

Research Article

Environmental Fate of Toxic Volatile Organics from Oil Spills in the Niger Delta Region, Nigeria

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Abstract: Over the years, the environmental degradation of ecological resources from crude oil pollution and its human health impacts is receiving more global attention. The utilization of environmental models capable of predicting the fate, transport, and toxicity of chemicals in spilt crude oil can provide essential knowledge required to deal with the complexity associated with the fate of volatile petroleum chemicals in the environment. This paper explores the environmental fate of toxic volatile organics from an oil spill in the Niger Delta Region of Nigeria. Results from the literature implicated sabotage and operational failures from pipelines as primary causes of crude oil spillages. The generation of a fugacity model using EPI Suite™ revealed that K_{oc} values greatly influence the behavior of BTN. Benzene, Toluene, and Naphthalene (BTN) were partitioned into three compartments based on organic-carbon partitioning coefficient (K_{oc}). The organic-carbon partitioning coefficient (K_{oc}) was computed as a function of soil-water distribution coefficient (K_d) and percentage organic matter (%OM). K_{oc} was used to determine the possible risk posed on delicate ecological resources. Aquatic toxicology estimation using Ecological Structural Activity Relationship revealed that all chemicals were not toxic even at over-estimated K_{oc} values. This research established the usefulness of screening level environmental modeling tools in assessing ecological risk and hence helpful in developing site-specific models for monitoring chemicals in the environment, which can assist governments, policymakers, and industries in designing appropriate regional disaster management plans.

Keywords: Benzene, Toluene and Naphthalene (BTN), Niger Delta Region (NDR), Organic-carbon partitioning coefficient (K_{oc}), Soil-water distribution coefficient (K_d).

1. Introduction

Societal growing concern and man's yearning for development have fueled his quest to explore his environment to harness its vast but limited resources over the past hundreds of years [1], [2]. In the current global pandemic situation caused by COVID-19, the pressure on the environment has increased with an intensified release of waste [3]–[8]. Sadly, much attention was not paid to the environmental impact of the processes carried out [8]–[13]. Deposits of crude oil can be found in almost all continents

of the world. With its discovery, petroleum and its associated products have become the primary source of energy that [14]–[16]. However, its exploration and exploitation have been accompanied by an alarming degree of environmental degradation, hence threatening the health and wellbeing of humans and other vital ecological resources [1], [17], [18]. It is indubitable that crude oil and gas have contributed immensely to societal development. However, its exploration, exploitation, and

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trade have contributed their quota in the current global environmental challenges [13], [14].

Before the 1960s, little attention was paid to the effects of crude oil spillages. However, three notable incidents sparked international attention: the Torrey Canyon wreck of 1967 (off the coast of England), the 1989 Exxon Valdez spill off the coast of Alaska, and the 1991 massive release of crude oil during the Gulf war. These led to increased environmental research and the adoption of several national and international control practices such as the Oil Pollution Act of 1990. Despite these controls, ecological hazards, petroleum contamination remains a prevalent issue [14], [19]. This awareness has contributed to development in the field of environmental toxicology. Environmental toxicology is an element of ecological science and environmental studies, covering several aspects, including protecting water, soil, fisheries, wildlife management, protecting endangered species, and habitat and ecosystem conservation [19]–[26].

In the Nigerian context, oil was discovered in the Niger Delta Region (NDR) in 1956. This resulted in an inflow of several multinational oil companies (MNOCs) to the region to prospect for petroleum and natural gas. With the oil boom of the 1970s, excessive exploitation of the region's environmental resources began. This exploitation of crude oil has become the mainstay of the nation's economy. The oil boom's impact gradually created a shift of focus by the Nigerian government from Agriculture to crude oil exploration, which made more wealth for the country and more environmental and socio-economic crisis for the NDR [27]–[29].

Claims by the MNOCs suggest that most spillages in the NDR result from vandalization/sabotage. However, the public has counter-accusations, blaming spill accidents on the corroded pipelines, negligence, and poor maintenance by the MNOCs. The 2011 UNEP environmental assessment of oil spill and gas flaring of Ogoniland in the Niger Delta stated that, since the discovery of crude in the region, about 600 million gallons of crude oil have been spilt, which have been ignored or poorly managed by the oil companies. These spills have contaminated many lands, damaging farmlands, affecting fisheries, and causing food scarcity and suffering. UNEP found the hydrocarbon contamination levels to be over 1000 times higher than the country's standard for drinking water and benzene contamination of about 900 times higher than the WHO level guideline [30]–[33]. In the light of these, an evaluation of the fate and partitioning of petroleum chemicals in the environment is imperative, as it can serve as a guide to environmental forensics experts during investigations and in the remediation of contaminated sites.

1.1. Environmental Fate of Crude Oil

When oil is spilt into the environment, it undergoes weathering process. Some hydrocarbons are dissolved in water during the weathering process, while others are absorbed into the soil, and the rest volatilizes. Compared to aliphatic and polyaromatic hydrocarbons, monoaromatic hydrocarbon in crude oil dissolves more in water. This is because of their low organic carbon partition coefficients (K_{oc}). Conversely, they tend to distribute into groundwater. On the other hand, polyaromatic hydrocarbon has low solubility in water; hence, it will partition more into soil and sediment compartments. However, crude oil generally has low solubility in water [34]–[36].

