Geochemical Fingerprinting for Oil Spill Source Identification and Environmental Impact Assessment: A Step Towards Decarbonization and Sustainability

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ABSTRACT

In Nigeria, offshore oil spills represent a great source of environmental pollution especially in the Niger-Delta region. Oil spillage is the accidental discharge of liquid petroleum hydrocarbon into the environment, especially marine areas, due to various reasons such as corrosion of pipelines, sabotage/vandalism, and during oil production operations. It is an issue of national urgency that affect wetlands, biodiversity and also contaminate the host community fertile soil and water. This technical paper is a contribution to a conversation that has been going on for years. Modern geochemical fingerprinting techniques were employed to investigate the extent of the oil spill, serving as the initial approach in conducting an environmental remediation exercise. Geochemical methods used in this study include Fluorometric On-site Analysis, Gas chromatography (GC), Mass Spectrometry (MS) and other supporting methods which includes visual observation and GIS. The study shows that geochemical fingerprinting plays an important role in providing legal evidence to show the linkage between the spilled oil and the exposure of the target environments, which supports to determine the level of environmental damage caused by oil spill using the Hebei Spirit Oil Spill (HSOS) in the Republic of Korea as a case study, and to employ the geochemical method used in resolving the Niger-Delta Oil spill issue and extent of environmental contamination. Advanced oil fingerprinting techniques like the comprehensive two-dimensional gas chromatography (GCxGC) and fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) can also be used. This is aimed at knowing the length of time an environmental remediation exercise will take, and also proffering the best possible environmental remediation method to be employed in the Niger-Delta region, so as to bring the wetlands and river to a condition closer to its former state. The limitations of the methods/techniques are discussed, and the future technological prospects are highlighted in this review.

Keywords: Crude Oil, Environmental, Niger Delta, HSOS, Oil Spill, Remediation, Geochemical Fingerprinting

INTRODUCTION

Oil spill is one of the major impacts of oil exploitation. It is the accidental discharge of crude oil into the environment during pumping of oil from oil wells or transportation of oil through pipelines and shipping vessels. Most of the oil exploration in Nigeria is done in the Niger Delta region, which contains the oil reserves of the country. The Niger Delta is the largest mangrove forest in Africa, and it is a major global wetland with an abundant biological diversity like arable land that supports a wide variety of crops and trees. It also has more freshwater fish species than any ecosystem in West Africa (Ohanmu *et al.,* 2019). This rich biodiversity is under threat from oil spill incidents that regularly occur in different parts of the region and at various times (Sam *et al.,* 2016). Offshore oil spills represent a great source of pollution in the marine environment (Bayer *et al.,* 2016; Nissanka & Yapa, 2018), therefore, advanced techniques like the geochemical fingerprinting methods should be devised to assess the extent of pollution and geochemical fingerprint of the oil spilled. Oil spills can be caused by human error, natural disasters, technical failures, or deliberate releases. 30-50% of all spills are human error, with 20-40% due to equipment failure. Causes are divided into deliberate releases, such as operational discharges or sabotage, and accidental releases.

Nigeria, where oil spill is a major challenge, requires an effective management of oil spills. Numerous organizations collect and compile data on oil spills in Nigeria; the government organization in charge of keeping an eye on and responding to oil spills in Nigeria is the National Oil Spill Detection and Response Agency (NOSDRA), founded in 2006. With data on oil and gas spills from 2006 to the present, its oil spill monitoring website offers the most easily accessed information. The Department of Petroleum Resources (DPR) and the Nigerian National Petroleum Corporation (NNPC) are two other government organizations that gather data on oil

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spills. However, unless spill data has been published in academic publications or research papers where authors were granted access, it is challenging to collect spill data from them (Watts & Zalik, 2020).

