier gas to produce a steady flow of 1.5 ml/min. Additional pre-set working parameters included a split ratio of 10:1, a split flow of 31.0 mL/min, a total flow of 36.6 mL/min, a saver flow of 20.0 mL/min, a saver time of 2.00 min, an average velocity of 48 cm/sec, a hydrogen flow of 35.0 mL/min, and an air flow of 350.0 mL/min. make-up flow : 20.0 mL/min, injection temperature of 250o C, and 320o C for the flame ionization detector. The column temperature was originally maintained at 50°C for 2 minutes before being raised to 300°C at a rate of 24°C/min and maintained for 15 minutes. Since each aliphatic compound has a unique retention time in the column, the aliphatic compound identification time was based on retention time. The individuals with the lowest retention times were found first, then those with the highest retention times.

Determination of Total Organ Carbon (TOC)

Wet chemistry technique was used for the determination of the TOC in the soil samples. Two phases were involved which are the samples extraction and the samples quantitation. Samples air-dried for 4 days and grounded in ceramic mortar, the samples were sieved in a 2mm mesh.

Materials and Chemicals

500ml conical flask, Burettes, 100ml measuring cylinder, Sodiumflouride salt, Concentrated Tetraoxosulphate (VI) acid, 1N potassium heptaoxodichromate (VI) (K2Cr2O7), Distilled water, Diphenylamine indicator, 0.5N Ferrous ammonium tetraoxosulphate (VI) (NH4)2FeSO4.6H2O).

TOC Determination Procedure

The Walkley-Black method was used to calculate total organic carbon. To oxidize the organic components in the sample, 1.0g of soil was weighed into a 500ml conical flask, 10cm3 of 1N potassium heptaoxodichromate (VI), and then 20cm3 of concentrated tetraoxosulphate (VI) acid were added through two distinct burettes. After a brief spin, the mixture was left for 30 minutes. Tetraoxophospate (v) and 100ml of distilled water were added to the solution to dilute it and stop the diphenylamine indicator from oxidizing. In order to bind any refractory metals like Ca, Mg, etc., 0.2g of sodium fluoride was added. A second burette filled with acidified Iron (II) sulphate was filled with the mixture and titrated against it using 2 drops of phenyl amine indicator. Titration was done slowly and meticulously with a distinct color compared to the blank (without sample), which had gone through the same process as above, and changed from dark brown to green. Samples' Titre values were noted, and the percentage of organic carbon was computed.

III. RESULT AND DISCUSSION

Fractionation of the samples shows, there were more saturated hydrocarbons than Aromatics and NSOs in all samples fractionated. The average weight of saturates (AHCs) in soils JA to JJ and OKA TO OKJ are 1.724g and 0.136g respectively. This indicates that the soils from Ijalla contains more contaminants of aliphatic hydrocarbons which is the main composition of petroleum compounds. The above figures shows the different masses of AHCs, Aromatics and NSOs present in both soils. In all cases the quantity in Ijalla is more than in Okere-Urhobo soils.

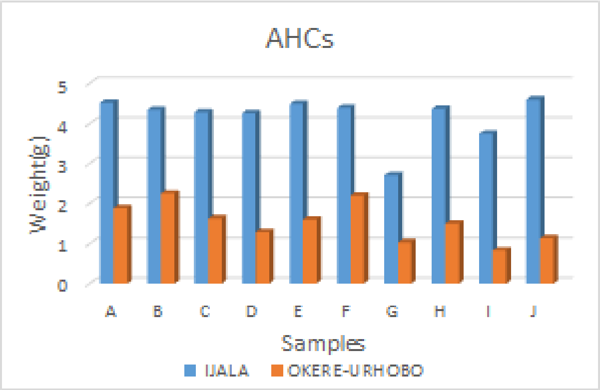


figure1: graph of AHCs of both sites

Aliphatic Hydrocarbons in both sites shows that more AHCs were present in IJalla sites than Okere-Urhobo. From the figure above, sample JA has the highest AHCs of value 2.382g while the lowest is JG. For Okere-Urhobo ranges from 0.057g to 0.283g, with OKE having the highest and OKF having the lowest value. It can be stated that there are more aliphatic also known as saturated hydrocarbons in Ijalla soil than Okere-Urhobo.

