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Petroleum Hydrocarbon Fingerprinting and Heavy Metal Distribution in Selected Oil Spill Impacted Sites in Rivers State, Nigeria

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ABSTRACT

Oil spills in the Niger Delta, have caused severe environmental degradation. This study investigated petroleum hydrocarbon contamination and diagnostic fingerprinting of oil spill-impacted soils from K-Dere and B-Dere communities in Rivers State, Nigeria. Six soil samples were collected from two impacted sites and analyzed for heavy metals using Atomic Absorption Spectroscopy and for Total petroleum hydrocarbons using Gas Chromatography-Flame Ionization Detection. Diagnostic ratios, including Pr/Ph, nC17/Pr, nC18/Ph and Carbon Preference Index (CPI), were calculated. Heavy metal concentrations varied across sites: Cadmium (0.16 – 0.60 mg/kg), Cobalt (0.40–5.30 mg/kg), Mercury (0.010–0.073 mg/kg), Copper (1.30 –6.50 mg/kg), Lead (0.11–1.01 mg/kg), Nickel (0.55–5.50 mg/kg), Vanadium (0.23–1.53 mg/kg), Chromium (0.91–6.70 mg/kg) and Iron (1042.5–2321.3 mg/kg). TPH concentrations ranged from 202.32 mg/kg to 20,326.5 mg/kg. K-Dere-01 (16,360.4 mg/kg), K-Dere-02 (13,369.3 mg/kg) and B-Dere-03 (20,326.5 mg/kg) exceeded the EGASPIN intervention value of 5000 mg/kg, indicating severe petroleum contamination. Gas Chromatography-Flame Ionization Detection chromatograms revealed n-alkane distributions (C15– C35) with unresolved complex mixtures and biomarkers (pristane, phytane). Diagnostic ratios showed Pr/Ph: 1.18–1.45, nC17/Pr: 0.74–1.48, nC18/Ph: 0.69 –1.36 and CPI: 1.01–1.10, confirming marine crude oil contamination with varying degrees of biodegradation. K-Dere samples contained relatively fresher hydrocarbons, while B-Dere samples showed more weathered and biodegraded residues. Contamination Factor, Geo-accumulation Index and Pollution Load Index indicated generally low heavy metal pollution. Urgent remediation is recommended for highly contaminated sites.

Keywords: Petroleum hydrocarbons, Fingerprinting, diagnostic ratios, oil spill, Heavy metals, biodegradation

Introduction

Oil spills represent one of the greatest environmental risks associated with oil production and exploration, particularly in the Niger Delta region of Nigeria[1]. The release of oil into terrestrial and aquatic ecosystems causes significant damage to soil fertility, biodiversity and human health[2]. The Ogoni area of Rivers State has been chronically polluted for decades as a result of sabotage, ageing infrastructure and poor enforcement of environmental regulations[3].

Complex mixtures of aliphatic, aromatic and unresolved complex mixtures (UCM) comprising hydrocarbons vary according to their source, maturation and alteration history[4]. Two principal analytical techniques used in environmental forensics for the detection and attribution of hydrocarbons in contaminated sites are fingerprinting and diagnostic ratio analysis[5]. While diagnostic ratios use specific compound ratios to infer processes such as weathering or biodegradation, fingerprinting employs qualitative and quantitative assessment of hydrocarbon constituents for the characterization of petroleum residues[6].

Because of frequent oil spills from pipeline breaks, artisanal refining and operational discharges, Ogoni communities have suffered severe environmental degradation[7]. According to Nwankwoala and Nwankwoala [8], these spills have resulted in persistent contamination of soil and water, reducing agricultural productivity and creating public health risks. Despite multiple remediation efforts, many affected sites have not been evaluated with thorough molecular-level characterization of petroleum hydrocarbons. Without accurate fingerprinting and diagnostic ratio analysis, the ability to distinguish between weathered residues and fresh petroleum inputs is limited, complicating both remediation planning and liability assessments[9].

