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DELINEATING THE TRAJECTORY OF A SPILL USING GENETIC BIOMARKERS IN IBAA AREA, EASTERN NIGER DELTA

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Abstract:

Oil spills(petroleumspills)are of frequent occurrences, and in this age of high level awareness, it is importanttoaccuratelydefine the trajectory of a spill to ensureknowledge of spill impactedarea/points. In this study, itismolecular markers (biomarkers),which are consideredcustodian of paleo information ofoil, as reliable tooltodetermine the trajectory (pathway) of spills. Samples were collected as tills from different locations alongwith the GPS coordinates of the suspected spill, using hand auger.Theoil in the samples was extracted and analysed for various biomarkersusingGC-MS.Anumberofparametric biomarker ratios were derived from the peak areas, and they showed consistency of values along sample points from sample 1 to sample 20. Consistency of values implies that the oilextracted from soil samples areof same source andare of a recent spill that has not been overwritten by any other. This method can be used to verify spill trajectories/pathways and can also be used to define or establish suspected trajectories of a spilled oil. The Oleanane/C_{30} Hopane and the $(Pr+Ph)/(C_{17}+C_{18})$ ratio showed good consistency and is being recommended as reliable parameters for delineating oil spilltrajectories.

Keywords **—oil spills, biomarkers, GC-MS, parametric, tills, trajectory, consistency.**

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1.0 INTRODUCTION

Spill trajectory is the pathwayfollowedby a spill in a marine or terrestrial environment. Even in the absence of wind or water current, the oilspreadshorizontallyonthesurface of the water.Onland, the topography of the surface directs its flow, winds and currents also disperse oil and accelerate the process. Theoil forms astream as itspreads.Delineating a spill trajectory canhelp understand potentiallyimpactedlocations along the pathway of a spill. It also provides informationabout the particular area where the spill has been active.This is the state of the art in oil spillsource and impacted areacorrelation, using genetic biomarkers for source identification.

An oil spill is the release of liquid petroleum hydrocarbons into the environmentby human activity, and it's a form of pollutionthatcan occur in coastal watersaswellas on land. Oil spills canoccur from tankers, offshore platforms, drilling platforms,releasesofcrudeoilfrom wells, releases of refined petroleum products (gasoline,diesel,luxury motor spirits,etc.) and their by-products.

Major oil spillattracts public and mediaattention. In recent years, this focushasincreased global awareness of the risks of oil spills and the associated damage to the environment. Largeoilspillshavedeclinedin recent years(Dagmar, 2011). The general public is usually aware of large spills, but areunaware that spills occuron a daily basis. Oil is a necessity of an industrial society and animportantpart of our lifestyle.Inmanydevelopedcountries,most of the energy is used for transportation, which isfuelledby oil and petroleum products. As current energy consumption trends show, this situation is unlikely to change significantly in the future. Industriesusepetroleum and petroleum derivatives to produceessentialproducts such as plastics, fertilizers and basicchemicalsthat will be needed in the future. In fact, the production and consumption of petroleum and petroleum products is increasing aroundtheworld, and the risks of oil explorationarecorrespondinglyincreasing.Transportingoil from the field to the consumer requiresup to 10-15transshipments between various modes of transportsuchastanktrucks, pipelines and roadtankers. Oil is stored at transshipmentpoints, terminals and refineries along the route. Accidentsmay occur during these transportation stagesandstorage. Fortunately, the actual number of spills has beenonthedeclineinrecentyears.Clearly, an important part of environmentalprotection is minimizingoilspills. Both government and industry are working to reduce the risk of oil spills by introducing draconian new laws and stringent operationalregulations.The industry isadopting new operational and maintenance practices to reduce incidentsleading to oil spills. Despite these measures, spill experts estimate that 40-55% of all spills are directly or indirectly caused by human error, equipment failure or malfunction and sabotage.

Geologic Setting of the Study Area

The Niger Delta Basin also referred to as the Niger Delta province, is an extensional rift basin located in the Niger Delta and the Gulf of Guinea on the passive continental margin near the western west of Nigeria. (Rayment 1965; Amajor, 1986, 1987).

