Oil Spill Pathway and Receptor: The Obrikom Experience

V. A. Ndukwe*, O. S Ndukwe, S. Abrakasa*, N. E. Ekeocha*****

*Department of Geology
University of Port Harcourt. Port Harcourt.
**Department of Geology
Federal University Oye Ekiti, Ekiti State
***Department of Geology
Gregory University, Uturu, Abia State

Corresponding Author & Email: V A Ndukwe bykaconcept@gmail.com

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Abstract: Oil spills occur frequently during production, transportation and processing of hydrocarbons. Rivers State is one of the Niger Delta' States that have experienced oil spills, with several cases such as the Bodo oil spill (2008), Bille oil spill (1999), Amusia oil spill (2009), among others. In this study, the Obrikom Spill was assessed to unravel potential pathway and possible recipient of oil in order to aid establish the level of impact of this spill around the study area. Possible traces of hydrocarbon (Oil spill) were found on the gills, fins of fishes around the study area. Samples were collected from the sources, soils, groundwater and surface water. Oil in the water samples was extracted using dichloromethane (DCM) and the extract was allowed to stand in a fume cupboard to convert the extraction solvent for evaporation, prior to being analyzed by the Gas Chromatography-Flame Ionization Detector (GC-FID). The gas chromatographic fingerprint indicates the presence of hydrocarbon class range of nC_{12} to nC_{32} implying the predominant presence of petroleum hydrocarbon. The presence of unresolved complex mixture (UCM) is consistent with biodegradation of hydrocarbon molecules, which is characteristic of exposed hydrocarbon. The GC profiles for River water samples, show significant low concentrations of Polycyclic Aromatic Hydrocarbons (PAHs). The low concentrations could be attributed to persistent dilution of runoffs which undoubtedly reduce concentration of PAHs over time within the River body. The pathway remains drainages and runoffs into the River Orashi and farmlands. Similarities were seen on the biomarker finger prints from samples collected from source, soil, ground water and surface water. Regardless of the containment of the spill, the river water still showed some traces of Polycyclic Aromatic Hydrocarbons (PAHs) with potential to affect marine organisms, and by extension humans, who are the end receptor.

Keywords- Biodegradation, ionization, Chromatography, Adsorption, Microbial.

Introduction:

The likelihood of the occurrence of accidental spills in the course of exploration, production and transportation of petroleum is high. It is one of the inherent risks in the business of oil exploration and production. The processes that are at play when a spill occurs are evaporation, dissolution, dispersion, photochemical oxidation, water-oil emulsification, microbial degradation, adsorption onto suspended particulate matter, sinking and sedimentation (Venosa and Holder, 2007). These processes also include weathering of the spilled petroleum hydrocarbon.

Rivers State, one of the Niger Delta States, has recorded large number of oil spills, with such examples as Bodo (2008), Bille (1999), Amusia and Joinkrama (2009).

The consequences of oil spills are numerous and include the destruction of livelihoods of the people who are either primarily engaged in fishing or farming. Most of the farmers undertake bush burning as the fastest way of clearing the intended land for farming. The proximity of the spill site to the farms and fishing ports determines the length of exposure time of the spill and eventually explains the effect the oil spill will have on their occupations (Swartjes, 2011).

The environment that is impacted by the spill could be onshore land or offshore marine. Spills sparingly occur on land, are mobile and mostly static except when affected by runoffs during rainfall, while offshore in marine environment, spilled oil could drift to an unpredictable wider area by the direction of current for high energy environment and direction of wind for turbulent/stormy weathers (Abrakasa and Onojake, 2012). When spill occurs, it becomes pertinent for a number of steps to be taken that will lead to the assessment of the spill to establish extent of coverage both in the vertical dimension as well as the horizontal and eventually to determine the chemical composition of the spilt oil for the profiling of its source, type and the potential recipient and the pathway of the spill, which describes avenues through which spill impacts its recipient. This knowledge could contribute to possible design of remediation processes (Swartjes, 2011; Abrakasa, 2013)

Osuji et.al. (2010), Odu et.al. (1985), Ojimgba and Iyagba (2012), Wegwu et.al (2011) and Birke (2007) have variously pointed out the occurrence of contaminating substances in oil spills and the effects they have on the soil and by extension on the human health.

This study seeks to assess the spill at Obrikom, in Rivers State, adopting the use of Gas Chromatography (GC), to establish the spill type and determine the end recipient.

Study Area:

The Study area is Obrikom town in Ogba/Egbema/Ndoni Local Government Area of Rivers State (Figure 1) in the Niger Delta region of Nigeria. The area is bound within Latitutde 5°10’13.11” to 5°43’59.16”N and Longitude 6°28’4.58”E to 6°47’43.21E”

The Niger Delta is divided into three main sedimentary environments namely the continental, transitional and marine environments that are stratigraphically represented as the Benin Formation (youngest in age), Agbada Formation and the Akata Formation, being the oldest (Short & Stauble, 1967).

The Benin Formation (the Coastal Plain Sands) are Eocene in age and constitute the groundwater extraction horizon in the region, being composed of unconsolidated sands that range from fine to very coarse textures. They are overlain by Quaternary deposits with a composition of sand and gravel with silts and clays in places. On the other hand, the Agbada Formation underlies the Benin Formation and principally serves as the reservoir for hydrocarbons in the delta region. The Akata Formation is the hydrocarbon generation (kitchen) layer within the region.

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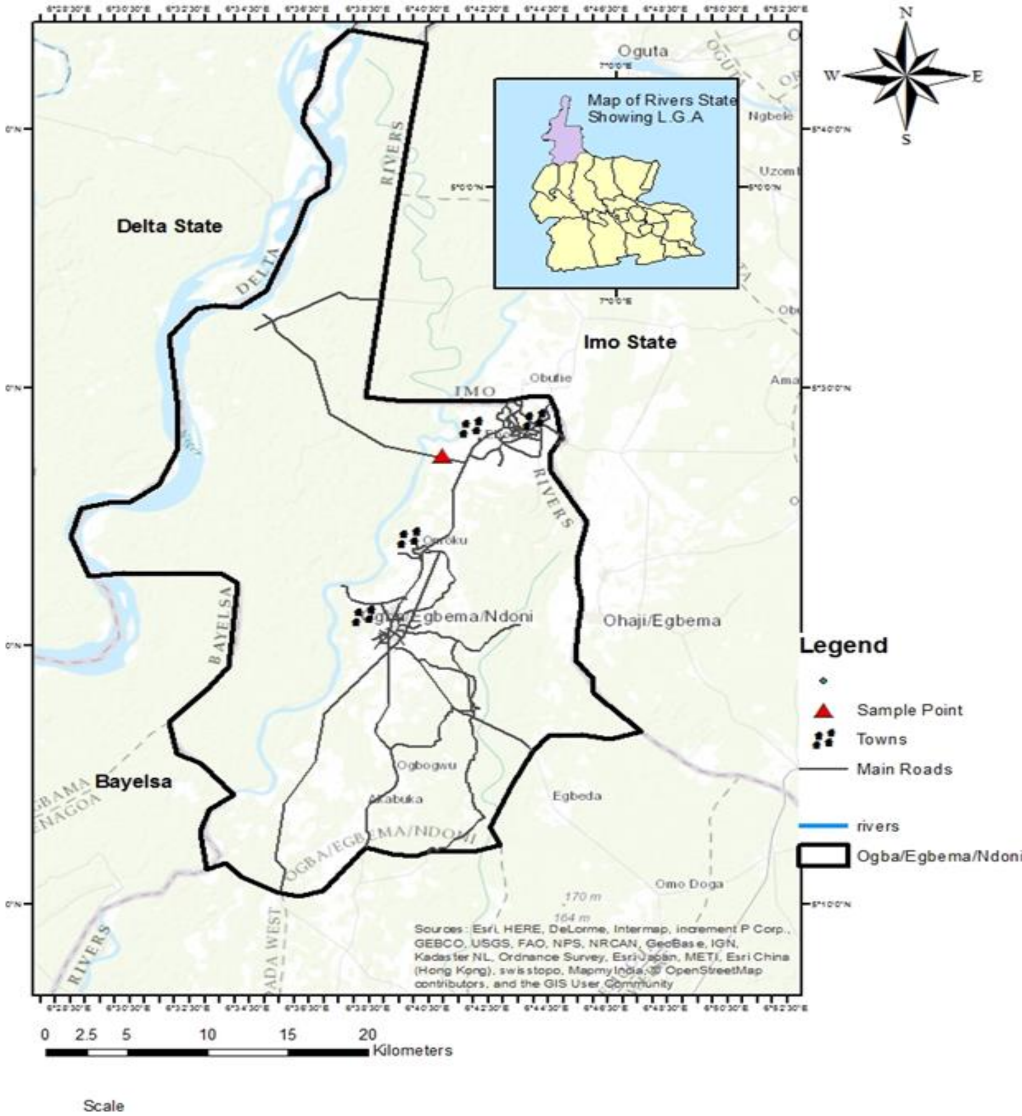