The purpose of this study was to assess the diagnostic ratios and petroleum hydrocarbon fingerprints of two oil spill-affected locations in Rivers State. The specific objectives were to: (1) use GC-FID to identify the compositional profiles (fingerprints) of petroleum hydrocarbons in soil samples from K-Dere and B-Dere impacted sites; (2) determine the concentration of selected heavy metals (Ni, V, Co, Pb, Cd, Cu, Cr, Fe, K, Hg) using AAS; (3) calculate diagnostic ratios to differentiate fresh petroleum inputs from weathered residues; (4) evaluate the impact of weathering and biodegradation on hydrocarbon distribution; and (5) perform statistical analysis to support source identification.

Materials and Methods

The study was conducted in selected oil spill-impacted sites of K-Dere and B-Dere communities within Ogoni land, Rivers State, southern Nigeria. Ogoni land lies within the eastern Niger Delta between latitudes 4°30′-4°45′N and longitudes 7°10′-7°30′E. The area has a tropical monsoon climate with annual rainfall of 2000-2500 mm. The terrain is generally low-lying with clayey to sandy-loam soils **(Figure 1)**.

Sample collection and preparation

Six surface soil samples (0–15 cm depth) were collected from two impacted locations (K-Dere and B-Dere; three samples each) using a pre-cleaned stainless-steel auger. Multiple subsamples within a 5 m radius were homogenized to form composite samples. Approximately 500 g of soil was placed into solvent-rinsed amber glass jars with Teflon-lined caps and stored at 4°C prior to analysis. A control sample was collected from an unimpacted site approximately 2 km from the nearest spill location.

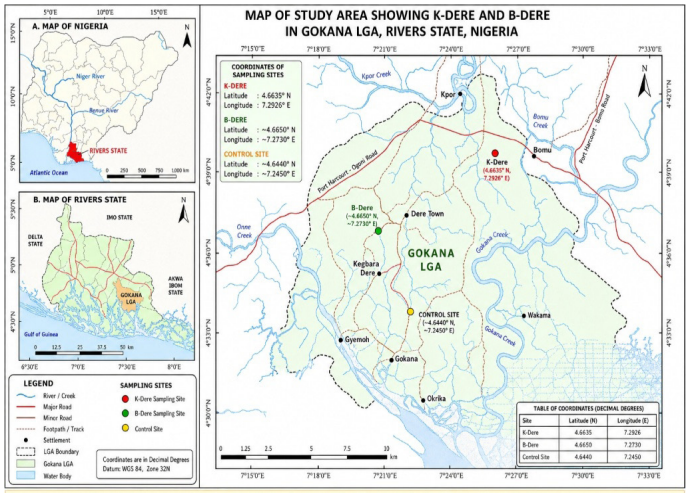

Figure 1: Map of Rivers State showing the Study Location.

Samples were air-dried at room temperature, sieved through a 2 mm mesh and extracted using Soxhlet extraction (USEPA Method 3540C) with n-hexane:dichloromethane (1:1 v/v) for 16 hours. Extracts were concentrated using a rotary evaporator, reduced under nitrogen to 1 mL and cleaned up using silica gel column chromatography (USEPA Method 3630C).

Instrumental analysis

GC-FID analysis: Hydrocarbon fingerprinting was performed using a GC-FID system equipped with an HP-5MS fused silica capillary column (30 m × 0.25 mm × 0.25 µm film thickness). Oven temperature was programmed from 60°C (2 min hold) to 300°C at 6°C/min (20 min hold). Injector and detector temperatures were 280°C and 320°C, respectively. Helium carrier gas flow rate was 1.2 mL/min, with 1 µL splitless injection[10,11].

AAS analysis: Heavy metals (Cd, Co, Hg, Cu, Pb, Ni, V, Cr, Fe, K) were analyzed using Atomic Absorption Spectroscopy (Shimadzu AA-7000) after acid digestion (USEPA Method 3050B).