This basin is very complex, and it carried high economic value as it contains a very productive petroleum system. The Niger Delta basin is one of the largest sub-aerial areas of about 75,000km^2 a total area of 300,000km^2 and sediment fill of 500,000km^3. The sediment fill has a depth between 9-12km^2 (United States Geophysical Survey 1999). It is composed of several different geologic formations that indicates how this basin could have formed, as well as the regional and large scale tectonics of the area.

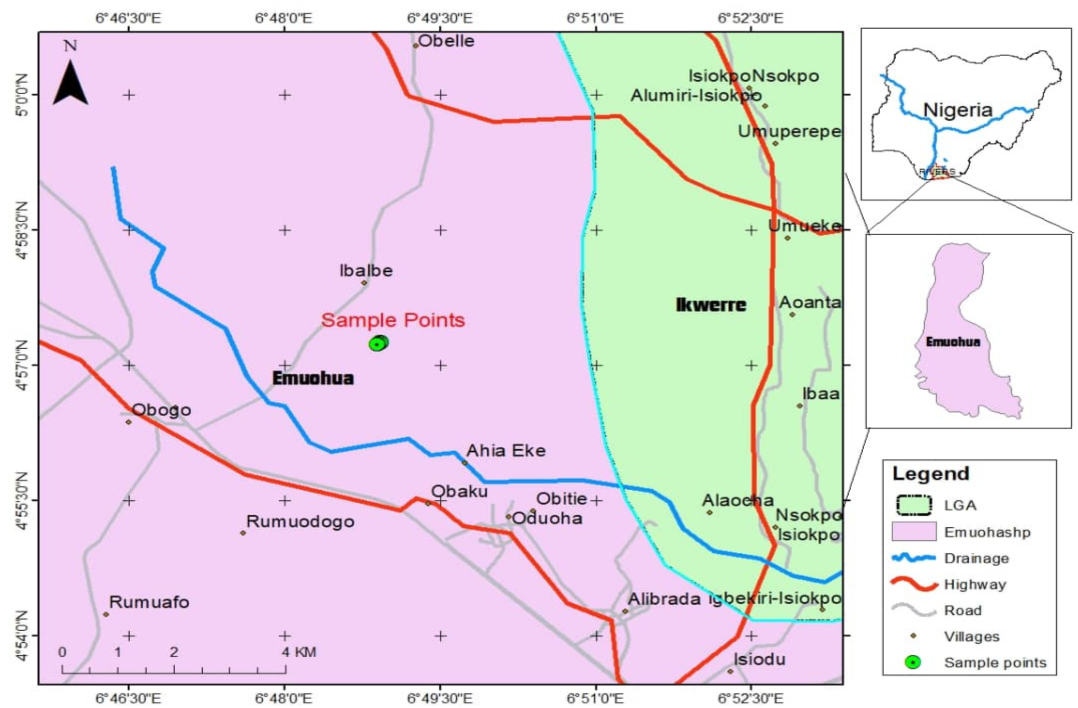
The Niger Delta Basin lies in the South-Western most part of a larger tectonic structure, the Benue trough (Olade *et al.,* 1975).

The Niger Delta Basin was formed by a failed right junction during the separation of the South American plate, as the South Atlantic began to open. (Amajor 1987, Grent 1971) Rifting in this basin started in the Late Triassic and ended in the Mid Cretaceous. Drifting continued, several faults formed, many of them thrust, faults. Also at this time syn-right sands and shale were deposited in the Late cretaceous. This indicates that the shoreline regressed during this time. (Murat 1972, Ladipo, 1988).

Concurrently, the basin had been undergoing extension resulting in high angle normal faults and faults block rotation. At the beginning of the Paleocene there was a significant shoreline transgression. During the Paleocene, the Akata formation was deposited followed by the Agbada formation during the Eocene. This loading caused the underlying shale Akata formation to be squeezed into shale diapers. Then in the Oligocene the Benin formation was deposited, which is still being deposited today.