Figure 1: Map of study area and sample point.

Method of Study.

Four different samples were collected as follows:

1. 1 crude oil sample from a drainage that is located at the base of the well head that serves as the source or the point of occurrence of the spill.
2. 1 sample was collected from a land space that showed evidence of spillage
3. 1 water sample from the Orashi River
4. 1 water sample from a nearby borehole.

All the samples were stored in sample bottles, were properly labelled and stored prior to movement to the laboratory.
Oil in the water samples was extracted using Dichloromethane (DCM). The extract was allowed to stand in a fume cupboard to allow for the evaporation of the extraction solvent. The uncontaminated soil was examined and the debris removed before the extraction process. The wet soil sample and wet soil and oil samples were also examined to remove plant remains before the extraction process.

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The extracts from the samples were analyzed using GC–FID for both the aliphatic and aromatic hydrocarbon contents. The total aliphatic and the total aromatic hydrocarbons were determined from the resolved peaks of the chromatographic fingerprints (CEN, 2006; CEN, 2002; Hansen et al., 2001).

Results and Discussion

The results of the analysis are shown in Figures 2 to 7. The similarity of the profile of the fingerprint infers similarity of oil in each of the analyzed samples. Table 1 shows the diagnostic ratios derived from the GC-FID for aromatic compounds in the hydrocarbon, which include P/A (Phenanthrene/Anthracene), FL/Py (Fluoranthene/Pyrene), Ant/(Anthracene+Phenanthrene), and Flt/(Flouranthenet+Pyrene).

Table.1: Diagnostic ratios for PAH compounds

SAMPLES	**DIAGNOSTIC RATIOS**					
	P/A	**FL/Py**	**BaA/(BaA+Chr)**	**BaP/(BaP+Chr)**	**Ant/(Ant=Phen)**	**Flt/(Flt=Pyr)**
Life Crude	0.8	1.5	0.5	0.4	0.55	0.61
Crude+Soil+Water	0.4	1.1	0.64	0.2	0.71	0.53
Crude+Soil	0.67	1.1	N/A	N/A	0.6	0.53
Uncontaminated Soil	0.75	0.87	0.4	0.55	0.57	0.46
Groundwater	0.5	0.69	0.4	0.7	0.67	0.55
Riverwater	0	0.61	0.48	0.52	1	0.37

Where P= Phenanthrene, A = Acenaphthylene, FL= Flourene, Py = Pyrene
BaA = Benz (a) antracene, Chr = Chrysene, BaP = Benzo (a) pyrene
Ant = Anthracene, Phen = Phenanthrene Flt = Flouranthene

Table 2 shows the diagnostic ratios for $n\mathrm{C}_{17}$/Pristane, $n\mathrm{C}_{18}$/Phytane, Pristane/Phytane derived from the GC-FID for the saturated or aliphatic hydrocarbons. These ratios provide valuable information on biodegradation, maturation and diagenetic conditions. The PAH ratios that are derived from the Aromatic fraction include anthracene/phenanthrene (*m*/*z* 178); BaA/Chrysene (*m*/*z* 228); BeP/BaP (*m*/*z* 252); and indeno [1, 2, 3-cd] pyrene/benzo[ghi]perylene (*m*/*z* 276).

Table 2: Diagnostic ratios for Aliphatics (Saturates).

SAMPLES					
	$n\mathrm{C}_{17}$/Pr	**$n\mathrm{C}_{18}$/Ph**	**$n\mathrm{C}_{23}/n\mathrm{C}_{24}$**	**$n\mathrm{C}_{29}/n\mathrm{C}_{30}$**	**WI**
Life Crude	0.05	0.91	1.55	3.26	0.25
Crude+Soil+Water	2.8	0.21	1.66	1.02	0.84
Crude+Soil		0.66	2.69	3.5	0.53
Uncontaminated Soil	0.02	0	0	0	0
Groundwater	0.002	0	0	0	0
Surface water	0.01	0	0	0	0

Where: **$n\mathrm{C}_{17}$, $n\mathrm{C}_{18}$, $n\mathrm{C}_{23}$, $n\mathrm{C}_{24}$, $n\mathrm{C}_{29}$, *and* $n\mathrm{C}_{30}$ are n-alkanes**
Pr = Pristane, **Ph** = Phytane and **WI** = Weathering index

The diagnostic ratio values for particular emission sources are shown in Table. 3. They enhance the distinction between PAH pollution originating from petrogenic (liquid fuel spills), pyrolytic (combustion of fuels) and burning biomass or coal sources.

Table 3: Some diagnostic ratio values for particular emission sources

Diagnostic Ratio	**Petrogenic**	**Fuel combustion**	**Coal, grass, wood burning**
Ant/(Ant+Phen)	< 0.1	> 0.1	-
BaA/(BaA + CHR)	< 0.2	> 0.35	0.2 - 0.35
Flt/(Flt +Pyr)	< 0.4	0.4 - 0.5	0.5

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Spill type

The spill types were determined greatly on the basis of some observations and the adopted analytical method. Ordinarily, any spill that occurs near a wellhead will be assumed to be petroleum related, as it would not have undergone biodegradation or weathering. In this wise, samples obtained were analyzed using GC-FID. The gas chromatogram showed the presence of hydrocarbons in the range of nC_9-nC_{31}, which observation is typical for Nigerian Deltaic crude oils. The hump within the baseline of the GC trace indicates the presence of modified hydrocarbon compounds such as Alkanones, Alkanals, Alkanoic acids, Alkanoates. These are the byproducts of oxidation and biodegradation of crude oils, and indicate that the spill type is petroleum hydrocarbons (Wang et al., 1994, Wang et al., 1998).

Contaminant transport media

Soil and surface water constitute the potential contaminant transport and residency media for spilled oil. Observations have shown that the spilled oil undergoes weathering/degradation when exposed to the constantly changing atmospheric conditions. The extent of weathering gives a pointer to the effect of the microbial degradation, which is accounted for by the loss of hydrocarbons at the spill site. This happens because the physical and chemical properties of spilled oil are measurably altered by weathering. Results of analyses of samples of soil, groundwater and surface water from the nearby Orashi River showed presence of hydrocarbon (Figures 2b and 4b) similar to that of the source (Figure 2a) which is from the wellhead. This indicates migration and spread of the contaminant spill over the surface of the soil and nearby river. The morphology of the soil and the undulating surfaces provide the least resistance pathway for the spill to percolate into the soil as well as flow on the surface of the soil way from the spill point (Wang et.al., 1998). The consistent similarity of the fingerprints with reduced abundance of the hydrocarbon compounds shows the reducing trend expected from the spill point. This infers that the transport media for the spilled oil from the spill point (wellhead) to the potential receptor (River Orashi) are the surface water and soil.

