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# Biomarkers, A Reliable Tool for Delineating Spill Trajectory

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## Abstract.

Oil (Petroleum) spill occur frequently and in this era of higher degree of awareness, it is pertinent that the trajectory of the spill be properly defined, to make certain the area of impact by the spill. In this study, biomarkers that are known as the custodian of paleo information in oils are suggested to be used as reliable tool for defining the pathway of a spill. Samples were collected as tills alongside the GPS coordinates of the sample points suspected to have been impacted by a spill.Oils in the samples were extracted and analyzed as whole oil using GC–MS. Some biomarker parametric ratios were derived, and the ratio showed consistency of values along the sample trail from sample 1 to sample 20. The consistency of the values indicates that the oils at each sample points are same hence same value. This method can be used to validate the trajectory/pathway of a spill and also used to define or establish a suspected pathway for a spill. The Oleanane/$C_{30}$Hopane ratio showed a good consistency and suggested as a reliable parameter for establishing a trajectory of an oil spill.

Keywords**: Spill. Oil (petroleum), trajectory, pathway, biomarker ratio.**

## 1.0 INTRODUCTION.

Oil spill delineation studies is an aspect of environmental oil fingerprinting studies which is an aspect of petroleum geochemistry(Jones, 2004).The day-to-day survival ofmost businesses largely depend on the availability of energy (petroleum), which drives and sustains economic activities. The consistent availability of (energy) petroleum is due to successful petroleum exploration. The exploration, production and transportation of petroleum provides for possibility of spillages during any or combination of the mentioned processes. Spillages could be onshore on land or offshore within marine environment.

Onshore spillages have the potential of impacting farmlands, fishfarms, recreational environments, and other privately own properties, these considerations become pertinent, because oil field that were hosted by communities may expand to host the communities and these considerations become more vital.

In contemporary times, the awareness and the concept of the spiller pays has become a pivotal point in considering the social cooperate responsibilities of operating IOCs (international oil companies), thus, each spillage event must have a source and hence a potential spiller who bears the responsibilities of clean up and site remediation. In most cases, the tendency of shifting the responsibility may arise, thus delineating the pathway (trajectory) of the spill becomes very vital, this will foster knowing the impacted areas, using the concept of biomarker to relate the source to the spill(Wang, et al., 2016). The fact that, if the spill is from a particular source, the spill and source will have similar biomarker characteristics can be used to identify areas of impact of the spill during spill flow and percolation.

The trajectory of a spilled oil can be delineated based on biomarker, this will help to decipher the areas the spill has impacted and will aid to sort out potential conflicts on mitigation and litigation. This is indirectly tracing the pathway of the spill-flow(Wang, et al., 2016), the undulated surfaces and the surface elevation will affect the flow rate and flow direction of the spill.

  

## 2.0 GEOLOGY OF NIGER DELTA BASIN.

The Niger Delta Basin was deposited as mega sequences within regular interval of 5Ma, these sequences linked together to form the Niger Delta Basin.Stratigraphically, the Niger Delta Basin is divided into three stratigraphic formations, these are the Benin Formation that is lithologically, composed of sand, sandstone, and shale intercalations in the lower series of the Formation. The underlaying formation to the Benin Formation is the Agbada Formation, whose descriptive lithology entails intercalations of sandstone and shale facies in the upper series and mainly shale in the lower series, while Akata Formation which is the last in the series is composed of mainly marine shales(Reijers, 2011), (Short & Stauble, 1967).

The surface soils vary from lose sandy soil to loamy and clay soils, in most areas the sandy soil are always the surface soils, while other areas such as wetlands have loamy soil and or clay as the surface soils, in wetland areas and other areas that are prone to erosions, clay soils are the surface soils.

## 3.0 MATERIAL AND METHODS

The materials entail the samples and chemicals that were used, the samples used were surface samples of suspected spill impacted areas obtained as tillsamples specifically,from along areas thatcovers the suspected pathway/flowpathof the flowing/spreading spill using sampling trowels. Samples were store in sample bags and in a chest of ice to preserve the sample compositional integrity, the chain of custody was not broken until samples were submitted from sample analysis.