Materials and Methods

Materialsused include the samples and chemicals.The samples used were surface samples fromareas suspected tohavebeenimpactedbythespill,specifically as sampling along theareacovering the suspected spill runoffpath using a sampling trowel.Collected Samples were stored in sample bags and ice boxes to preserve the integrityofthe sample composition.The chain of custody was not interrupteduntil samples weresubmitted for analysis. The method used forsample processinginvolvesextracting oil (petroleum) from soil samples using DCM (dichloromethane).Extracts were then subjected to biomarker/molecular marker analysis using aGC-MSmethod for m/z 191 and m/z 218 (Wang& Brown, 2009). Biomarkers of choice are aliphatic markers that resist biodegradation. The hypothesis is that in the absence of biodegradation,spilled samples and source samples wouldhave similar ratios of selectedparameters.Extracts were prepared for GC-MS analysis by adding0.2mg of extract to0.2mL of hexane andmeasuring to 1µg/µL.This is the recommended concentration usedforGC-MSanalysis injected into full scan analysis. GC-MS analysis was performedonan HP5890 II GC with a split/splitless injector connected to an HP 5972 MSD (Mass Selective Detector). The GC temperature was programmed from40to300°C at 4°C/min and held at the final temperature for 20 minutes. The carrier gas was helium(1ml/minflowrate,50kPapressure,30ml/minslotvelocity).Ionization and identification were performedonan HP 5972 MSD with an electron voltage of 70 eV, filament current of 220µA, source temperature of 160°C, multiplier voltage of 1600V, and interface temperature of 300°C.Acquisitionswere monitored usingan HP Vectra 48 PC Chemstation computer in full scan mode (30ions, 0.7 cps,35mindwelltime). HP is now known as Agilentinthe UK. Peak integration was performed using the RTE integrator. Data are from AgilentTechnologies'2011 Enhanced MSD Chemstation software percentagereport (Peters et al., 2005). Mass chromatograms at m/z 85, 191, 218, and 217 were extracted from various data files generated from analysis withAgilentTechnologies Enhanced MSD Chemstation 2011 software.Peak ratioswereusedtocalculate parametric ratios extracted from the corresponding percentagereports.