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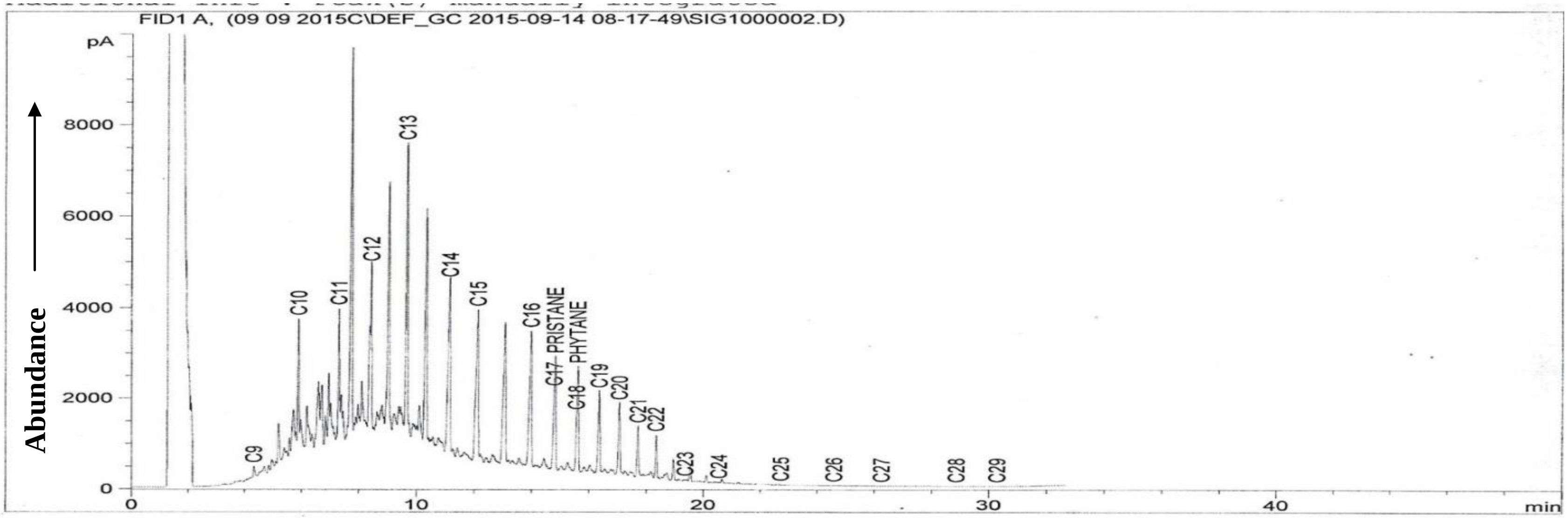

Figure 2a: GC FID profile of Crude sample from Source

Retention Time

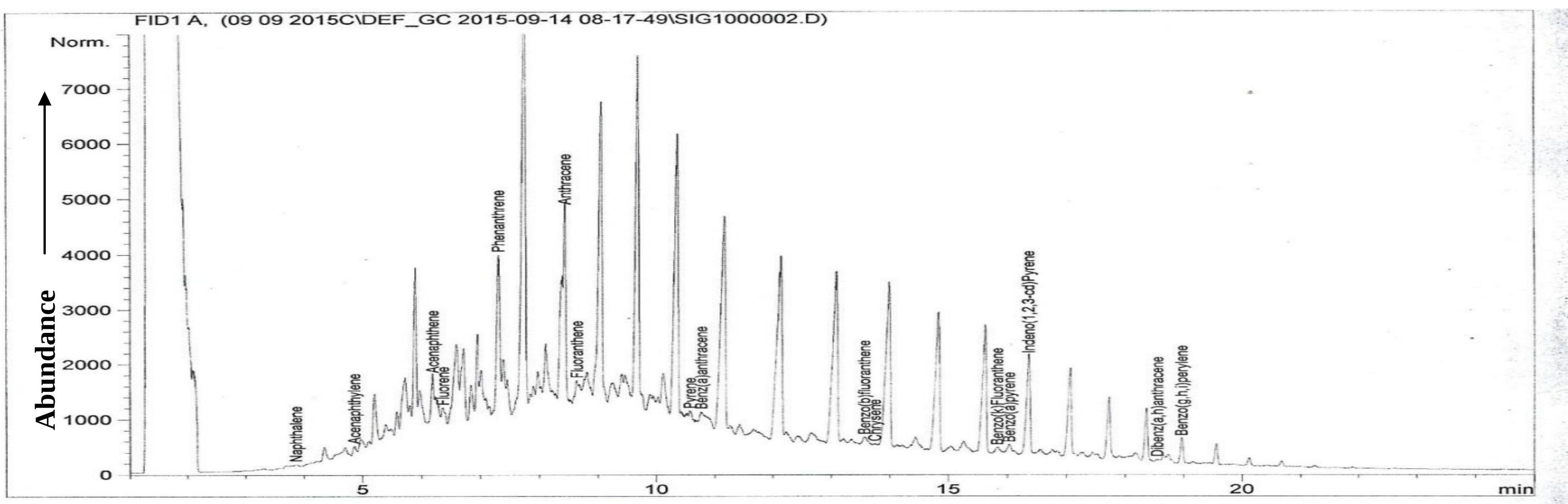

Figure 2b: GC – FID PAH profile for source oil

Retention Time

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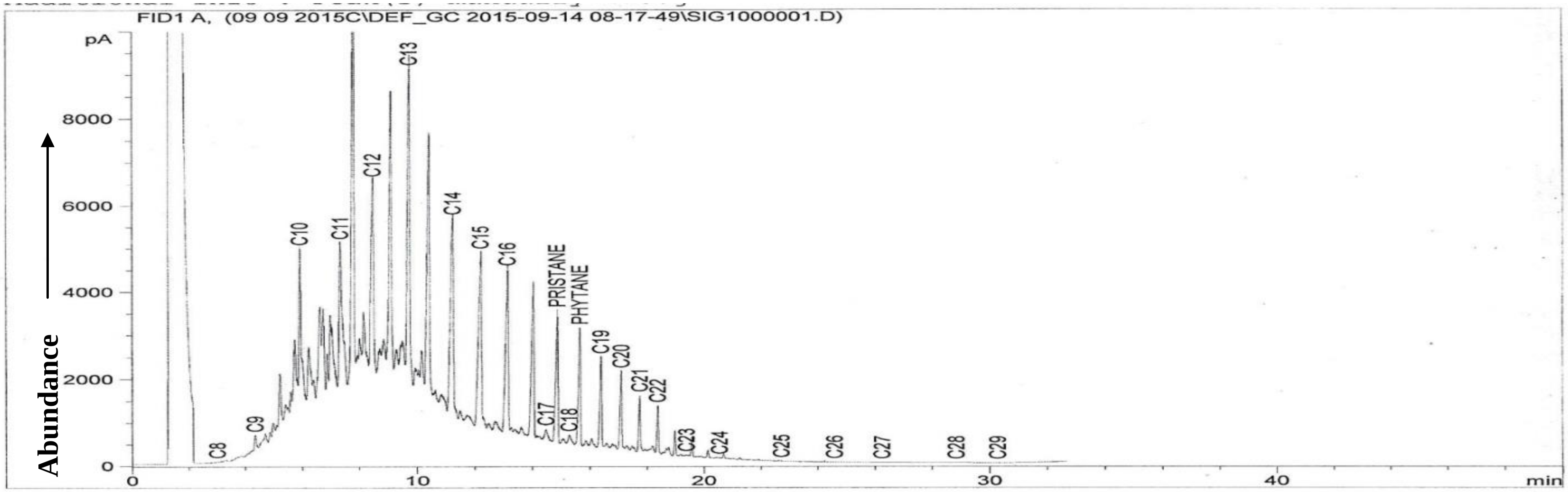

Figure 3a: GC-FID Aliphatics of crude+soil+water sample.