Diagnostic ratio analysis

The following diagnostic ratios were calculated from GC-FID peak areas following established protocols[6,10,11]:

Pristane/Phytane (Pr/Ph)

nC_{17}/Pristane (nC_{17}/Pr)

nC_{18}/Phytane (nC_{18}/Ph)

Carbon Preference Index (CPI) = ½ × [$(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})$ + $(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})$]

Data analysis

Contamination Factor (CF), Geo-accumulation Index (Igeo) and Pollution Load Index (PLI) were calculated according to Tomlinson, et al.[12]. Descriptive statistics were computed using SPSS version 25.

Results and Discussion

Heavy metal concentrations

The concentrations of selected heavy metals in soil samples are presented in **(Table 1)**. Cadmium ranged from 0.16–0.60 mg/kg, cobalt from 0.40-5.30 mg/kg, mercury from 0.010–0.073 mg/kg, copper from 1.30-6.50 mg/kg, lead from 0.11–1.01 mg/kg, nickel from 0.55–5.50 mg/kg, vanadium from 0.23-1.53 mg/kg, chromium from 0.91-6.70 mg/kg, while iron recorded the highest concentrations (1042.5–2321.3 mg/kg) **(Figure 2)**.

Table 1: Heavy Metal Concentrations (mg/kg) in Oil Spill Impacted Soils.

Heavy Metal	K- Dere-01	K-Dere-02	K-Dere-03	B-Dere-01	B-Dere-02	B-Dere-03	Control
Cd	0.55	0.16	0.3	0.6	0.41	0.2	ND
Co	5.24	4.06	0.95	5.3	0.85	0.4	ND
Hg	0.051	0.073	0.011	0.021	0.014	0.01	ND
Cu	6.18	4.1	2.43	6.5	3.2	1.3	ND
Pb	0.43	0.21	0.32	0.11	0.32	1.01	0.01
Ni	4.88	5.33	1.67	5.5	4.8	0.55	ND
V	1.02	0.82	0.23	1.53	0.9	0.32	ND
Fe	2235	2137.4	1745.1	2321.3	2139.5	1042.5	94.01
K	930.31	614.49	51.95	867.17	379.96	68.4	87.03
Cr	6.55	5.96	2.91	6.7	4.1	0.91	ND

ND = Not Detected

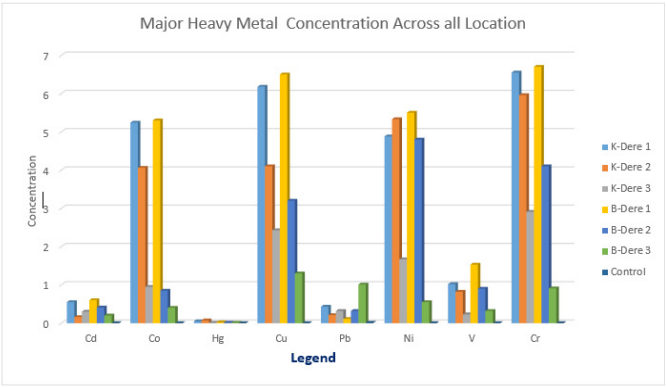

Figure 2: Major heavy metal concentration across all locations with control.

Elevated concentrations of nickel and vanadium key petroleum-associated metals in all impacted samples confirm crude oil as the contamination source[13,14]. However, all pollution indices (CF < 1, Igeo < 0, PLI = 0.09) indicated low heavy metal contamination relative to regulatory standards, confirming that hydrocarbon contamination represents the greater environmental risk.

Total petroleum hydrocarbon (TPH) concentrations

TPH concentrations varied substantially across sampling locations **(Table 2)**, ranging from 202.32 mg/kg to 20,326.5 mg/kg.

