

ASSOCIATED PETROLEUM HYDROCARBONS AND HEAVY METALS OF AN OIL SPILLED SITE IN THE NIGER DELTA, NIGERIA

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ABSTRACT

Soil samples were collected from an oil polluted site in the Niger - Delta, of the southern region of Nigeria, and were analyzed for petroleum hydrocarbons and heavy metals, which may have been introduced to the soil as a result of the oil spillage that was incidence at the site. The total extractable hydrocarbon content (THC) of $1.13 \times 10^5 \pm 2.91 \times 10^4$ mg/kg of the affected soil revealed a high level of petroleum hydrocarbon contamination that far exceeds compliance limits. The gas chromatographic analyses conducted on the samples showed significant contamination in the n-C12 - n-C17 range, especially the n-C13 and n-C17 fractions, and pristane being more abundant than phytane. It also showed a significant concentration of the polycyclic aromatic hydrocarbons (PAHs) with naphthalene which may actually be oxidized before many saturates which are the most prone to biodegradation and attenuation, while indeno 1, 2, 3 cd pyrene was the most abundant. The results also depicted a substantial concentration of the benzene, toluene, ethyl benzene and xylene (BTEX) fractions with 1, 3, dichlorobenzene as the most abundant fraction while o-xylene had the least concentration. Heavy metals were detected in varying concentration in polluted soils. Zinc had the highest concentration of 9.84 ± 0.93 mg/kg while Arsenic had the least concentration of 0.12 ± 0.04 mg/kg. These results suggest that as at the time of sample collection, the spilled oil was still fresh on site. That pristane was more abundant than phytane inferred an oxic depositional environment of a probable non-waxy, marine derived organic matter and a phytoplankton input for the spilled oil.

KEYWORDS: Petroleum hydrocarbons, Heavy metals, Oil spillage, Pollution, Attenuation

INTRODUCTION

Petroleum, in common parlance, refers to the three major forms of hydrocarbons namely crude oil, natural gas and condensates. Crude oil, the liquid form of petroleum, is a complex mixture of hydrocarbons or substituted hydrocarbons varying widely in both physical and chemical properties (Atlas, 1981; Leahy and Colwell, 1990). Crude oil may be characterized in terms of four primary fractions namely, saturates, aromatics, resins and asphaltenes with an average density of 850 kg/m³ (Connell and Miller, 1981). Saturates include straight or branched chain n-alkanes, and the cycloalkanes with one or more saturated rings, while aromatic include compounds with one or more fused aromatic rings, each of which may be attached saturated side chains (alkyl-substituent). In contrast to the saturated and aromatic fractions, both resins and asphaltenes consist of non-hydrocarbon polar compounds, with trace amounts of nitrogen, sulphur and/or oxygen in addition to carbon and hydrogen, and often forming complexes with heavy metals. Structurally, the predominant constituents of crude oils include its total petroleum hydrocarbon (TPH), the polycyclic aromatic hydrocarbon (PAH), and the volatile aromatics, benzene, toluene, ethyl benzene and xylene (BTEX) (Osuji, Udoetok and Ogali, 2006). The compositional variation of crude oils results from the geohistory of a particular crude oil, and this confers on it marked peculiarity in chemical and physical properties.

The Niger - Delta region bordering the Atlantic ocean from latitude 30 to 90 East and latitude 4030' to 5020' North (Short and Stouble, 1967; Agagu, 1978; Whiteman, 1982) is the petroleum resource base of Nigeria. However, the petroleum resource potential of this region is fundamental to massive oil spillages and its appurtenances. When crude oil is spilled, the consequence is the release of petroleum hydrocarbon into the environment. The characteristics of the oil affect the way the oil spreads as well as the hazard it might pose to the affected environment. Basically, the heavier crude fractions are more likely to cause more mechanical damage than the lighter fractions, which are apparently not as damaging physically but more toxic. The extent of contamination of the environment by these petroleum hydrocarbons is however determined by their concentration in the soil. When their concentrations reach a certain level, they become toxic to the resident flora and fauna (Osuji et al., 2004).

The present study examines the concentrations of petroleum hydrocarbons and heavy metals associated with oil spillage in the study area. The study site was selected from the petroliferous Niger - Delta of southern Nigeria, following reconnaissance surveys of oil impacted areas in the region. The interest of this study was focused on the level of contamination of the site as a result of the introduction of these hydrocarbons to the soil and the resultant consequences thereof.