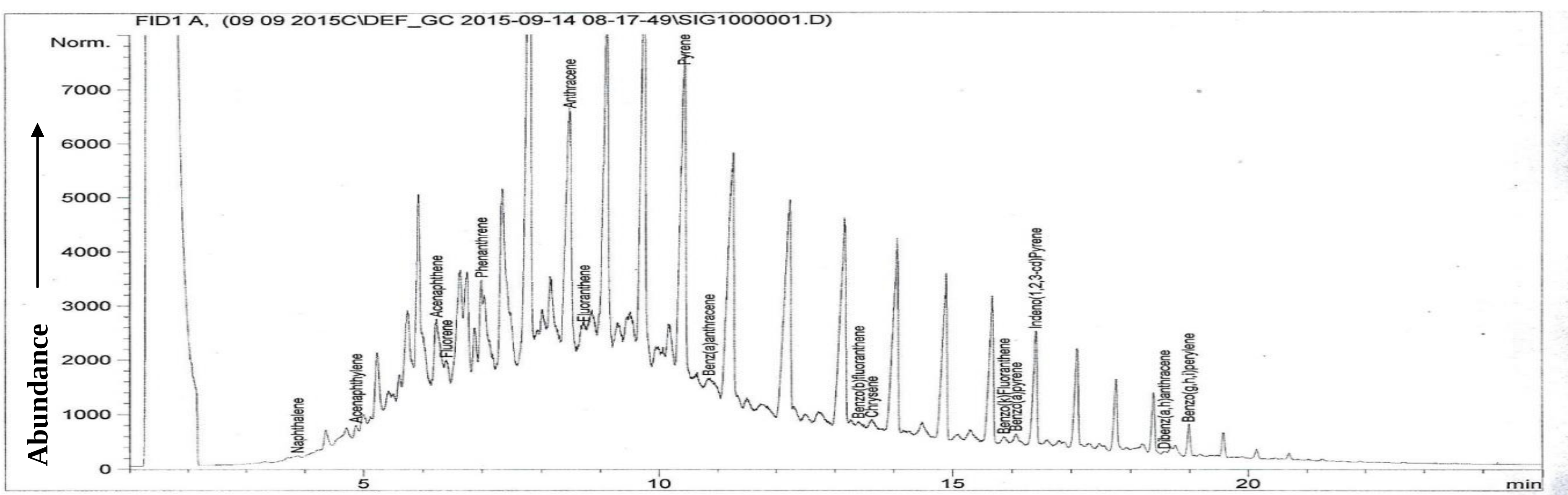

Figure 3b: GC-FID PAH of crude oil impacted soil+water sample.

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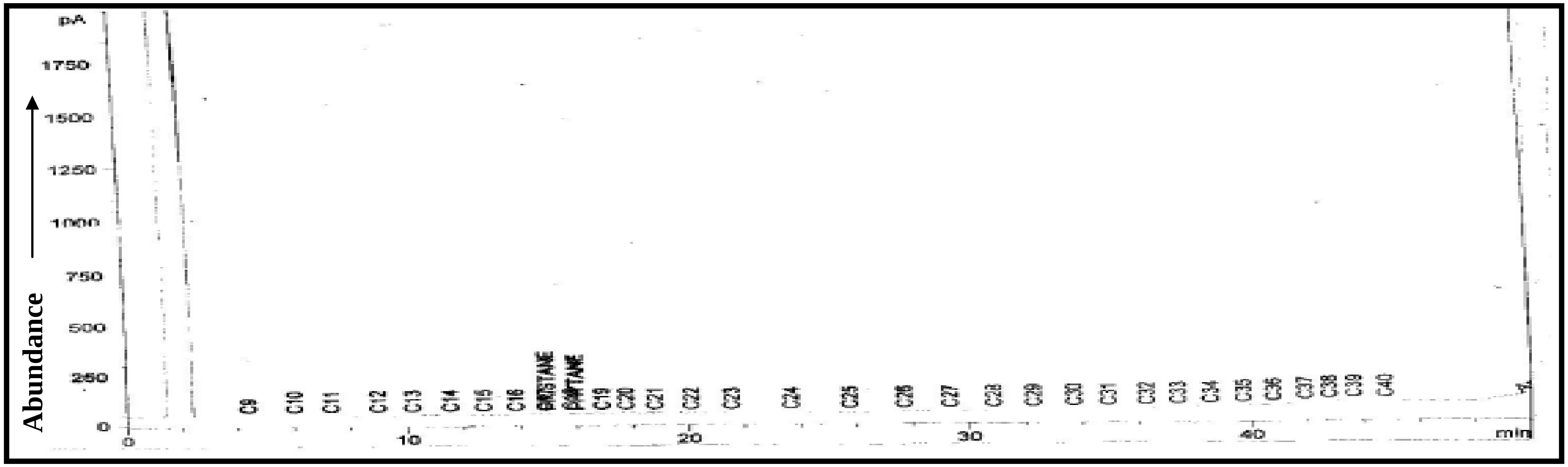

Figure 4a: GC-FID Aliphatics for Groundwater sample

Retention Time

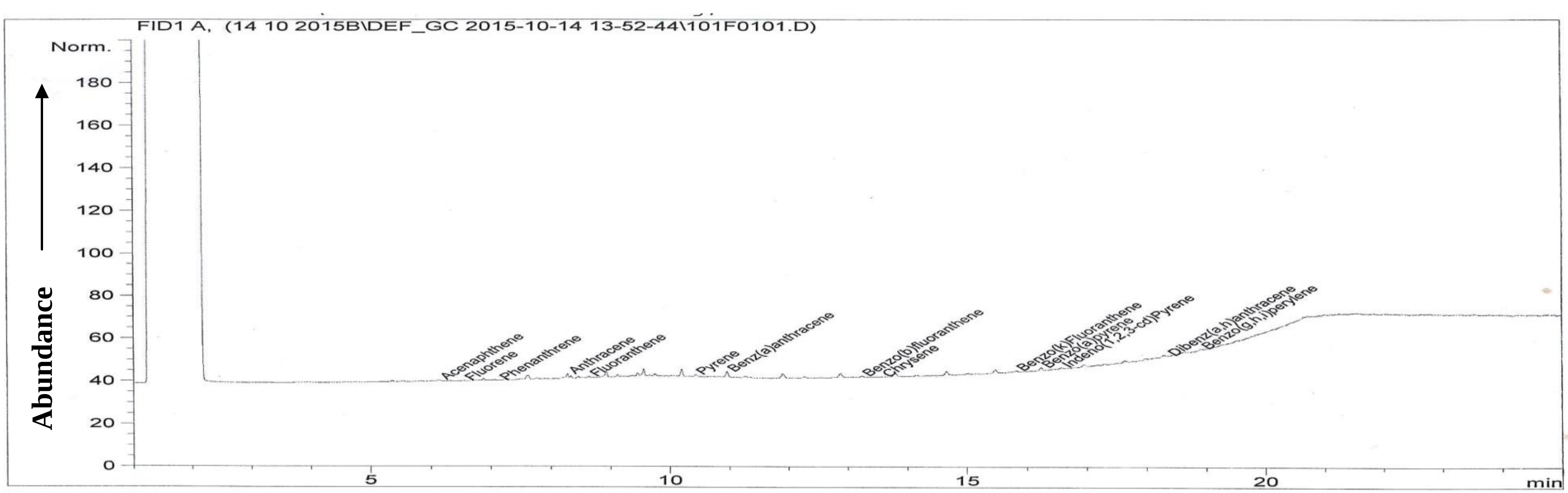

Figure 4b: GC-FID PAH of Groundwater sample.