Offshore oil spill is the most frequent source of pollution globally, causing aquatic organisms and some species of plant go extinct. The organic contaminants that make up crude oil are harmful when introduced into the environment (Ahmad *et al.,* 2020). Consequently, oil spill interferes with soil properties and functionalities thereby making the soil unsafe for biological activities (Wang *et al.,* 2017). Some hydrocarbons in crude oil have high lipophilicity which enhances their bioaccumulating activity in an aquatic ecosystem; hence, the soil, surface, and groundwater quality are constantly impacted by the spills (Nduka & Orisakwe, 2011). Oil is a complex mixture of different organic compounds, mostly hydrocarbons and other components, such as sulphur, nitrogen, and oxygen (Fingas, 2011). The chemical component of crude oil is mostly carcinogenic and affects the health of the people in the host community. According to the geological processes involved in its creation, the oil's compositional percentages fluctuate, giving it unique qualities and features (Vafaie & Kivi, 2020). Mineral oil can linger on the ocean surface in the form of several layers because it contains hydrophobic components (Alpers *et al.,* 2017). When oil spills, its behavior is determined by its chemical makeup as well as by oceanic and meteorological factors that affect weathering. In the event of an oil spill at sea, lighter items (such as gasoline, diesel, and light oils) will typically produce thinner layers of oil on the water's surface, while heavier products (such as heavy oils and Bunker C) will form thicker layers (Fingas, 2011).

Using the Heibei Spirit Oil Spill (HSOS) as a case study and simultaneously synchronizing the advanced geochemical forensic method used in investigating the extent of oil spill in the west coast of the Republic of Korea (ROK) with the offshore oil spill in the Niger-Delta region of Nigeria, it is certain this review will birth a modern method of investigating the extent of contamination of offshore oil spill in Nigeria. This study reviews the different geochemical methods and technologies used in analyzing the chemical composition of oil spilled in marine and onshore sites and the environmental remediation methods to be recommended for such oil spill site.

THEORY AND DEFINITIONS

Geochemical fingerprinting is a method for determining and differentiating the distinct chemical makeup of rocks, minerals, soils, and other geological objects. It entails examining the ratios and concentrations of different elements, isotopes, or compounds to produce a unique "fingerprint" that represents the sample. The use of geochemical fingerprints has a long tradition in Earth sciences. Already Goldschmidt (1924) proposed the application of so-called "geochemische Leitelemente" for elucidating genetic relationships among different rock types. A necessary prerequisite for applying geochemical fingerprints is that suitable analytical methods exist which allow the detection of fingerprints. A successful use of geochemical fingerprints, therefore, is much related to the development of analytical techniques for their precise determination. With the introduction of new analytical tools or with improvements in analytical precision and detection limits of older technologies new fingerprints might continue to emerge. Geochemical fingerprints are used for the identification of specific geological reservoirs on Earth, which includes the characterization of different environments (marine-freshwater; oxic-anoxic, mantle-crust etc.) that play a role in the origin of a rock of interest. According to the definition given to it in the context of oil spill investigations, it is a method recently used to recognize and distinguish the distinct chemical signature of oil spilled into the environment, which may be onshore or offshore depending on the location of the spill. In industrialized nations, it is often used to determine the magnitude of oil spills and to identify the corporation responsible for the spill in order to enforce the legal obligation of environmental remediation.

CASE STUDY: HEIBEI SPIRIT OIL SPILL INCIDENT IN REPUBLIC OF KOREA

On December 7, 2007 while anchored about five miles off Taean, on the west coast of the Republic of Korea (ROK), the Hong Kong-registered tanker M/V Hebei Spirit (146 848 GT), loaded with 209,000 tons of crude oil, was struck by the crane barge Samsung No. 1. The Hebei Spirit caused about 10,900 tons of crude oil to leak into the ocean. Three distinct types of crudes were spilled as a result of the collision: Kuwait export crude (KEC), Iranian heavy crude (IHC), and UAE Upper Zakum crude (UZC). The oil ship sustained punctures on tanks No. 1, 3, and 5. Over 375 km of shoreline were in various states of pollution due to the spilled oil. The biggest event in recent memory was the HSOs. Emergency response operations for bulk oil removal were conducted until January 2008, with secondary response continuing until October 2008. Over 1.3 million volunteers from ROK helped in shoreline cleanup operations, resulting in the rapid removal of oil from the environment. However, lingering oils were found along heavily impacted shorelines.

Based on the Marine Environmental Management Act in ROK, the responsible party should immediately commence natural resource damage assessment (NRDA) through the predesignated ad hoc institutes by Korean government when the volume of spilled oil is over 100 kL. The HSOS incident heavily impacted areas like Taean National Seashore Park, which had 32 recreational beaches. Rapid assessment and quantification of shoreline contamination was necessary to prioritize cleanup operations and make decisions for beach reopening. A modified fluorometric on-site analysis of pore water was applied to the affected area. Long-term monitoring of residual petroleum hydrocarbons in multimedia environments was established as part of NRDA. Geochemical fingerprinting is crucial for the oil spill environmental forensics, providing legal evidence to show the linkage between spilled oil and target environments. The spill involved three different Middle East crude oils with varying mixing ratios in marine environments. There was a lack of background contamination data and the alteration of oil chemical composition by weathering and chemical dispersion.