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MATERIALS AND METHODS

Site Description and Sample Collection

The study site, Idu – Ekpeye, (Fig. 1) is located at Ahoada West Local Government Area of Rivers State, where an oil pipeline passing through a farmland in the village, was vandalized. It is found between longitudes 6025' – 6035' East and latitudes 4045' – 5010' North, and is located in the humid rainforest of the Niger Delta basin of Nigeria. It records a mean daily temperature of 26°C and rainfall of 180mm; and nearness to the sea influences high precipitation and relative humidity. Sampling was carried out on September 30, 2004 and at the time of sampling, clean up activities were going on at the site. The sampling was done as part of the field reconnaissance survey. The area was divided into 100 grid plots, each measuring 20m x 20m. Soil samples were collected at surface (0-15cm) and subsurface (15-30cm) depths by the use of hand driven augur, and were homogenized. The homogenized soil samples were put in aluminum foil plates, labeled accordingly and taken to the laboratory for analysis.

Laboratory Analyses

Total Hydrocarbon Content (THC)

Soil samples (1g each) were put into a conical flask and 50ml of xylene (10ml at a time), was added to ensure that all the crude is extracted from the soil samples. The xylene/oil mixture was shaken with a wrist action for about five minutes and filtered into a centrifuge tube. This mixture was centrifuged for fifteen minutes at 250 revolutions per minute. The total petroleum hydrocarbon of the mixture was thereafter determined by spectrophotometric method using the HACH DR/2010, at 425nm.

Oil Extraction and Chromatographic Analysis

Five grams (5g) of homogenized samples were accurately weighed into clean, dry beakers. The weighed samples were extracted with 10ml of hexane respectively and passed through a filter paper. The extract (the hydrocarbon/hexane mix), now ready for gas chromatography, was injected into a Varian model 3400 gas chromatograph (GC) with the following operational conditions; flow rate (H₂ 30ml/min, air 300ml/min and N₂ 30ml/min), injection temperature (50°C), detector temperature (320°C), recorder's voltage (1MV), and

chart speed 1cm/min. For interpretation of results, the GC recorder was interfaced to a Hewlett Parker (hp) Computer (6207AA Software, Kayak XA PIT/350 W/48 megabytes CD-ROM). The chromatograms were quantified with respect to the internal standards.

Heavy Metal Analysis

Ten grams (10g) of the granulated sample was weighed into a beaker and 100ml of distilled water was added. An additional 5ml of concentrated nitric acid and boiling chips were added. The mixture in the beaker was heated continuously with addition of small volumes of nitric acid until digestion was complete. Complete digestion was marked by a clear solution. The digested samples was evaporated to a final volume of 10 - 20ml, thereafter, the solution was transferred to a 100ml volumetric flask and diluted to mark. Concentrations of the heavy metals in the extract were determined thereafter using Perkin Elmer model 2280/2380 Atomic Absorption Spectrophotometer. Readings were taken at appropriate wavelengths for each metal.

RESULTS AND DISCUSSION

Total extractable hydrocarbon content (THC) of soils is frequently used to assess and ascertain the extent of contamination at an oil polluted site. The result of the THCs of $1.13 \times 10^5 \pm 2.91 \times 10^4$ mg/kg (Table 1) of the oil-affected soils indicates a high level of hydrocarbon contamination at the study site. This THC level exceeds the 50ppm limit set for petroleum industries in Nigeria (DPR, 1991). Though there have been reported cases of microorganisms using hydrocarbons as a source of energy, the presence of petroleum hydrocarbons at high concentrations creates anaerobiosis, which depletes available oxygen and also reduce gaseous diffusion into the soil (Osuji, 2001). Additionally, such concentration of hydrocarbons on site is capable of endangering plant species such *Solanum anomalum*, *Symphonia globulifera* and other agricultural crops. Osuji et al. (2004) report a percentage decrease of 85% for *Andropogon gayanus* in a post impact survey of an oil-impacted area. Therefore there is need for remedial and control measures to be taken at the study site so as to forestall further negative impacts on the socio-economic activities in the area.