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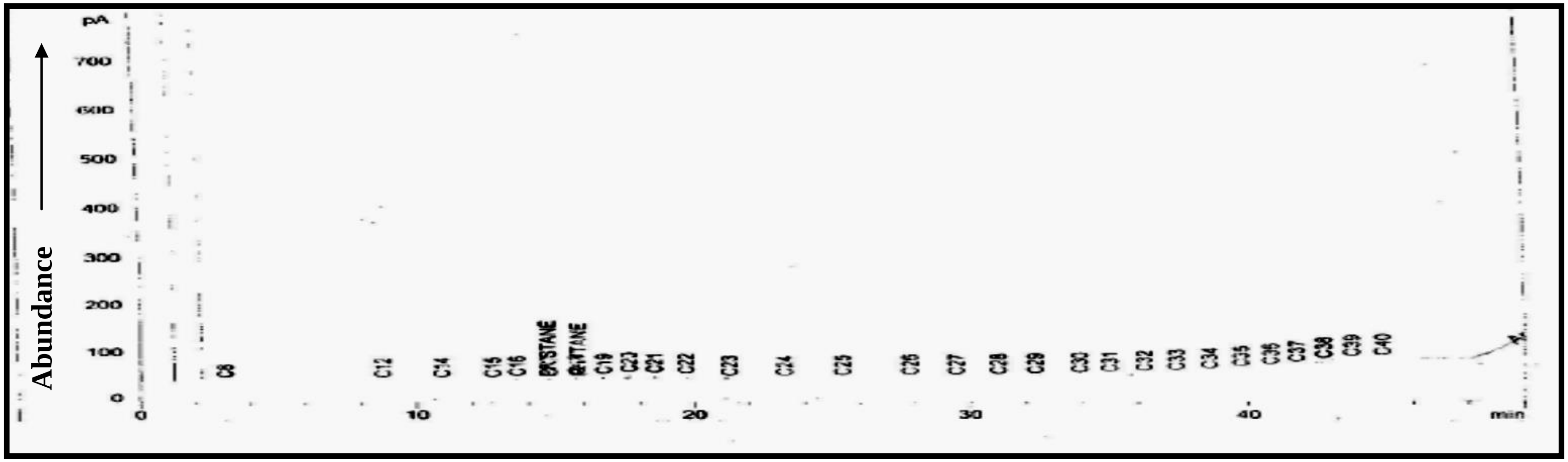

Figure 5a: GC-FID Aliphatics for uncontaminated soil sample

Retention Time

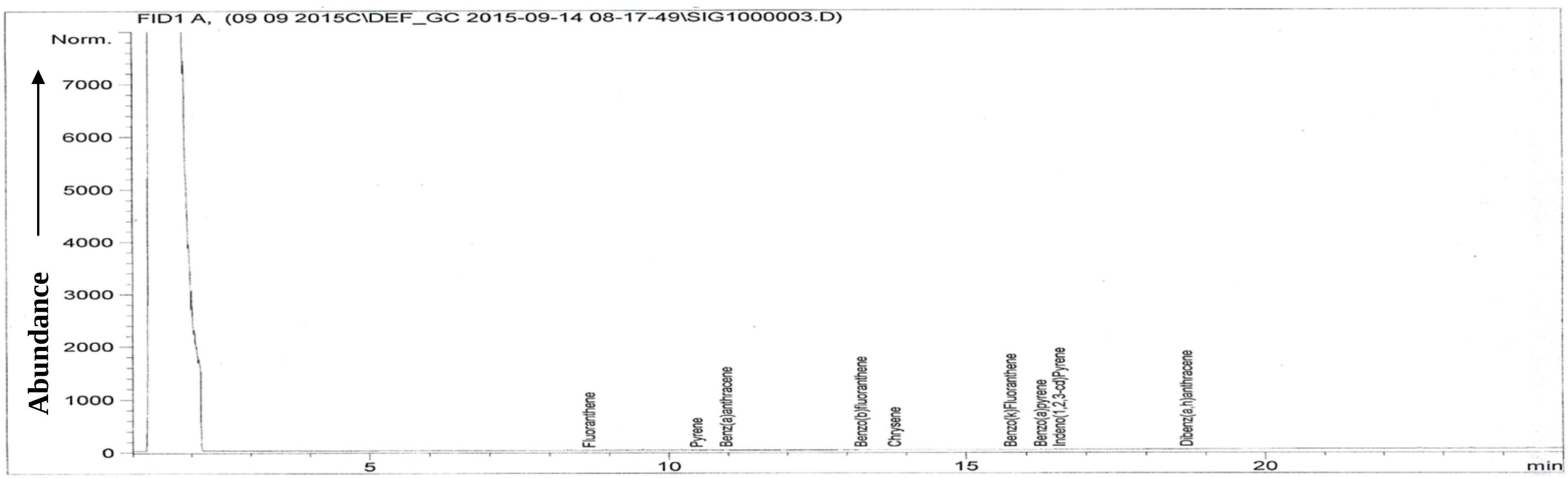

Figure 5b: GC-FID PAH of uncontaminated soil sample.

Retention Time

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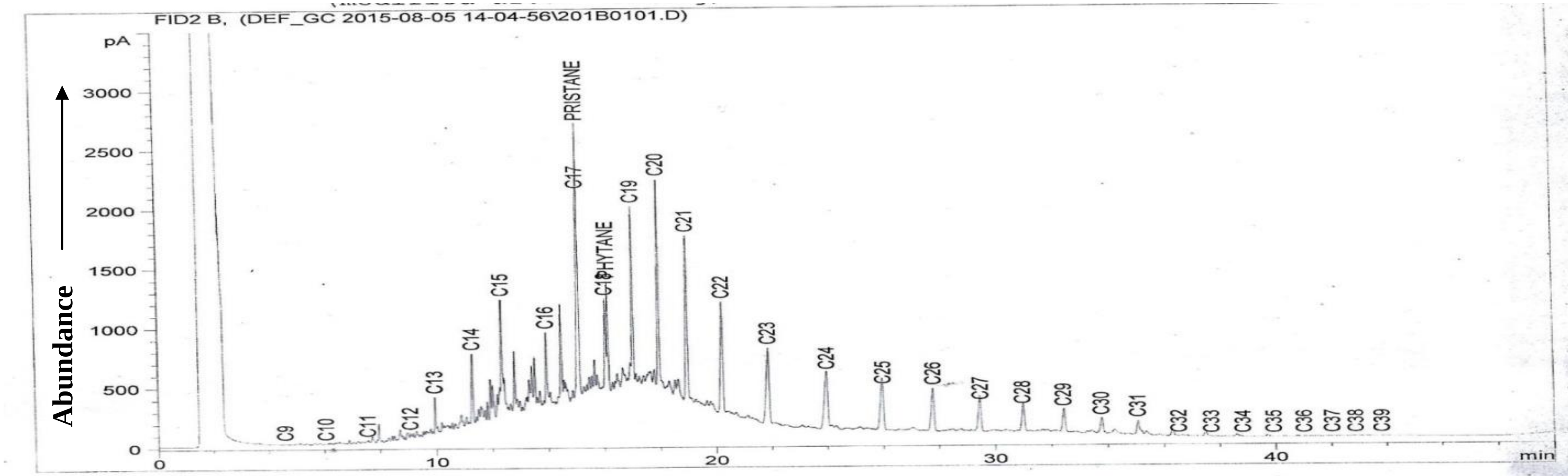

Figure 6a: GC-FID Aliphatics for crude+soil sample.