Samples K-Dere-01, K-Dere-02 and B-Dere-03 exceeded the EGASPIN intervention value of 5000 mg/kg by factors of 3.3-4.1, indicating severe petroleum contamination requiring urgent remediation. The mean TPH concentration was 8984.37 mg/kg (SD = 8798.29 mg/kg), suggesting localized spill events rather than uniform contamination[9,15].

GC-FID chromatogram interpretation

Representative GC-FID chromatograms **(Figures 4-9)** exhibited characteristic features of weathered crude oils:

n-Alkane distribution from n-C_{15} to n-C_{35}. Absence of lower molecular weight alkanes (< n-C_{15}) suggests evaporative loss during weathering[10].

Pristane and phytane biomarkers clearly resolved, confirming petroleum origin[11].

Unresolved complex mixture (UCM) humps prominent in B-Dere samples, indicating advanced weathering and biodegradation[5,6].

Bimodal distribution in some samples (e.g., B-Dere-03) suggesting mixed marine and terrestrial organic matter input[16].

Table 2: TPH Concentrations in Soil Samples.

Sample	Location	TPH (mg/kg)
A	K-Dere-01	16,360.40
B	K-Dere-02	13,369.30
C	K-Dere-03	226.68
D	Bolo-01	202.32
E	Bolo-02	3,421.00
F	Bolo-03	20,326.50

EGASPIN Target Value: 50 mg/kg; EGASPIN Intervention Value: 5000 mg/kg.

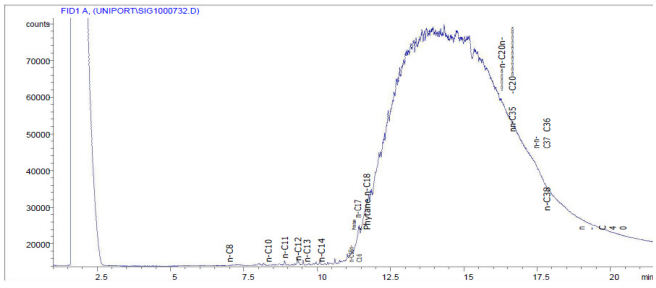

Figure 3: GC-FID chromatogram of K-Dere-01 (fresher oil).

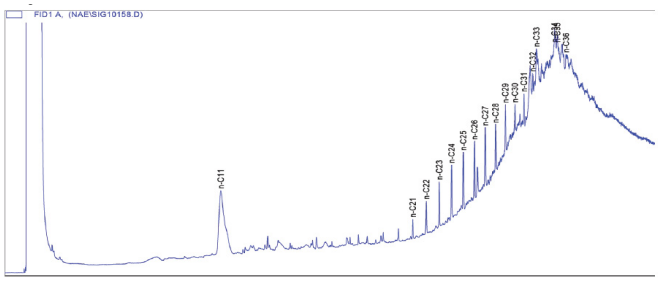

Figure 4: GC-FID chromatogram of K-Dere 02.

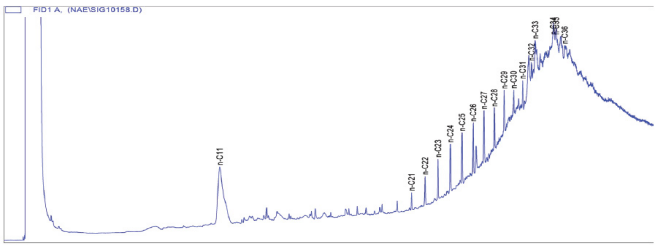

Figure 5: GC-FID chromatogram of K-Dere-03.

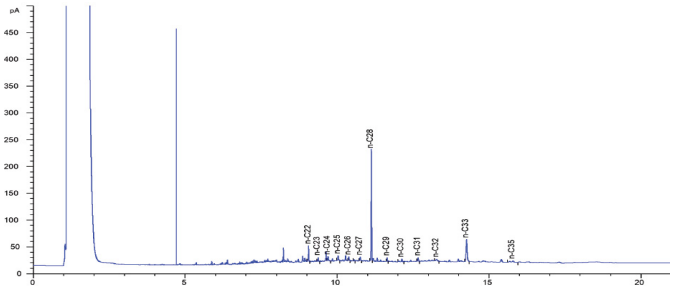

Figure 6: GC-FID chromatogram of B-Dere-01 (moderately weathered).