Table 1: Total Hydrocarbon Content (THC) of soil samples from an oil spilled site in the Niger - Delta, Nigeria.

Sample locations	THC (mg/kg)
IDU 024	1.87×10^5
IDU 048	9.99×10^4
IDU 052	8.33×10^4
IDU 065	8.94×10^4
IDU 078	7.91×10^4
IDU 083	1.08×10^5
IDU 095	1.45×10^5
Mean ± S.E	$1.13 \times 10^5 \pm 2.91 \times 10^4$

Results of the total petroleum hydrocarbon (TPH), polycyclic aromatic hydrocarbons (PAH) and benzene, toluene, ethyl benzene and xylene (BTEX) contents of the oil-impacted soils are presented in Tables 2 - 4. The gas chromatographic analyses conducted on the samples showed an abundance of n-C8 - n-C23 (Table

2); it showed a substantial concentration of the polycyclic aromatic hydrocarbons (Table 3) and also a significant concentration of benzene, toluene, ethyl benzene and xylene fractions (Table 4). These results show that the spilled oil was still fresh on site with high level of hydrocarbon fractions in the n-C12 - n-C17

range, especially the n-C13 and n-C17 fractions. The results also show that pristane was more abundant than phytane. Pristane is a product of decarboxylation and tend to be more abundant in more oxidizing environments such as peat swamps and low in strongly

reducing environments (Kaufman et al., 1990). Hence this high concentration of pristane suggests an oxic depositional environment and a phytoplankton input for the spilled oil.

Table 2: Total petroleum Hydrocarbon (TPH) content of soil samples from an oil spilled site in the Niger - Delta, Nigeria

TOTAL PETROLEUM HYDROCARBON	
Hydrocarbon fraction	Amount (mean \pm S.E mg/kg)
C8	385.83 \pm 425.19
C9	346.92 \pm 200.82
C10	117.12 \pm 119.13
C11	125.00 \pm 226.84
C12	726.05 \pm 409.58
C13	3946.58 \pm 2711.99
C14	1179.40 \pm 1114.16
C15	1172.18 \pm 2711.99
C16	675.92 \pm 239.64
C17	1851.45 \pm 1771.43
Pristane	662.71 \pm 750.10
C18	322.90 \pm 329.49
Phytane	116.37 \pm 101.05
C19	77.64 \pm 94.11
C20	89.37 \pm 65.87
C21	105.30 \pm 151.74
C22	255.32 \pm 372.05
C23	404.08 \pm 750.09

Table 3: Polycyclic aromatic Hydrocarbon (PAH) Content of soil samples from an oil spilled site in the Niger - Delta, Nigeria.

POLYCYCLIC AROMATIC HYDROCARBON	
Hydrocarbon fraction	Amount (mean \pm S.E mg/kg)
Naphthalene	8.16 \pm 6.3
Acenaphthylene	69.15 \pm 48
Acenaphthene	88.58 \pm 31.66
Fluorine	126.25 \pm 46.73
Phenanthrene	151.1 \pm 65.27
Anthracene	158.64 \pm 47.26
Fluoranthene	281.96 \pm 145.85
Pyrene	126.26 \pm 381.63
Benzo(a) anthracene	313.09 \pm 351.86
Chrysene	269.31 \pm 191.18
Benzo (b) fluoranthene	355.48 \pm 333.27
Benzo (k) fluoranthene	134.23 \pm 63.9
Benzo (a) Pyrene	63.9 \pm 310.96
Indo 1,2,3 cd Pyrene	375.81 \pm 287.31
Dibenzo (a,b) anthracene	73.66 \pm 24.85
Benzo (ghi) perylene	231.37 \pm 192.87

The results obtained for the polycyclic aromatic hydrocarbons (PAHs) revealed that naphthalene which may actually be oxidized before many saturates (Fotgh and Westlake, 1987) was the most prone to biodegradation and attenuation as depicted by its least concentration (Table 4). Also, indeno 1, 2, 3 cd pyrene was the most abundant PAH fraction.