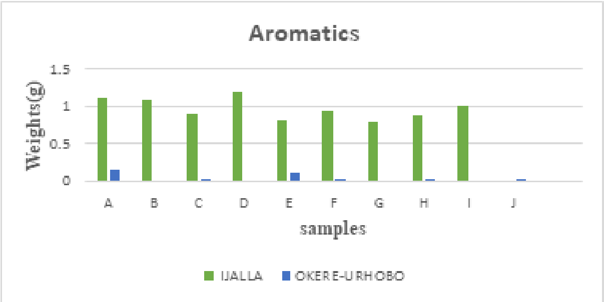


figure2: graph of aromatics weights of both sites

Aromatics fraction as seen from figure shows sample JD has 1.204g while JJ has 0.741g (lowest value) and Okere-Urhobo samples ranges from 0g to 0.101g. In comparing the sites for aromatic content, site Ijalla has more of aromatics. In comparing the concentration of aliphatic with Aromatics in Soil Ijalla, the Aliphatic were much present in all the samples than the aromatics.

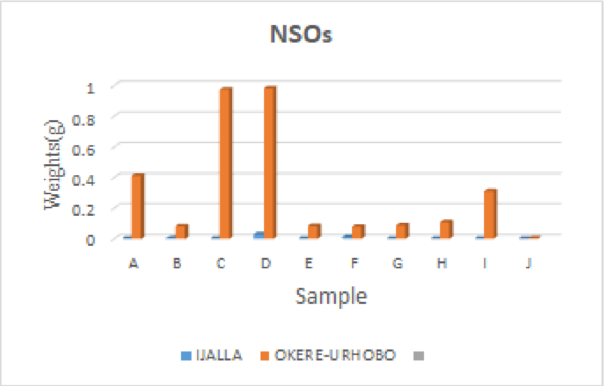


Figure 3 graphical representation of NSOs

Nitrogen, Sulphur and Oxygen compounds in both soils were small when compared to aliphatic and Aromatics. From figure it seen that the NSOs of samples Ijalla are much higher than Okere-Urhobo, where the values ranges from 0g to 0.012g in Okere-Urhobo and 0.082g to 0.981g.

CPI of the soils

According to this study's CPI values in the contaminated soils, which ranged from 0.95 to 2.51, the soils JA to JJ were primarily contaminated by petrogenic hydrocarbons, which are an oil pollutant source. Data obtained for Soil JB, JE, JF, JH and JI fall in this category. On the other hand, a CPI value less than 1 or close to 1 indicates a dominance of even-numbered hydrocarbons, which could indicate a higher proportion of microbial or bacterial contributions. Similarly, a CPI close to 1 suggests minimal microbial degradation and a predominantly terrestrial source. Data obtained for Soil JA, JC, JD, JG and JJ fall in this category. CPI values in the contaminated soils, which ranged from 0.95 to 2.51, the soils JA to JJ were primarily contaminated by petrogenic hydrocarbons, which are an oil pollutant source.

A CPI that is near to 1 in the context of the okere-urhobo assumed non-petroleum soil, which indicates that the organic matter contained in the soil is probably of mixed origin. The soil OK-A is an obvious example of one whose organic matter source may have both terrestrial and marine origins. Since there is no isoprenoid biomarker in soils like OK-C, OK-G, OK-I, and OK-J, their source of organic matter is most likely of terrestrial origin because terrestrial organic matter normally has lower ratios.

Analysis of Total Organic Carbon (Toc)

The percentage of soil that is made up of plant or animal tissue that has undergone various phases of breakdown (decomposition) is known as total organic matter. Between 3 and 6% of our productive agricultural soils are organically rich.

The amount of Carbon found in soil organic matter is known as total organic Carbon. (Ibe, 2006) states that carbon makes up around 58% of the bulk of organic matter, with water and other inorganic components like nitrogen, potassium, etc. making up the remainder. Since carbon is the most abundant and simple to measure component of organic matter, soil organic carbon is frequently assessed in conventional soil tests. (Ibe, 2006). Using the following formula, the percentage of organic carbon was determined:

POC= 10(1-T/S) x F (Peng S., 2019)
Where T = sample titration
S = blank titration = 20cm3 bb
F= factor derived as follows
=1.0x 12 x 1.72 x 100
1
4000 W

Where W = weight (in grams) of sieved samples = 1g. (Ibe, 2006)

The result below shows the percentage Organic content per 1g of soil from each samples:

Table1: percentage of TOC

	A	B	C	D	E	F	G	H	I	J
POC (J)	4.52	4.33	4.28	4.26	4.49	4.39	2.71	4.36	3.74	4.59
POC (OK)	1.88	2.25	1.63	1.29	1.60	2.19	1.032	1.50	0.83	1.14

The EPA's (Environmental Protection Agency) soil screening guidance recommends 0.2% (0.002g/g) as the default concentration of Organic Carbon for sub –surface soils. Therefore percentage organic carbon (POC) above 0.2% needs to be investigated for its sources. (IDEM, 2007).