The method applied for sample treatment entails extraction of the oil (petroleum) from the soil sample using DCM (Dichloromethane), extracts were later subjected to whole oil analysis for biomarkers using GC–MS method(Wang & Brown, 2009). The biomarkers of choice are aliphatic markers that are recalcitrant to biodegradation. The hypothesis is that the source and the spilled oil will bear similar ratios of the parameters of choice where biodegradation did not prevail.

Extracts were prepared for GC–MS analysis by measuring 0.2mg of the extract into 0.2mL of hexane to achieve 1µg/µL which is the recommended concentration that was injected into GC–MS for full scan analysis. The GC-MS analysis was done using a HP5890 II GC with a split/spiltless injector linked to a HP 5972 MSD (Mass Selective Detector). The GC was temperature programmed for 40ºC–300ºC at 4ºC per minute and held at final temperature for 20 min. The carrier gas was Helium (flow rate 1ml/min., pressure of 50kPa, slit at 30ml/min). The ionization and identification were carried out in the HP 5972 MSD, which was equipped with electron voltage of 70 eV, filament current of 220µA, source temperature of 160ºC, a multiplier voltage of 1600V and interface temperature of 300ºC. The acquisition was monitored by HP Vectra 48 PC chemstation computer in full scan mode (30ions 0.7 cps 35m dwell). HP is currently known as Agilent, UK. Peak integration was done using the RTE integrator. Data was obtained from the percentage report from the Enhanced MSD Chemstation 2011 software by Agilent Technologies(Peters et al., 2005).

Mass chromatograms of m/z 85, 191, 218 and 217 were extracted from the various data file generated from the analysis using Enhanced MSD Chemstation 2011 software by Agilent Technologies. The abundances wereused for the calculation of the parametric ratios which were extracted from the corresponding percent report.

  