To unravel these relationships, conventional tiered fingerprint approach including gas chromatography (GC) and mass spectrometry (MS) was applied to analyze fingerprint characteristics of spilled oil. Additionally, emerging fingerprinting techniques were also employed for further detail analysis.

METHODOLOGY USED IN THE HSOS INCIDENT

Rapid Screening of Shoreline Contamination; Fluorometric On-Site Analysis of Pore Water

Oil spill sites often use various assessment techniques to evaluate oil contamination, such as TPH or PAH concentrations in sediments. However, these methods can be impractical due to the grain size and weight of the sediments. Instead, oil contamination at a sandy shoreline can be better assessed by measuring oil concentrations in pore water, which can reflect sediment contamination and is not dependent on grain size. Conventional GC methods can be used for oil quantification in pore water, but this method is often impractical due to time, cost, and sample processing. On-site fluorometric detection was introduced to measure oil concentration in pore water in a timely manner. The fluorometric detection method estimates total petroleum hydrocarbon concentration in a sample, with a detection limit of 0.13 μg/L. Although it may not directly relate to GC measurement of oil content, it is capable of generating data comparable to GC but more rapidly and cost-effectively than conventional GC techniques. This study monitored the contamination level and temporal variation of dissolved/dispersed oil in pore water on a monthly basis using a portable fluorometer, and the results were illustrated using GIS mapping. The results showed spatial and temporal variations of oil contamination at the beach, with most beaches showing local variations approaching pre-spill contamination levels. However, continuous elevations in oil concentration were also observed at certain local sites until January 2011.

Extended Observation of Remaining Oils in Multimedia Oil spreads and divides into seawater, sediment, and biota, three distinct aquatic system compartments when it reaches marine settings. Remaining oils remained in the multimedia environments even after visible oils were eliminated by a cleansing procedure. The long-term multimedia monitoring was aimed to determine the persistence of leftover oiling and gauge the amount of oil contamination throughout the region. The sampling area and frequencies were modified in accordance with the state of oiling. Taean County's highly polluted locations constituted the majority of fieldwork, while isolated offshore islands were also visited. Researchers visited Taean four days after the HSOS and collected data on saltwater, sediment, and biota from various areas. Taean's heavily contaminated intertidal sections underwent more thorough investigation, and remote locations were visited periodically. Analyses included total petroleum hydrocarbons, biomarker chemicals, alkylated PAHs, and polycyclic aromatic hydrocarbons, including 16 listed by the US Environmental Protection Agency. After the spill, intertidal seawater had a high PAH content, reaching 5170 ng/L. Oysters from the Taean had a higher alkylated PAH content than the background level. Long-term monitoring data showed a dramatic decline in petroleum hydrocarbon concentration in multimedia for the first five months. One month after the spill, PAH concentrations dropped significantly to 100 ng/L, then fluctuated within background concentrations. The average concentration of TPH, 16 PAHs, and alkylated PAHs in intertidal sediments dropped seven, ten, and twenty times, respectively, from the original concentration level one year after the spill. Over time, the total concentration of PAHs in oysters dropped rapidly, and seasonal changes were observed at most sites, with levels nearing pre-spill contamination. On the other hand, year-round oyster populations at mud flat, boulder-armored beaches were comparatively greater. Specifically, in September 2009, oysters from Garumi, a boulder-armored beach, had increased PAH values of 22 400 ng/g.

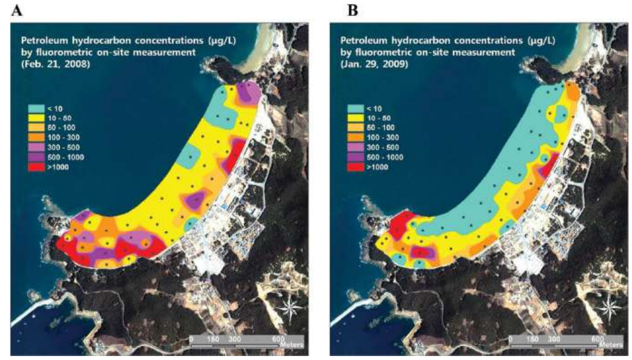

Figure 1: Spatial distributions of petroleum hydrocarbon concentrations in pore water measured using an on-site fluorometric pore water analysis method by Kim *et al.* (2010). Spatial distributions on Feb. 21, 2008 (A) and on Jan. 29, 2009 (B).