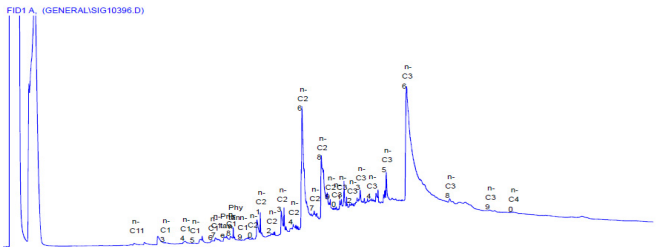

Figure 7: GC-FID chromatogram of B-Dere-02.

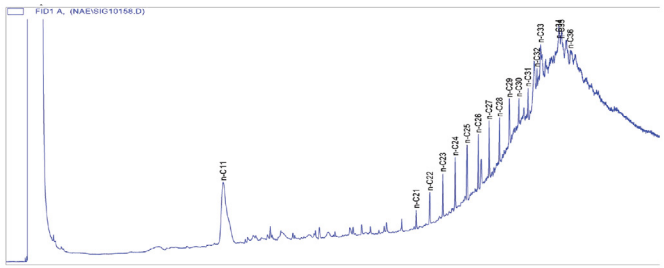

Figure 8: GC-FID chromatogram of B-Dere-03 (heavily weathered/biodegraded).

Diagnostic ratios

Diagnostic ratios calculated from GC-FID chromatograms are presented in **(Table 3)**.

Pristane/Phytane (Pr/Ph)

Pr/Ph values ranged from 1.18 to 1.45 for all impacted samples. Pr/Ph > 1.0 indicates terrestrial organic matter input deposited in an oxic paleoenvironment[17,18]. These values are consistent with crude oils from the Niger Delta petroleum province, which derive from mixed marine and terrestrial organic sources[10,19].

Table 3: Petroleum Fingerprint Diagnostic Ratios.

Sample	Pr/Ph	nC17/Pr	nC18/Ph	CPI
K-Dere-01	1.32	1.48	1.36	1.05
K-Dere-02	1.28	1.33	1.25	1.07
K-Dere-03	1.45	1.15	1.1	1.1
B-Dere-01	1.2	0.98	0.94	1.03
B-Dere-02	1.18	0.85	0.82	1.02
B-Dere-03	1.25	0.74	0.69	1.01

nC_{17}/Pristane and nC_{18}/Phytane Ratios

nC_{17}/Pr ratios were >1.0 for all K-Dere samples (1.15–1.48) but <1.0 for all B-Dere samples (0.74–0.98). Similarly, nC_{18}/Ph ratios were >1.0 for K-Dere samples (1.10–1.36) and <1.0 for B-Dere samples (0.69–0.94). Under aerobic biodegradation, n-alkanes are preferentially degraded over branched isoprenoids, causing these ratios to decrease with increasing biodegradation[11]. The significantly lower ratios in B-Dere samples indicate more advanced microbial degradation, consistent with larger UCM humps in their chromatograms.

Carbon preference index (CPI)

CPI values for impacted samples ranged from 1.01 to 1.10, close to unity. CPI near 1.0 is characteristic of mature crude oils of petrogenic origin[10,20]. The control sample CPI of 1.85 indicates biogenic n-alkanes from higher plant waxes, confirming that contamination in impacted sites is derived from crude oil.