From the analysis conducted, samples from both soils has POC aboved the recommended limits. With soil JJ having the highest POC of 4.59% while the lowest is OkI with POC 0.83%. Below is the graphical representation of TOCs in both communities.

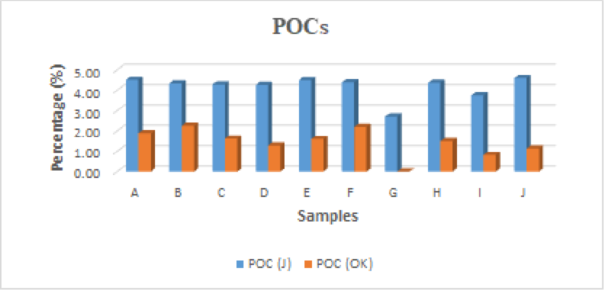


Figure 4: barchart of POCs of both sites

The TOC results shows that all soil samples has POC greater than 0.2%, which indicates that both soil has other source carbon. But that of Ijalla site is much higher than that of Okere-Urhobo when compared. The lowest value of Ijalla which is JG (2.709%), is higher than the highest value of Okere-Urhobo, OKB (2.245%).

Analysis of Oil and Grease

A mixture of substances known as "oil and grease" are those that do not readily mix with water. Results of oil and grease analysed from each soil samples are given below:

The summary of the concentration between the oil and grease in both communities is presented in the figure below:

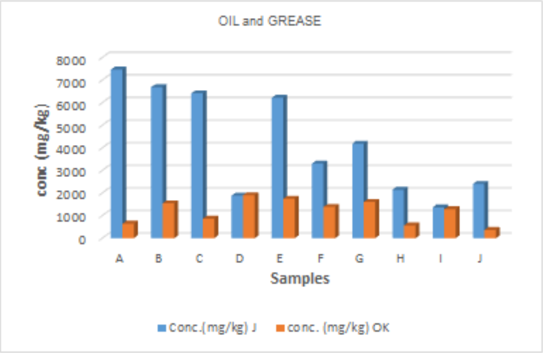
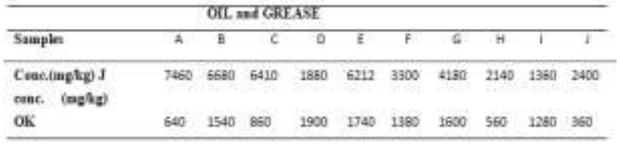


Figure: 5 graphical representation of oil and grease in both communities

Table 2: Oil and Grease



OIL and GREASE										
Samples	A	B	C	D	E	F	G	H	I	J
Conc.(mg/kg) J conc. (mg/kg)	7460	6680	6410	1880	6212	3300	4180	2140	1360	2400
OK	640	1540	860	1900	1740	1380	1600	560	1280	360

On analysis of O%G, the samples from Ijalla has an average concentration of oil and grease of 5440mg/kg with soil JA having 7460mg/kg, which far exceeds the DPR, (Department of Pesticides Regulation), California, 2007 states the maximum permissible concentration of oil and grease is 1000mg/kg in an average of 30cm depth.

IV. CONCLUSION

The analysis of extent of pollution caused as a result of the storage, marketing and transportation of artisanal crude oil refined products in the creeks of Ijalla, has made the soils of the mini-urban settlement, to contain high concentration of saturated hydrocarbons analysed. The soils have high percentage of TOC and O&G (Oil and grease) content, also from the analysis AHCs, the concentration of n-Alkanes was very high. The individual results summarized above, when compared to Okere-Urhobo has low or no concentrations, levels, percentage or content as the case may be for all the parameters tested.

It can be deduce that the soils of Ijalla community are highly contaminated with Crude oil products which can be linked to the discrete operations of marketing artisanal crude oil products , such as PMS(petrol), PKO(kerosene) and AGO(diesel).

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