Varying Degree Mixture of Three Source Oils

Every year, ROK imports more than 870 million barrels of crude oil from various oil producers, and it is ranked as the seventh world consumer of crude oil. According to recent three-year statistics (2006–2008), more than 80% of crude oil imported to ROK came from the Middle East. Among the Middle Eastern countries, Saudi Arabia is the largest oil exporter, followed by the United Arab Emirates (UAE), Kuwait, Iran, Qatar and Oman. These statistics are well reflected in the cargo oils of the M/V Hebei Spirit; four different types of Middle Eastern crude oil, including KEC, IHC, UZC, and Saudi Arabia Khafj, were loaded, and three of them were spilled. The proportional spill volumes of the three cargo oils were estimated to 43.4%, 42.8%, and 13.8% for KEC, IHC, and UZC, respectively. Their physical properties, such as density, viscosity and pour point, were similar each other. However, their asphalthene and resin contents showed significant differences among them. Laboratory experiments revealed that IHC and KEC produced stable water-in-oil emulsions, while UZC resulted in a meso-stable emulsion. These three cargo oils showed similar but distinguishable hydrocarbon fingerprints. Their normal alkane distribution showed a similar pattern, but the diagnostic ratio of pristane to phytane was source specific and was a good source indicator. Likewise, double ratios using alkylated PAHs and biomarker compounds including hopanes and steranes were very useful for source identification. However, the challenge in oil fingerprinting for this spill was the continuous miXing, to varying degrees, of the three crude oils during the spill. The puncture sizes of each hole were different, and thus, their miXing rate varied according to time.

Background Contamination

Natural seeping, coal, shale, and anthropogenic activities were discussed as sources of background hydrocarbons. Natural seeping is one of the most masking hydrocarbon backgrounds when the reservoir of spilled oil was near the seeping region. Over the past 19 years, ROK experienced an average of 354 spills and 3406 kL of oil, despite a decline in middle- to large-scale spill events. Small-scale leaks, often off the west coast, leave residue and complicate identifying the source of oil. These spills sparked discussions about buried oil resuspension, prompting the use of tier-based fingerprinting techniques for source identification. Most of the newly stranded oils at the beach were found to be unmatched with HSOS oil; illegal disposal or unintentional spills were proposed as the main causes.

The Impact of Weathering on Oil Fingerprints

When oil is spilled in the marine environment, it is immediately subjected to various weathering processes including evaporation, dissolution, emulsification, degradation and photooxidation. Evaporation and dissolution are the primary processes that affects the chemical composition/fingerprint of oil spilled in hours or days after the spill. While Photooxidation and biodegradation are the only two natural processes that remove spilled oil from the environment. In the HSOS case, four level categorizations were used to describe the weathering degree of stranded oil: initial, moderate, advanced, and extreme stages. The pattern changes in the distributions of saturated hydrocarbon (SHC), PAH target analytes, and their weathering ratios were used to identify weathering characteristics and their evolution. As the internal conservative reference, weathering percentages of residual oil were calculated using C30-17α(H), 22β(H)-hopane. Evaporation was discovered to be the most important weathering process during the spill's early stages. 28.9% of the initial spilled oil was lost by oils categorized as the first weathering stage in the HSOS case. Oils in a moderate weathering stage lost 8.8% more of their original weathered content due to evaporation and dissolution. Oils belonging to these stages were stranded oils collected within 3 months after the spill. Advanced and extreme weathering stage samples exhibited the time-lagged effects of biodegradation, resulting up to total loss of 60.3% combined with other weathering processes. The weathering of this spill complicated the source identification.