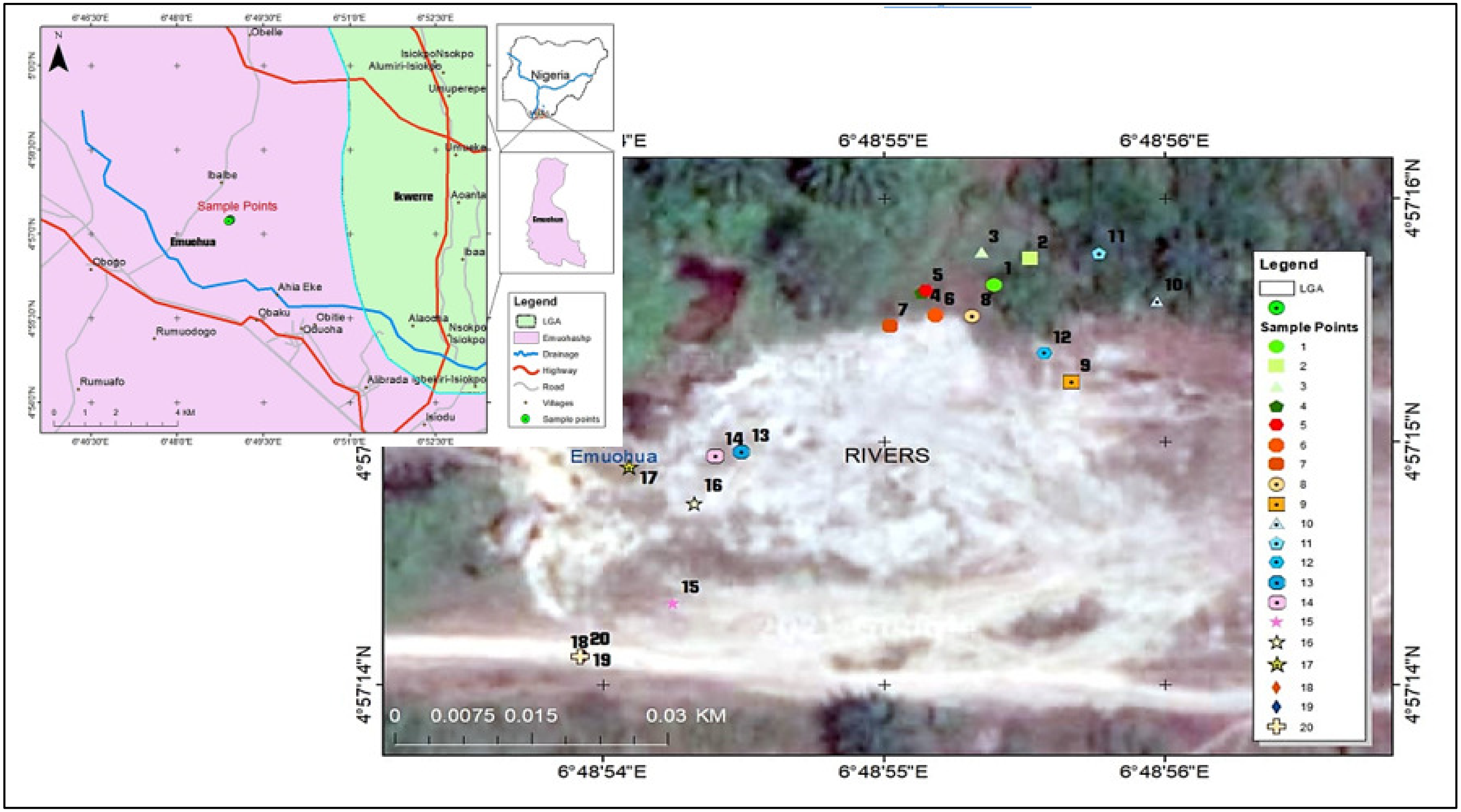

Figure 1. Map showing Sample location

  

Table 1. Table showing the GPS coordinates and parametric ratios obtained from the GC–MS analysis

| Sample Points | Latitude (N) | Longitude (E) | $(C_{17}+C_{18})/(Pr+Ph)$ | $C_{17}/C_{18}$ | $OL/C_{30}$ | $C_{31}S/C_{31}R$ | $C_{32}S/C_{32}R$ |
|---|---|---|---|---|---|---|---|
| P001 | 4.954346389 | 6.8153875 | 0.4 | 1.2 | 0.7 | 0.9 | 1.3 |
| P002 | 4.954376389 | 6.8154225 | 0.4 | 1.3 | 0.7 | 0.9 | 1.2 |
| P003 | 4.954383611 | 6.815375 | 0.6 | 1.6 | 0.7 | 1.0 | 1.4 |
| P004 | 4.954336944 | 6.815316111 | 0.3 | 2.3 | 0.7 | 0.8 | 1.5 |
| P005 | 4.954339167 | 6.815319722 | 0.4 | 1.4 | 0.7 | 0.8 | 1.3 |
| P006 | 4.954311667 | 6.815329167 | 0.4 | 1.5 | 0.9 | 1.0 | 0.8 |
| P007 | 4.954299167 | 6.815284444 | 0.6 | 2.1 | 0.8 | 1.6 | 1.8 |
| P008 | 4.954310278 | 6.815366111 | 0.4 | 1.1 | 0.9 | 0.8 | 0.7 |
| P009 | 4.954235278 | 6.815464167 | 0.4 | 0.6 | 0.7 | 1.6 | 1.2 |
| P010 | 4.954328333 | 6.815548056 | 0.2 | 1.2 | 0.7 | 0.7 | 1.4 |
| P011 | 4.9543825 | 6.815491111 | 0.3 | 1.8 | 0.7 | 0.9 | 1.3 |
| P012 | 4.9542675 | 6.815437222 | 0.3 | 0.7 | 0.7 | 0.9 | 1.4 |
| P013 | 4.954155278 | 6.8151375 | 0.9 | 2.4 | 0.8 | 1.0 | 1.1 |
| P014 | 4.954151111 | 6.815111389 | 0.4 | 0.9 | 0.7 | 0.9 | 1.4 |
| P015 | 4.9539825 | 6.815069167 | 0.3 | 1.7 | 0.8 | 0.8 | 1.4 |
| P016 | 4.954096111 | 6.81509 | 0.4 | 1.1 | 0.8 | 1.0 | 1.4 |
| P017 | 4.954138611 | 6.815025278 | 0.6 | 2.9 | 0.8 | 1.0 | 1.0 |
| P018 | 4.953922222 | 6.814983056 | 0.4 | 1.5 | 0.7 | 0.9 | 1.4 |
| P019 | 4.953921944 | 6.814981111 | 0.4 | 0.9 | 0.8 | 1.0 | 1.2 |
| P020 | 4.953921389 | 6.814978333 | 0.5 | 1.2 | 0.7 | 0.9 | 1.1 |

## 4.0 RESULTS AND DISCUSSION

The table of results as in Table 1, consists the GPS coordinates and various parametric ratios that were obtained from the GC–MS results. Figure 1 shows the map of the location of sample points as an insert and then a more detailed map showing the various sample points according to their GPS locations.