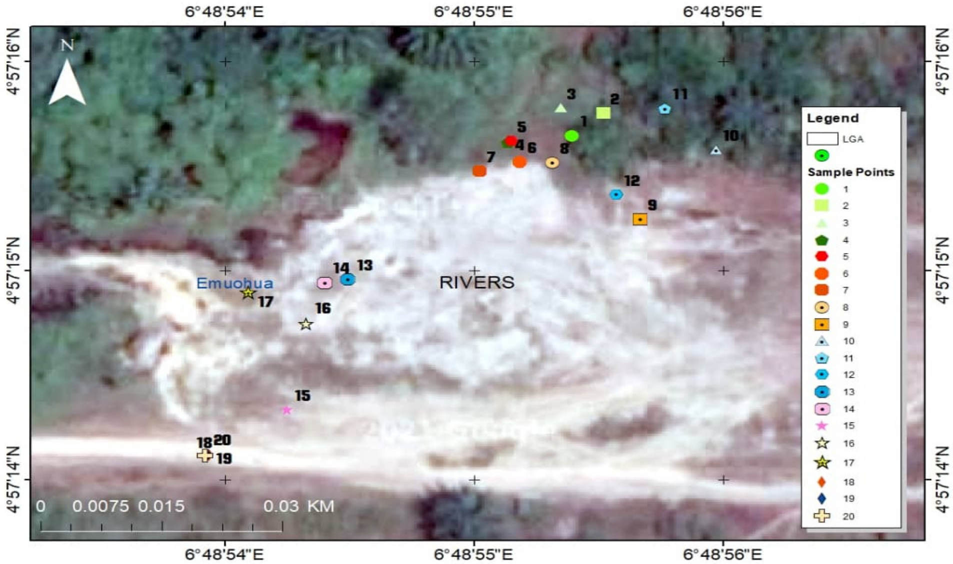
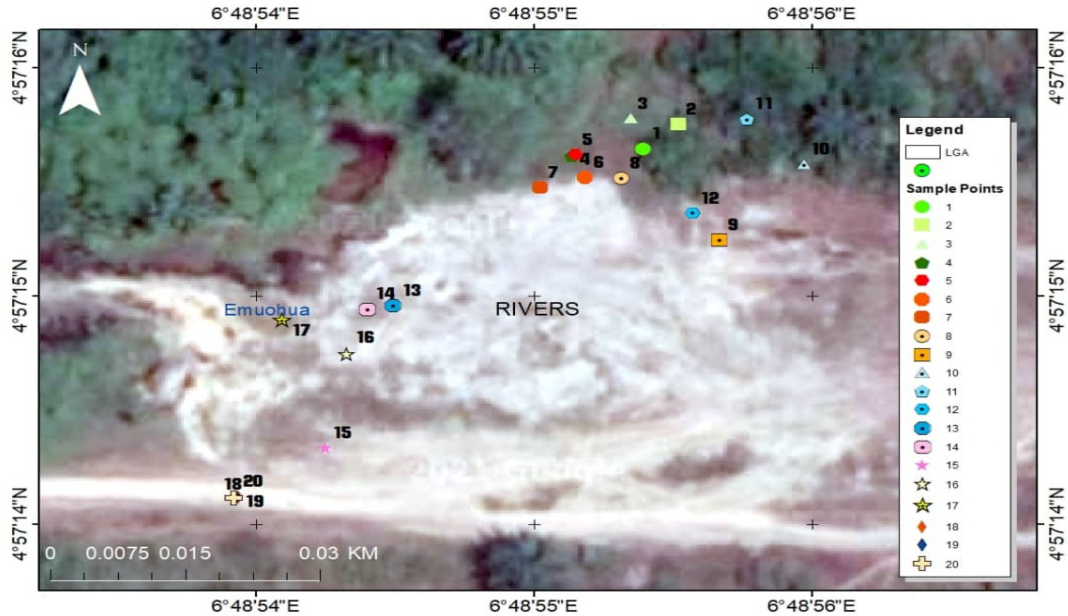


Fig. 1a and 1b, Map of the study area and sample locations and sample collection points.

Sample Points	Latitudes (N)	Longitude(E)	Elevation	C32S/C32R	$(C_{17}+C_{18})/(Pr+Ph)$
P001	**4.954346389**	**6.8153874**	**17**	**1.28**	
P002	**4.954376389**	**6.8154224**	**17**	**1.24**	**0.60**
P003	**4.954383611**	**6.815375**	**17**	**1.44**	**0.29**
P004	**4.954336944**	**6.815316111**	**17**	**1.46**	**0.38**
P005	**4.954339167**	**6.815319722**	**17**	**1.33**	**0.45**
P006	**4.954311667**	**6.815329167**	**17.5**	**0.80**	**0.59**
P007	**4.954299167**	**6.815284444**	**17**	**1.84**	**0.42**
P008	**4.954310278**	**6.815366111**	**17**	**0.71**	**0.45**
P009	**4.954235278**	**6.815464167**	**17**	**0.21**	**0.18**
P010	**4.954328333**	**6.815548056**	**17**	**1.36**	**0.31**
P011	**4.9543825**	**6.815491111**	**17**	**1.31**	**0.31**
P012	**4.9542675**	**6.815437222**	**17**	**1.44**	**0.95**
P013	**4.954155278**	**6.8151375**	**17**	**1.11**	**0.42**
P014	**4.954151111**	**6.815111389**	**17**	**-**	**0.32**
P015	**4.9539825**	**6.815069167**	**17**	**1.37**	**0.41**
P016	**4.954096111**	**6.81509**	**17**	**1.44**	**0.57**
P017	**4.954138611**	**6.815025278**	**16**	**1.38**	**0.37**
P018	**4.953922222**	**6.814983056**	**16**	**1.00**	**0.42**
P019	**4.953921944**	**6.814981111**	**16**	**1.44**	**0.51**
P020	**4.953921389**	**6.814978333**	**16**	**1.23**	**0.40**