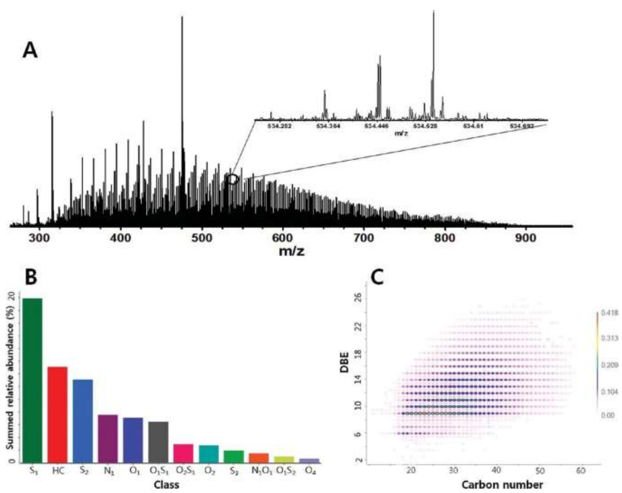

Figure 2: (A) High-resolution mass spectrum and expanded mass spectrum of weathered oil spilled from the HSOS. (B) Class distribution of the oil sample and (C) the carbon number vs DBE plot of S1 class compounds. (Yim *et al* 2012).

Emerging Oil Fingerprinting Techniques Used

Gas Chromatography/Isotope Ratio Mass Spectrometry

Gas chromatography/isotope ratio mass spectrometry (GC/IRMS) was used to analyze stranded oils in order to find the stable carbon isotope ratios of n-alkanes. They had their isotopic compositions compared to potential source oils. According to the preliminary findings, the cargo oils' stable carbon isotopic compositions that allowed them to be distinguished from ambient contaminations were still present in the stranded oils that were collected within three months of the spill. Stable isotope ratios of alkanes have remained relatively unchanged, despite significant changes in compositional signatures brought about by weathering processes. As a result, they can be used, in conjunction with conventional molecular markers, to effectively trace HSOS or assign pollution sources among the three spilled oils.

Comprehensive Two-Dimensional Gas Chromatography

Comprehensive two-dimensional gas chromatography (GCXGC) has the potential to revolutionize forensic oil spill analysis. GC×GC is capable of separating an order of magnitude more compounds from complex mixtures than traditional GC. The increased chromatographic resolution is achieved by using two chromatographic columns with different selectivities coupled together by a modulator. Also, the GC×GC detectors need to have a fast response. Flame ionization detectors are widely used, and fast time-of-flight mass spectrometers (TOF MS) are well-suited for GC×GC. GC×GC facilitates the understanding of the sources, weathering, and toxicity of unresolved complex mixtures (UCM) hydrocarbons. In the HSOS case, GC×GC was promising to comprehensively evaluate the varying degree of mixing effects of the three spill sources and the abiotic and/or biotic effects of weathering. GC×GC facilitated the initial screening of various types of hydrocarbons using group type analysis and the application of isoprenoid compounds like biphytane and methyl hopanoids with the help of enhanced separation. These compounds were found to be used as conservative fingerprint for HSOS case.

FT-ICR MS

FT-ICR MS, or Fourier transform ion cyclotron resonance mass spectrometry, is one of the most effective methods for molecular studies of oils. Crude oils that are exposed to microbial or photooxidation processes during weathering may produce a significant polar molecules. UCM may be caused by an increase in polar compounds, which are frequently present in samples of degraded crude oil. The polar and heavy components of crude oils can be effectively studied using FT-ICR MS in conjunction with atmospheric pressure photo-ionization or electro-spray. Using FT-ICR MS, stranded oil samples with different levels of weathering were examined to determine the precise compositional changes. Significant increase of polar compounds like N-, S-, O-containing heterocyclic aromatics were found in the resin fraction of the weathered oil. High-resolution mass spectrum of an oil sample contained over 20 peaks within a ~ 0.4 m/z window, which could be converted into elemental formulas using data interpretation like double bond equivalence (DBE).

The elemental composition and structural information obtained by FT-ICR MS are expected to be further used to develop new fingerprinting tools.

"Submerged Oil" After the HSOS Incident:

One of the misinformed environmental fates of oil relayed to the public during the HSOS was sunken or submerged oil. The specific gravities of the cargo oils in M/V Hebei Spirit were in the range of 0.85−0.87; theoretically, fresh spilled oil does not sink. However, when oil is stranded on sand beaches or mixed with sand in the surf zone, spilled oil can be settled down. In a strict sense, these phenomena could be classified as wash-out oil from the intertidal zone after aggregated in sand.