Retention Time

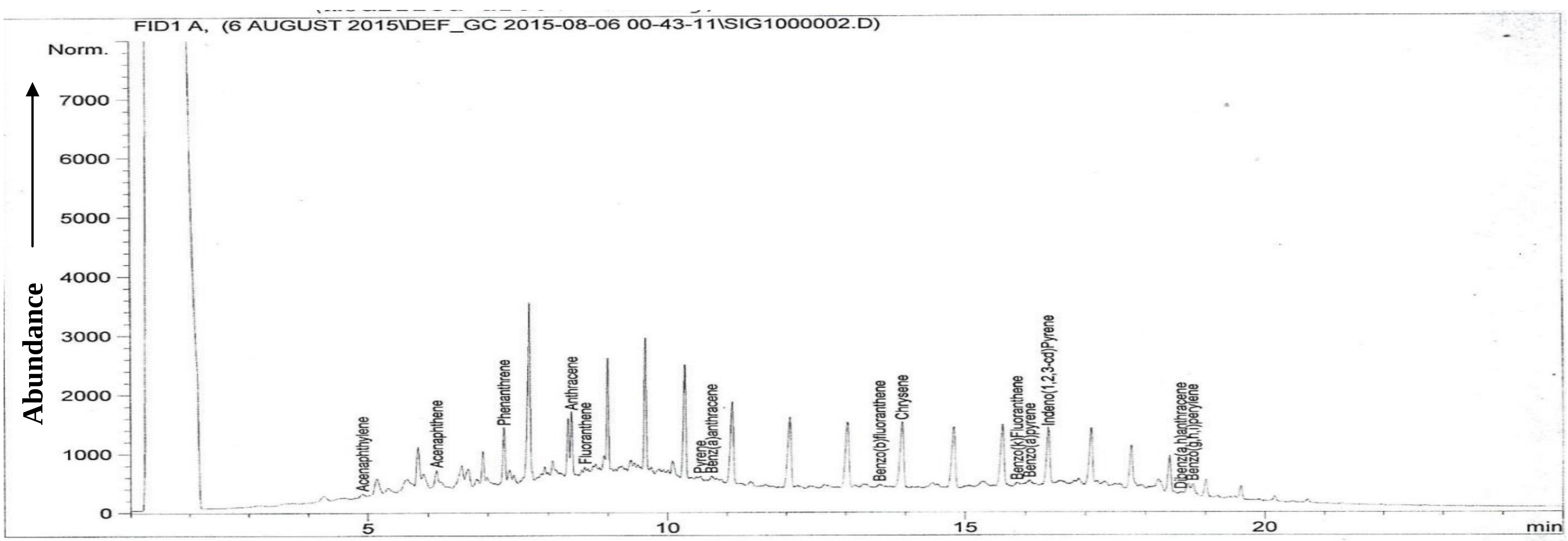

Figure 6b: GC-FID PAH Oil impacted soil

Retention Time

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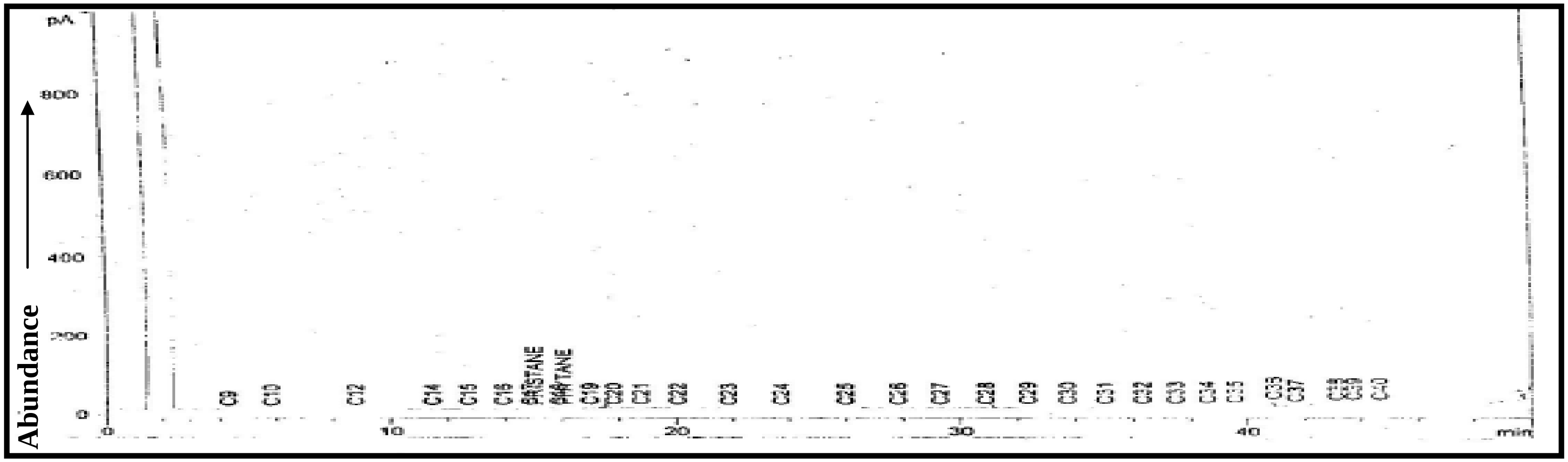

Figure 7a: GC-FID Aliphatics for Surface water sample.

Retention Time

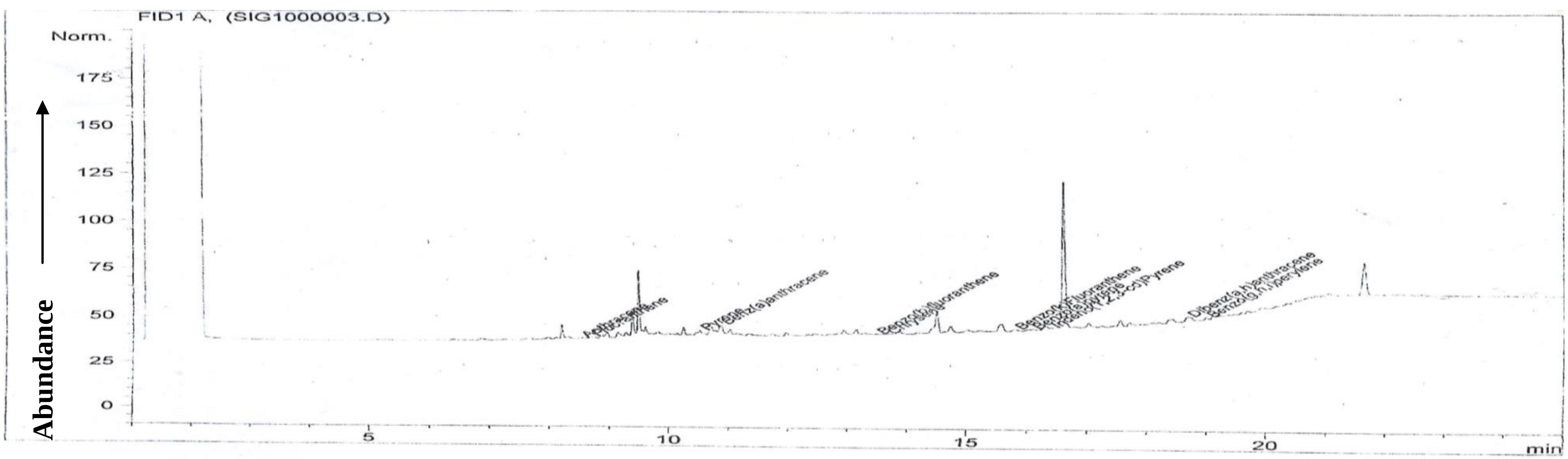

Figure 7b: GC-FID PAH Surface Water (River Orashi)