BTEX level in oils is an important parameter due to its toxicity and environmental concerns. BTEXs are hazardous carcinogenic and neurotoxic compounds and are classified as priority pollutants by the EPA (Wang et

al., 1995). The presence of peaks in the Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) fingerprints of the samples also suggests that the oil was only slightly degraded, as these hydrocarbon fractions are highly volatile and easily degraded under aerobic conditions. The result obtained in this study show that 1, 3, dichlorobenzene was the most abundant, while o-xylene, had the least concentration. Kaplan et al. (1996) used these hydrocarbon fractions to determine whether an oil spill is recent or not.

Table 4: Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) content of soil samples of an oil spill site in Niger - Delta, Nigeria

BTEX	
Hydrocarbon fraction	Amount (mean \pm S.E mg/kg)
Benzene	27.08 \pm 23.04
Chlorobenzene	16.76 \pm 14.06
1,2, dichlorobenzene	20.08 \pm 8.96
1,3, dichlorobenzene	29.05 \pm 28.01
1,4, dichlorobenzene	5.23 \pm 2.26
Ethyl benzene	12.06 \pm 5.91
Toluene	19.44 \pm 12.1
m,p - xylene	18.25 \pm 8.75
O - Xylene	3.66 \pm 3.23

Heavy metals were detected in varying concentration in polluted soil (Table 5). The results show a mean concentration (\pm S.E) mg/kg of 0.48 \pm 0.07 for Nickel, 0.34 \pm 0.13 for Lead, 0.32 \pm 0.07 for Chromium, 0.12 \pm 0.35 for arsenic, 0.24 \pm 0.10 for cobalt, 9.84 \pm 0.93 for zinc and 0.32 \pm 0.11 for copper. This result shows that Zinc was the most abundant heavy metal. Many studies on the Niger - Delta such as NDES (1999) have shown that soils naturally have varying but trace amounts of heavy metals even in undisturbed environment. Therefore it is normal to have obtained this varying amount of heavy metals at the study site. Enhanced concentrations of metals like nickel, copper and lead in the soils may result in absorption by plants,

which may bring about possible bioaccumulation by such plants and the animals that depend on the plants for survival, and all of these may lead to toxic reactions along the food chain (Osuji and Onojake, 2004). Therefore, in appraising the potential hazards of these heavy metals associated with crude oil, it is pertinent to consider appropriate depollution measures so as to check the possible biomagnification of these metals especially some of them like Nickel, which is persistent. The concentration of Nickel was by far higher than that of Vanadium, which was below detection limit suggesting that the spilled oil was sweet crude oil. Sweet crude oil generally has higher concentration of Nickel than Vanadium (Udoetok, 2005).

Table 5: Heavy metal contents of soil samples an oil spill site in Niger - Delta, Nigeria.

HEAVY METALS	Amount (mean \pm S.E mg/kg)
As	0.12 \pm 0.04
Cr	0.32 \pm 0.07
Ni	0.48 \pm 0.07
Pb	0.34 \pm 0.13
Co	0.24 \pm 0.10
Zn	9.84 \pm 0.93
Cu	0.32 \pm 0.11
V	BDL

* BDL = Below detectable limit (where detectable limit is 1 x 10³ mg/kg)

The introduction of petroleum hydrocarbons to the study site as a result of the oil spill incident there may have been responsible for the high level of petroleum hydrocarbons obtained at the site. This is evident by the high level of total hydrocarbon content (THC), significant concentration of total petroleum hydrocarbon fractions within the n-C12 - n-C17 range, especially the n-C13 and n-C17 fractions, the high concentration of polycyclic aromatic hydrocarbons (PAHs) and the substantial concentration of the volatile BTEX fractions. Indeed, the overall results suggest a very high level of hydrocarbon contamination at the study site.

Conclusion

The results obtained from this study reveal high concentration of hydrocarbons at the study site. Although clean up activities were on-going at the time of sampling, extra depollution measures should be

employed expeditiously at the site to avoid the spreading of these contaminants to unpolluted lands through weathering processes, and further consequences which may be inimical to the agricultural productivity of the area and the socio-economic well being of the residents. Remedial contingencies should include an immediate excavation of the oil-coated layer of soils and possible application of lime and fertilizer supplements to normalize pH and increase metabolic activities of hydrocarbon utilizing microbes at the site. Also, there is need for constant review of the Environmental Impact Assessment (EIA) regulations and guidelines to accommodate changing technology and public expectations so as to check the massive pollution and consequent degradation of our environment.

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