APPLICATION OF GEOCHEMICAL FINGERPRINTING USED IN HSOS TO OIL SPILL IN NIGERIA

The geochemical fingerprinting method in identifying the source of oil spilled in the HSOS case can find it application in investigating the source of oil spill both onshore and offshore in Nigeria, especially in the Niger-Delta region. The Heibei Spirit Oil Spill (HSOS) case demonstrated the effectiveness of geochemical fingerprinting in identifying the source of oil spills. This technique can be applied to investigate oil spills in Nigeria, to identify the corporation responsible for the spill in order to enforce the legal obligation of environmental remediation and also assist in recommending the best environmental remediation approach needed for such spill site.

NIGERIA'S OIL SPILL CHALLENGE

Nigeria's oil-rich Niger Delta region has faced numerous oil spills, causing environmental degradation and health issues for people in the host community. Nigeria's oil spill crisis can be attributed to a lack of effective regulation and enforcement. The existing regulatory framework has not been fully effective in preventing and addressing oil spills due to weak enforcement, inadequate resources, and overlapping responsibilities among regulatory agencies. This lack of oversight has led to devastating environmental and socioeconomic consequences, including widespread pollution, health risks, and economic losses. Identifying the source of oil spills is crucial for holding responsible corporations accountable and ensuring proper remediation approach. The geochemical methods used to investigate the Heibei Spirit Oil spill can be applied to oil spills in Nigeria by utilizing the following geochemical techniques;

1. Fingerprinting: the geochemical fingerprinting methods involves analyzing oil samples from the spill and potential sources (e.g., pipelines, wells) to identify unique chemical signatures, determining the spill's origin.

2. Polycyclic Aromatic Hydrocarbon (PAH) Analysis: the PAH analysis applied in the HSOS incident is an important tool for assessing the impact of oil spills on the environment. PAHs are a group of toxic, carcinogenic compounds found in crude oil and petroleum products. They are harmful to humans, wildlife, and ecosystems. Gas chromatography-mass spectrometry (GC-MS) is a widely used PAH analysis method for identifying and quantifying PAHs in oil samples.

3. Stable Isotope Analysis: is one of the techniques used in the HSOS case to analyze the stable isotopes of elements like carbon (C) and hydrogen (H) in the oil spilled. It is used to identify the source of the oil, as different sources have unique isotopic profile and also track the movement of oil in the environment for evaluating the effectiveness of the cleanup operations. The most commonly analyzed isotopes in oil spills is carbon-13 (C-13) and Hydrogen-2 (2H). Stable Isotope analysis is performed using mass spectrometry.

4. Fluorometric On-Site Analysis: the fluorometric on-site analysis can be introduced to measure oil concentration in pore water in a timely manner. The fluorometric detection method estimates total petroleum hydrocarbon concentration in a sample, with a detection limit of 0.13 µg/L. It is rapid and cost-effective than conventional GC techniques.

5. Collaboration and Data Sharing: the data on oil spills in Nigeria is gathered and organized by many agencies; the National Oil Spill Detection and Response Agency (NOSDRA), is the government agency responsible for monitoring and responding to oil spills in Nigeria. Oil spill data should be shared with geoscientist to work with, without any monetary demands.

OIL SPILL REMEDIATION TECHNIQUES AFTER SPILL INVESTIGATION

Remediation is the removal of pollution from the soil, groundwater, sediment, or surface water using physical, chemical, or biological methods depending on the properties of the contaminant, the type of media, and the conditions of the environment (Zabbey *et al.,* 2017). The selection of an appropriate remediation technology depends on site-specific conditions such as the characteristics of contaminants, properties of soil, and weather (Lim *et al.,* 2016). Different remediation methods can be applied depending on the contaminated media (e.g., water, air, or soil) and the contaminants present in the site (e.g., BTEX [benzene, toluene, ethylbenzene, xylene], heavy metals) (Gomes *et al.,* 2013). Soil is the most extensive media that has been contaminated with oil in the Niger delta (Ijah & Antai, 2003). Containment and RENA have been applied extensively to the soil in the Niger Delta (Sam *et al.,* 2016). However, containment is often inappropriate because it involves using impermeable barriers on the soil which could hinder the community from using the soil for their livelihood and RENA is also problematic in most of the sites considering that the contaminants have percolated deeper than 5 m where it is ineffective to use the method (UNEP, 2011).