### *4.1 Delineating Spill Trajectory*

The trajectory of a spill has been described variously as the pathway, the movement and location of a spill at any given time( Liu, et al., 2011)(Drozdowski, et al., 2011)(Chang , et al., 2011)(Apai, 2001). The trajectory of the spilled oil on the soil surface will depend on the undulation of the soil surface and the soil type on the surface.

The hypothesis on which this study rest are in two approaches, the first is that the soil's ability to adsorb the spilled oil also affects the abilityof the spill to flow and spread across the surface of the soil. The soil type on the surface varies from one place to another.The basic soil types are sand/gravel, loamy, clay and silt; soil can be considered as the loose unconsolidated material and these some-what corresponds to the different horizons of the soil, which are the topsoil, subsoil, and the parent rock. The topsoil is mainly organic and very porous and soft, in most areas topsoil is sandy loamy or loamy, while the subsoil is comparatively more compact relative to the upper horizon and the parent rock is basically broken bed rock.

If the topsoil is made up off consolidated material as in erosion prone areas, where the initial topsoil has been washed away, then the spilled oil will flow and spread rather than percolate/penetrate in the lower layer of the soil.

The second aspect of the study hypotheses is that, given that there is no significant change to the composition of the spilled oil, the spilled oil will have similar or same compositional distribution of the hydrocarbon compounds relative to the source/original oil. Based on this concept the trajectory of a spill can be delineated using biomarker compounds in crude oil.

The biomarker compounds are modified compounds that initially originate from the organic matter that constitutes the source rock generating the oil. These compounds form the basic genetic units on which the oils can be characterized (custodians of paleo information)(Wang, et al., 2016)(Stout & Wang, 2018).

The trajectory of a spilled oil can be complicated, it can be influence by the elevation and surface undulation, however, the different sample points are indicated by the GPS coordinates as in figure1, and the various biomarker ratios per sample are listed in table 1.

Figure1, essentially represents the assume pathway of the spill of interest, but the consistency of the values of various biomarker ratios will validate the pathway.

  