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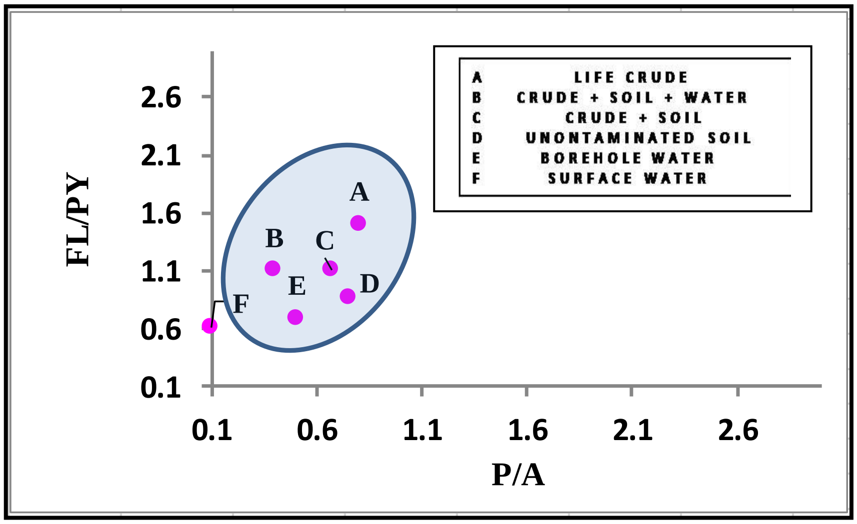

Figure 8: Plot of some diagnostic ratios, showing the distribution of compounds

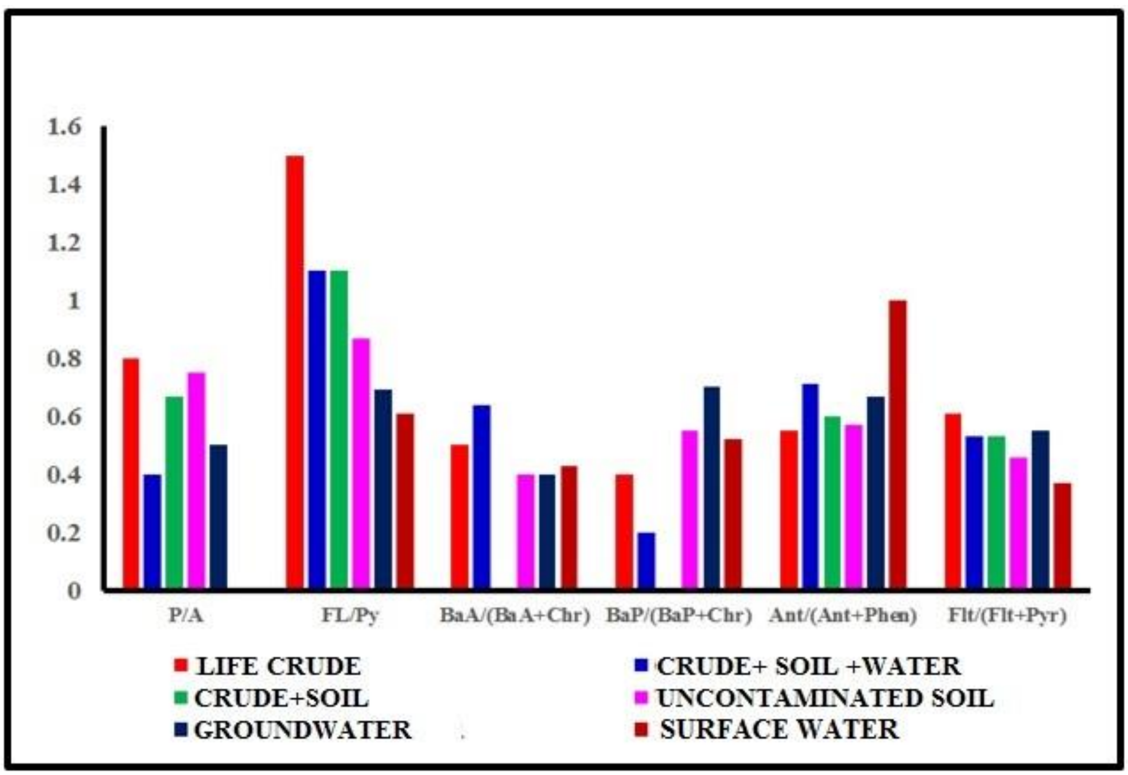

Figure 9: PAH diagnostic ratio of the source samples and the site samples.

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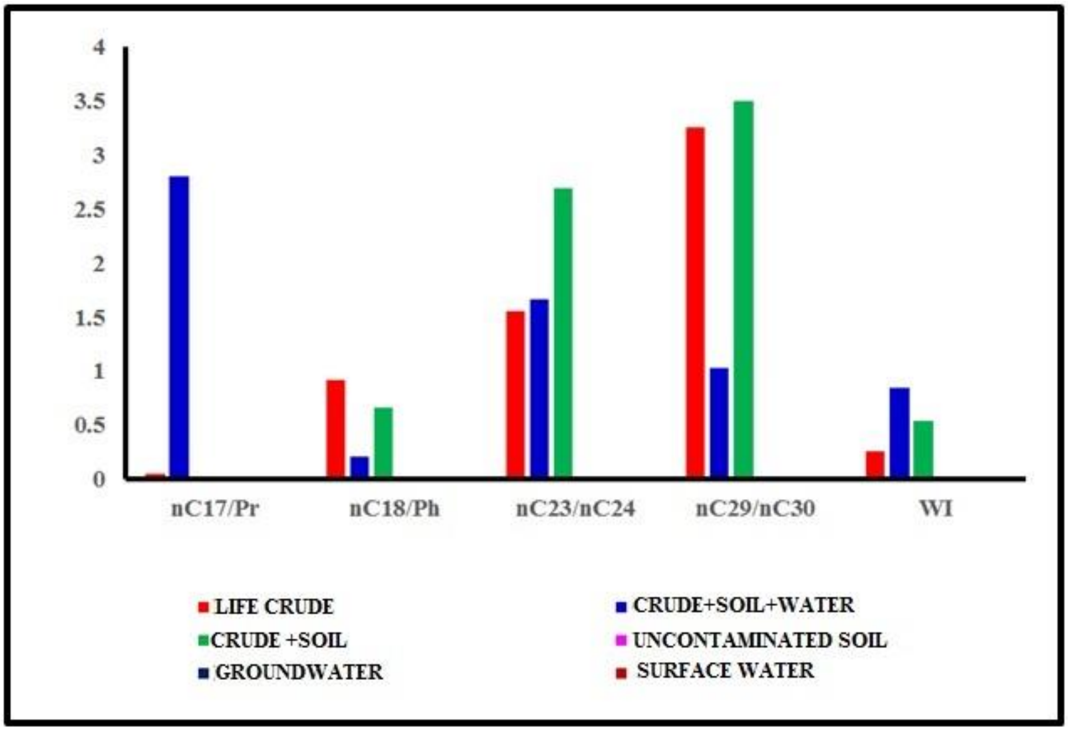

Figure 10: The saturated hydrocarbon ratios and weathering index for the samples.