BIOREMEDIATION AS THE BEST ENVIRONMENTAL REMEDIATION METHOD

Zabbey *et al.* (2017) suggested that bioremediation is the best soil remediation option for Niger Delta's mangrove environment. The use of bioremediation innovations has been proven to be one of the most effective methods to the restoration of contaminated environments, which is a method that is both environment-friendly and financially rewarding, and also able to support the needed funding to carry out the restoration process. The process of bioremediation involves the use of natural biological processes such as biochemical solubilization and mineralization in an effort to remove or clean soil contaminated by industrial contaminants (Jimoh & Lin, 2019b). Moreover, it must be emphasized that biodegradation is one of the most important mechanisms for the removal or reduction of hydrophobic contaminants, and this process is undertaken by natural microbial populations. Several factors have made it difficult for a large amount of mass to be transferred to the process of biodegradation and bioremediation due to the extreme hydrophobic nature of pollutants, such as their low water solubility, strong soil particle attachment, and low biological availability (Jimoh & Lin, 2019b; Omokhagbor Adams *et al.,* 2020). It involves three distinct approaches: bioaugmentation, biostimulation, and bioventilation (Namkoong *et al.,* 2002).

BIOAUGMENTATION

Bioaugmentation involves importing some contaminant degrading strains to the existing microbial population at the remediation area to facilitate the degradation process (Abdulsalam *et al.,* 2011). Many microorganisms can degrade hydrocarbons in the soil, sediment, and water environment; however, studies suggest using different strains of bacteria and fungi because no single species can degrade all the compounds present in crude oil (Lim *et al.,* 2016).

BIOSTIMULATION

Biostimulation is the optimization of environmental conditions for the microbes through nutrient addition to speed up the degradation process (Jiang *et al.,* 2016). For example, in a lab-scale comparative study performed by Tanee and Kinako (2008), the authors reported that biostimulation of soil with an inorganic fertilizer is more effective in degrading crude oil than phytoremediation. In another pilot-scale experiment, Aghalibe *et al.* (2020) amended a soil polluted with Bonny light crude oil with cow dung, nitrogen, phosphorus, and potassium (NPK) fertilizer, and poultry droppings to stimulate biodegradation. During 8 weeks of experimentation, the authors observed that the NPK amendment stimulated the removal of 93% of polycyclic aromatic hydrocarbons (PAHs) from the soil. Poultry droppings removed 90% and cow dung showed 86.9% effectiveness. Biostimulation can also be used in heavily polluted soils without a need for dilution. The high oil concentration selectively stimulates the bacterial strains capable of tolerating and biodegrading crude oil. These microorganisms occurred in high numbers and showed a striking diversity in their identities and are active under oil-saturated conditions. However, the soils should be kept moistened, well-aerated and supplied with adequate dissolved oxygen (DO) and nutrients (Ali *et al.*, 2020).

BIOVENTILATION

Bioventing is the injection of oxygen to stimulate the activity of the microbes. Oxygen is necessary for the metabolism of microbes, and it is often the limiting factor in the biodegradation process (Lim *et al.,* 2016). In a previous pilot-scale experimental work, bioventing removed up to 85% of petroleum within 60 days (Thomé *et al.* (2014). Different remediation solutions have been applied to oil-polluted soil in Nigeria and bioremediation has been studied and applied in both the laboratory and the field, and it has proven to permanently degrade oil contaminants with little environmental footprints at a relatively low cost (Babalola *et al.,* 2021; Thomé *et al.*, 2014).