Weathering and biodegradation assessment

The combined evidence reveals distinct weathering histories between sites:

- **K-Dere samples:** Fresher hydrocarbons (nC_{17}/Pr > 1), smaller UCM humps, detectable higher molecular weight n-alkanes (up to n-C_{35}). Suggests relatively recent spill or continuous input[6].
- **B-Dere samples:** More weathered residues (nC_{17}/Pr < 1), prominent UCM humps and depletion of n-alkanes in C_{15}-C_{20} range. Indicates prolonged environmental exposure and advanced microbial degradation[5,21].

The presence of pristane and phytane in all samples, even where n-alkanes were significantly depleted, confirms predominantly aerobic biodegradation[11], consistent with oxic surface soil conditions in the Niger Delta.

Unimpacted site (Control)

The control sample further strengthens the interpretation of anthropogenic contamination within the study area. The control location exhibited substantially lower diagnostic ratio values compared to the polluted locations, particularly for the Fe/K ratio (1.08), indicating relatively lower metal enrichment and reduced anthropogenic influence.

The absence of detectable concentrations for cadmium, cobalt, copper, nickel and chromium within the control sample suggests that the elevated diagnostic ratios observed in the K-DERE and B-DERE locations are primarily associated with anthropogenic activities rather than natural background contributions.

The marked differences between the control and impacted locations, therefore, confirm that petroleum exploration activities, industrial discharge, metallic corrosion and hydrocarbon contamination significantly contributed to heavy metal enrichment within the study area.

Heavy metal diagnostic ratios

Calculated metal diagnostic ratios (Cu/Pb, Ni/Cr, Fe/K, Cd/Co) showed considerable variation. High Cu/Pb ratios at B-Dere-01 (59.09) suggested copper enrichment associated with petroleum contamination. Elevated Fe/K ratios at K-Dere-03 (33.59) indicated iron enrichment from weathering and corrosion.

The extremely high TPH concentrations recorded in K-Dere-01, K-Dere-02 and B-Dere-03 indicate severe environmental degradation requiring urgent remediation. The presence of pristane and phytane biomarkers, along with CPI values near unity, confirms that the contamination is derived from crude oil rather than biogenic sources. The observed variation in nC17/Pr and nC18/Ph ratios between K-Dere and B-Dere sites indicates different weathering histories: K-Dere samples contain relatively fresher hydrocarbons, while B-Dere samples have undergone more advanced biodegradation due to prolonged environmental exposure.

These findings are consistent with previous studies in the Niger Delta. Menkiti, et al. (2023) reported high TPH concentrations in Ogoni soils and Mark, et al. (2016) demonstrated that diagnostic ratios can distinguish between combustion-altered and biodegraded hydrocarbons. The present study extends these findings by providing detailed molecular fingerprinting of two distinct impacted sites.

Although heavy metal concentrations were generally low, the enrichment of nickel and vanadium, key petroleum-associated metals, supports the conclusion that crude oil contamination is the primary source of pollution. The low heavy metal pollution indices (CF, Igeo, PLI) indicate that metal contamination is not the principal concern; rather, hydrocarbon contamination poses the greater environmental risk.

Conclusions

This study established that soils from K-Dere and B-Dere communities in Ogoni land are significantly impacted by petroleum hydrocarbon contamination resulting from oil spill activities. Although heavy metal concentrations were generally within permissible limits, petroleum hydrocarbon contamination was severe in several locations. The extremely high TPH concentrations recorded in K-Dere-01, K-Dere-02 and B-Dere-03 indicate serious environmental degradation requiring urgent remediation measures.

Hydrocarbon fingerprinting and diagnostic ratio analyses proved effective in identifying the origin, transformation and weathering status of petroleum contaminants. The dominance of n-alkanes within the C15–C35 range, presence of pristane and phytane biomarkers, UCM humps and diagnostic ratio values confirmed contamination from marine-derived crude oil and revealed varying levels of biodegradation across the sites. K-Dere samples contained relatively fresher petroleum hydrocarbons, whereas B-Dere samples exhibited more weathered and biodegraded residues due to prolonged environmental exposure.

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