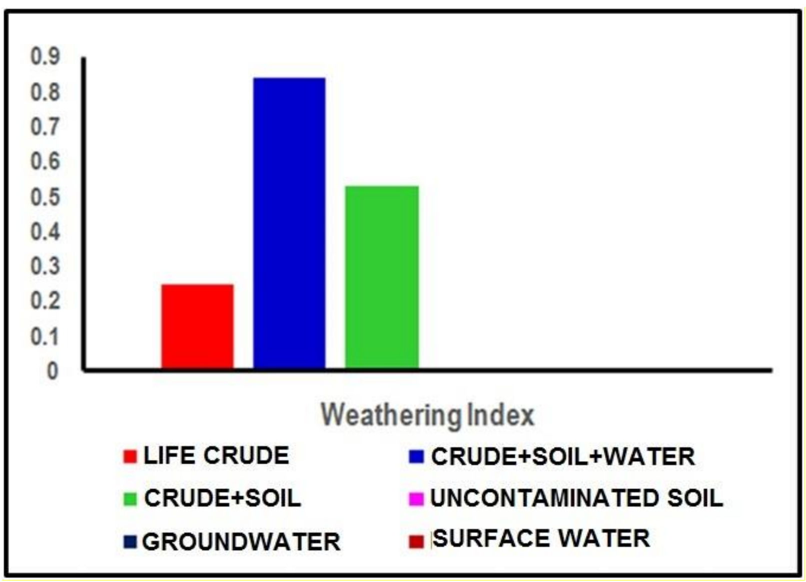

Figure 11: The weathering index for the site samples and suspected source sample

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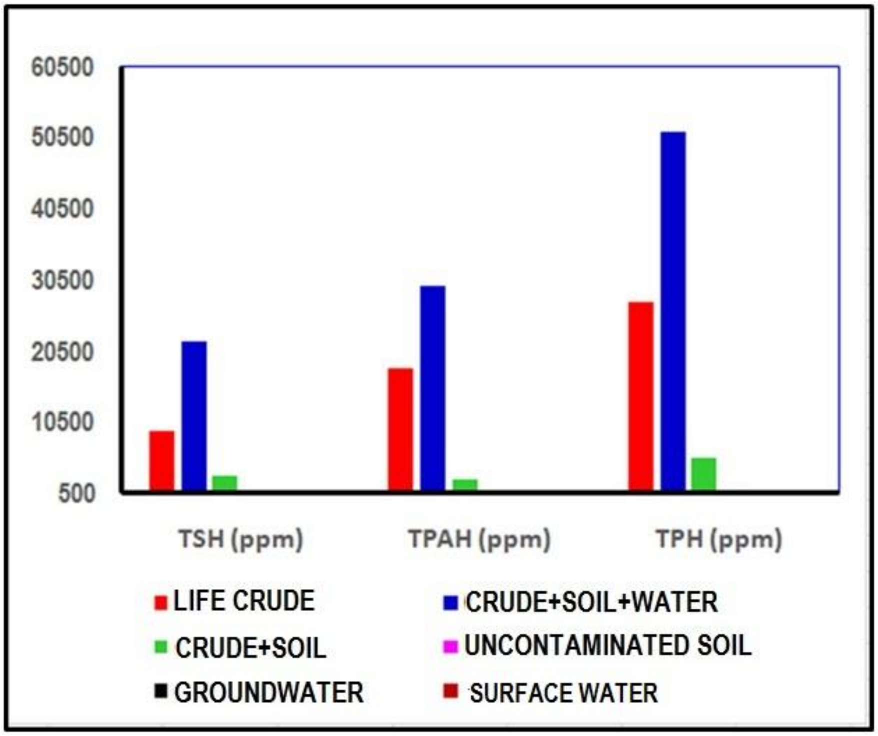

Figure 12: The total saturated hydrocarbon (TSH), total poly aromatic hydrocarbon (TPAH)

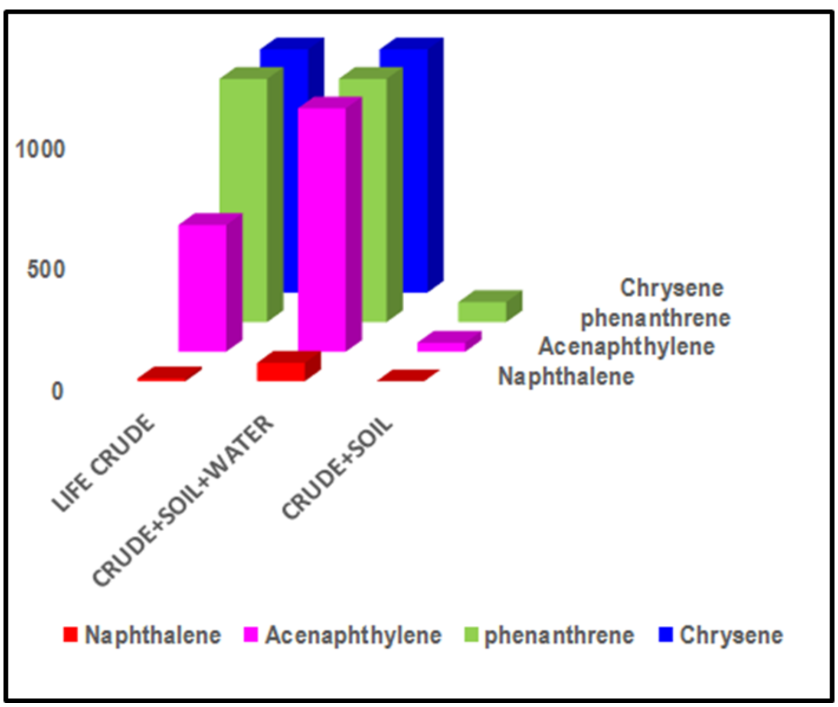

Figure 13: The distribution of some aromatic compounds in source sample and site samples.

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End receptor.

According to Goldstein et. al. (2011) and Swartjes (2011), living resources and their habitats constitute the end point of contaminant spills and include marine life, birds, mammal and human resources (i.e. fisheries, aquaculture, tourism and recreational areas). The study area together with the Orashi River manifests these components and consequently presents as a potential drainage point with the tendency to distribute the spilled oil. This implies that fish and any other animal caught from the River Orashi for human consumption would show contamination and as a consequence, have the humans as the most likely end receptors.

The GC profile for River water sample (figure 4b) showed significant but low concentrations of PAH hydrocarbon. River water ideally serves as the habitat media, particularly, marine life (animal and plants). The low concentration could be attributed to persistent dilution of runoffs which undoubtedly leads to reduced concentration of PAH over time within the River body. The GC fingerprint for the oil - impacted soil and water sample (Figure 2b) and the source sample (Figure 2a) showed a very high degree of similarity, which represents similar compositional distribution of PAH in both the source sample and the oil - impacted soil and water.

Conclusion.

The Obrikom 2014 spill was evaluated for the determination of its source, its transport and residency media and its end receptor. The GC fingerprints of samples collected at the source point indicate presence of hydrocarbon compounds, inferring petroleum spill. The transport media were established to be soil and surface water, as elucidated by the GC profiles of the soil, water, oil sample to that of the wellhead sample. The Orashi River serves as the end receptor, with input via runoffs and drainage due to the morphology and undulated nature of soil surface providing least resistance pathway for the flowing petroleum front into the river.

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