Media	Source	Remediation type	Results after remediation	References
Soil	Soil from University of Calabar spiked with crude oil	Bioremediation	*Bacillus, Pseudomonas, Vibrio, Micrococcus* and *Alcaligenes* reduced crude oil from 26.7% to 43.3% after 16 days	Ijah and Antai (2003)
Soil	Crude oil contaminated farmland in Rumuekpe	RENA	TPH reduction from 300 mg/kg to 282 mg/kg after 10 weeks	Ebuehi et al. (2005)
Soil	Soil from university of Port Harcourt spiked with crude oil	Biostimulation and phytoremediation	Biostimulation of soil with NPK was more effective than phytoremediation using *Vigna sp*.	Tanee and Kinako (2008)
Soil	Petroleum contaminated soil from Lagos spiked with PAHs	Chemical remediation	72% of acenaphthene, 42% of naphthalene, and 37% of anthracene were extracted using oxalic and tartaric acid	T.O. Oluseyi (2013)
Soil	Crude oil contaminated soil from Eleme	Nanotechnology biodegradation	CNB-technology removed 99% of TPH, 100% of PAHs, and 100% of heavy metals	Adekunle et al. (2015)
Soil	Simulated crude oil contaminated soil from Agbor	Chemical remediation	79.96% removal of TPH with Fenton oxidation was achieved at the end of 6 hours	Akpoveta (2016)
Soil	Crude oil polluted farmland in Bodo	Phytoremediation	In 90 days, *M. alternifolius* achieved 99% removal of TPH and 78% removal of PAHs while *F. ferruginea* also removed 99% of TPH	Chukwuma et al. (2019)
Soil	Soil spiked with crude oil from Abia State university	Biostimulation	NPK amendment stimulated 93% removal of PAHs, Poultry droppings and cow dung stimulated 90% and 86.9% removal	Aghalibe et al. (2020)
Soil and groundwater	Contaminated samples from a legacy site in Ejama Ebubu	Integrated remediation approach	Excavation, ex situ treatment, thermal desorption, fixation, skimming achieved > 95% removal of TPH, PAHs and BTEX in soil groundwater	Mmom and Igbuku (2015)
Water	Crude oil polluted water from Bodo creeks	Adsorption	*Dialium guineense* Seed Husk sorbent and its ammonium sulfate functionalized form were able to remove > 50% of crude oil from water	Eze et al. (2019)
Water	Lab simulated crude oil polluted water	Biostimulation	A consortium of *Aspergillus Niger*, and *Pseudomonas Aeruginosa* stimulated with NPK and urea fertilizer removed 99.09% of TPH	Anih et al. (2019)
Water	Crude oil contaminated water from Niger Delta	Bioremediation	Bacterial strains of *Serratia marcescens XYL7* removed 99.5% of xylene and 60% of pyrene while *Alcaligenes faecalis PYR5* degraded 97.4% of anthracene	Uba (2019)
Water	Contaminated groundwater from Baruwa community	Skimming and chemical oxidation	Skimming-off technology removes PNAPL and $KMnO_4$ oxidizes the hydrocarbons. Up to 100% TPH removal was achieved in 30 weeks	Ola et al. (2019)
Sediment	Kpene stream	Biostimulation of sediment with fertilizer and mineral salts	66.7% degradation of hydrocarbons was achieved in 6 weeks	Abu and Ogiji (1996)
Sediment	Bonny River loading jetty	Stirred tank bioreactor	After 56 days of treatment, more than 92% removal of 6 PAH compounds wasachieved	Chikere et al. (2012)

Abbreviations: BTEX, benzene, toluene, ethylbenzene, xylene; CNB, compost-based nanotechnology in bioremediation; NPK, nitrogen, phosphorus and potassium; PAHs, polycyclic aromatic hydrocarbons; PNAPL, pure nonaqueous phase liquid; RENA, remediation by enhanced natural attenuation; TPH, total

CONCLUSION

Using the Heibei Spirit Oil Spill (HSOS) as a case study and simultaneously synchronizing the advanced geochemical forensic method used in investigating the extent of oil spill in the west coast of the Republic of Korea (ROK), we can easily investigate offshore oil spill in the Nigeria, especially in the Niger-Delta region of Nigeria. Geochemical fingerprinting is crucial in oil spill environmental forensics, providing legal evidence to show the linkage between spilled oil and target environments. It is certain this review will birth a modern method of investigating the extent of contamination of offshore oil spill in Nigeria. This technique of Oil spill investigation is also very crucial in holding any Oil corporation responsible for the spill accountable so as to carry out the environmental remediation exercise the contaminated site needs.

The application of geochemical fingerprints crucially depends on the development of adequate analytical techniques. Further advances of the existing methods and the introduction of new techniques will undoubtedly strengthen the existing fingerprints or will establish new fingerprints. Nevertheless, what is sometimes neglected is the fact that geochemical fingerprints in most cases are not self-evident, but ambiguous and need to be supported by further techniques such as the Visual observation method and GIS; using the vegetation indices such as SAVI, and NDVI. In this respect, great care is necessary when applying geochemical fingerprints. This study reviews the different geochemical methods and technologies used in analyzing the chemical composition of oil spilled in marine and onshore sites and the environmental remediation methods to be recommended for such oil spill site.

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