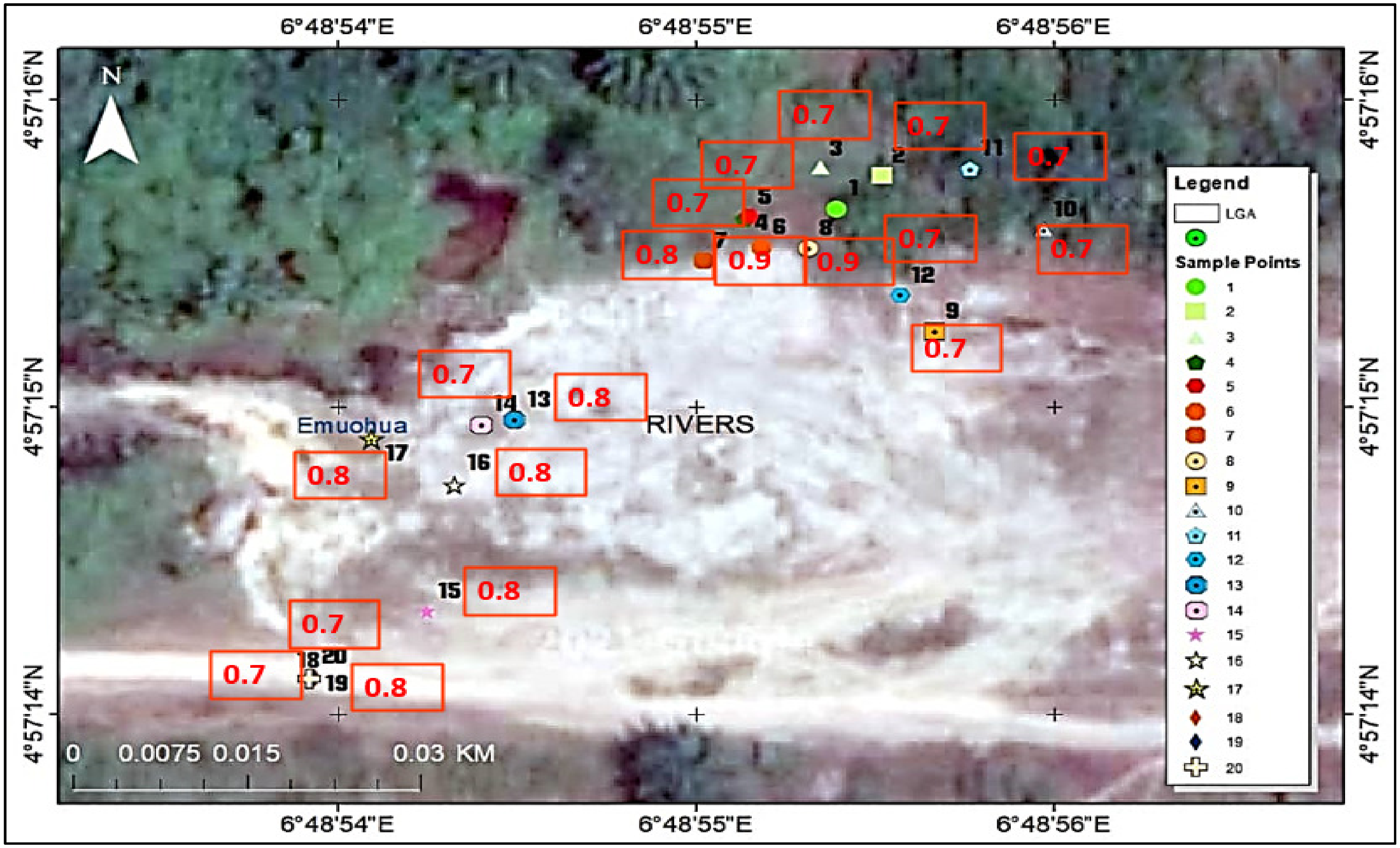


Figure 2. Map of Sample location and the Oleanane/$C_{30}$Hopane ratio posted to the sample for Profile.

Table1, shows the different ratios and the ratios show some degree of consistency for each biomarker ratio. The trend and the variableness of the ratio can be observed from sample No.1 to sample No. 20. The consistency of the values indicates the pathway that had been trailed by the flowing/spreading spill. This study can be used to validate claims by host communities on the aspect of areas that could have been impacted by the spilled oil, which could also serve the purpose of mitigation (prevention) and litigation (allocation of responsibilities for cleanup and remediation).

The trajectory of spills has been known to have been delineated using drifters in marine environments, drifters are monitored,and the average movement profile recorded using radio signals attached GPS equipment(Chang , et al., 2011).

Secondly, numerical modeling, and satellite remote sensing resources can be used for coastal and ocean observations. Surface oil locations inferred from satellite imagery were used to re-initiate positions of virtual particles, which are tracked using forecast surface currents( Liu, et al., 2011).

These studies are all within marine environment, however, studies on onshore environment have not been recorded but could have been carried out.

This study can serve as best practice method for delineating oil spill trajectory, which basically is redefining the pathway a spilled oil has trailed using the evidence the spill left behind which are basically soil samples bearing traces of the spilled oil.

Biomarker geochemistry has been an efficient method for correlating and identifying samples of the spill oil at different sample points and the original source samples(Wang & Brown, 2009).

Figure 2 shows the map of the sample location and the corresponding Oleanane/$C_{30}$Hopane ratio as assigned to each sample point to provide a better understand of the concept and the trend/profile of the ratio according to the delineated pathway of the spilled oil. The trend shows values that varies between 0.7 and 0.9 for which there is no significant difference and invariably shows that the spilled oil trailed that pathway. Similar mapping could be done for other ratios. Where there are significant differences in the ratios, it could represent an overwritten fingerprint or a contamination.

## 5.0 CONCLUSION

The biomarker ratio has served as a reliable parameter that can be used for delineating and validating spill trajectory/pathway. It could serve the double purpose of identifying areas that are / not impacted by the spill and it could be extended to mitigating and litigating purposes.

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