Table1.TableshowingtheGPS coordinatesandparametricratiosobtainedfromtheGC–MSanalysis



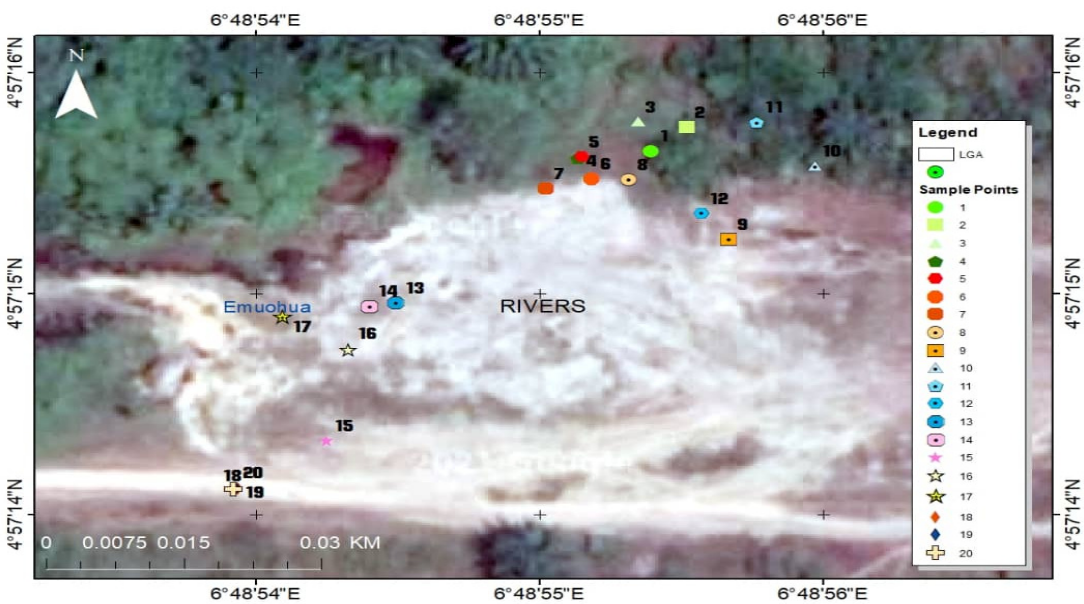


Fig. 2a and 2b shows the map of the sample location and the corresponding ratios of Oleanane/C_{30} and (Pr+Ph)/(C_{17}+C_{18}) respectively as assigned to each sample point to provide a better understanding of the concept and the trend/profile of the ratio according to the delineated pathway of the spilled oil.

4.0 RESULTSANDDISCUSSION

Delineating Spill Trajectory

Spill trajectory which entails 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. Studies show that, drifters, numerical modelling, remote sensing, coastal and oceanic observations have been used in delineating spill trajectories.
Software such as GNOME, METOCEAN have been used to carry out studies, all which are within marine environments, however, studies on onshore environment using biomarkers have not been recorded but could have been carried out.

This study is focused on the use of biomarkers to delineate the trajectory of a spill and correlating the source and spilled oil at various impacted points in IBAA Community of Rivers State.

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 1a and 1b 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.

Table 1, shows the Oleanane/C_{30} hopane and $(C_{17}+C_{18})/(Pr+Ph)$ ratios,the ratios show a consistent profile inferring that the spilled oil is recent and had not undergone any significant change and that it has not been over written by any other spill. The trend and the variableness of the ratio can be observed from sample No.1 to sample No. 20. In figure 2a and 2b. The consistency of the values indicates that the pathway had been trailed by the flowing/spreading spill.

Where there are significant differences in the ratios, it could represent an overwritten fingerprint or a contamination.

Conclusion

This research work has unravelledthe application of oil genetics and forensic based scientific concepts onprofiling the pathways of a spill, generating information of great importance to environmental forensic investigations in terms of determining the source of spilled oil, differentiating and correlating oils, and monitoring the degradation process and weathering state of oils under a wide variety of conditions using biomarkers,which provides science based forum for mitigation and litigation on the bases of the spiller pays.

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