1.2. Toxicity of Petroleum Hydrocarbons

The toxicity of petroleum hydrocarbons increases with the quantity of low boiling compounds [37] and in ascending order of alkanes, alkenes, and aromatics [38]. BTEX, an acronym for benzene, toluene, ethylbenzene, and xylene isomers, is more toxic to the environment than other hydrocarbons. They are the common aromatic compounds of crude oil that are most soluble and mobile and have a more significant influence on their physical and chemical properties [39]. BTEX is important for posing health risks when seeping into soil and groundwater from underground pipelines and storage tanks. It has been classified as hazardous, carcinogenic, and neurotic compounds by USEPA and Environment Canada [39], [40]. Researcher in toxicology has paid more attention to volatile organic compounds (VOCs) such as BTEX because of the health risk [41]. A wholesome environment is a bedrock for the existence of life. Life expectation in background with poor environmental values is usually low. Air and water-borne diseases are traditionally associated with chemical pollution in the environment, waste disposal. Is a global environmental health issue [42]–[44]. Acidic groundwater pollution attributed to oil and gas-related activities in the Niger Delta region has been predicted to tend to affect human health, depending on the dosage and inherent health status, thereby affecting productivity [45], [46].

1.3. Oil Spillages in Nigeria

Define oil spillage as the unrestrained flow of petroleum oil or petroleum products into the environment due to operational errors, disasters, failure from equipment, and vandalism (sabotage) [47]. Most oil spills in Nigeria occur in the NDR with devastating effects, such as fire outbreaks, drinking water contamination, fish kills [21], [45], [48]. The spill of oil and accompanying environmental degradation is still on the rise in the Niger Delta [1]. The key conundrum

for the Nigerian government is how to arrest the problem, with the burning question of how can they carry out remediation of the polluted environment without first modelling or predicting the volume of oil that has been spilled into the environment over the decades [49]. Now, altogether avoiding the spill of crude oil into the environment during operations seems implausible. However, the issue in the Niger Delta is with the regularity and volume of spill incidences and the poor control and response time. Terrestrial and marine resources are usually affected whenever oil spills are not properly recovered, spreading over a large area. Marine habitat, farmlands are the most affected, consequently threatening the existence of organisms in the affected area [50], [51]. Apart from crude oil spills, environmental contamination also stems from midstream operations, such as refining petroleum products. Examination of the treatment of wastewater from a refinery using activated carbon (although focused on the physiochemical phenomenon) confirms the presence of organic pollutants including phenol, benzene, Toluene and Xylene (which are vital volatile components in crude petroleum) being discharged with industrial wastewater into the environment [52], [53].

There have been multiple oil spills in the past. Reports published by Nigerian authorities and oil companies have revealed discrepancies in the number of incidences. In 2006, Shell Nigeria reported an average of 250 incidences per 2006 while the Nigerian National Oil Spill Detection and Response Agency (NOSDRA) confirmed 327 oil spill cases. The inconsistency of these reports displays laxity in harmonizing data by regulatory bodies or failure to disclose many oil spill incidents.

1.4. Niger Delta: Causes of Oil Spills

Spillages occur either from natural causes such as natural disasters or production activities, poor control of oil well, sabotage, poor loading, and offloading practices. Half of the oil spillages in the NDR are attributed to inadequate assets quality (corrosion), less than two percent due to production failure/crude transfer operations, and twenty-eight percent to sabotage [54]–[57]. Figure 2 shows the oil

spill data from January 2013 – to May 2021, showing the causes of the oil spill in the region under review.

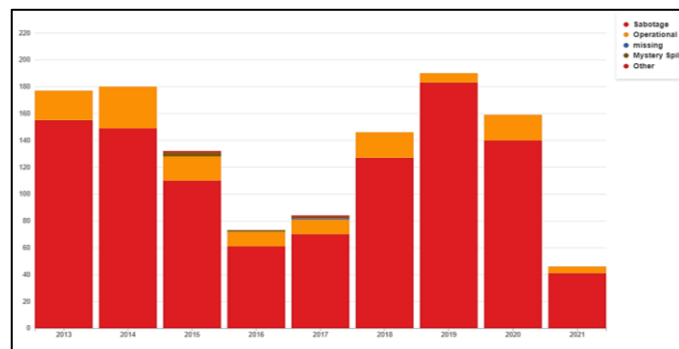


Figure 1. Annual Oil Spill Incidences by Cause for 2013-2021 [58].

If the data presented on the Shell Petroleum Development Company of Nigeria Limited (SPDC) website is anything to go by (as there are counterclaims by affected communities that spills are results of corroded pipelines), Figure 1 shows sabotage/theft to be the primary cause of spill of crude in the Niger Delta, followed by spills due to operations, in a total of 1142 spills.

1.5. Proximity assessment of NDR to spill Hazards

Accidents that are severe in a year are sparse and are assumed to follow a Poisson distribution; hence tough oil spills are thought to occur less frequently [59]. For risk assessment purposes, the probability and severity of environmental pollution on specific areas from hydrocarbons is logically determined by the quantity of spillage of every discharge, the likelihood of a spill occurring, and the level of exposure of vulnerable and delicate resources.

The proximity of ecological resources in the NDR to petroleum pipelines serves as potential hazards for the ecosystem and is critical in exposure assessment. Hence, there is the urgency to determine the possible degree of damage that can occur in the event of a spill to design a suitable remediation and disaster management response approach. Table 1 compares the rate of pipeline failure in the NDR compared to other regions in the world.

Table 1. Comparison of Pipeline Failure in Nigeria/Niger Delta and Other Regions in The World. *

Region	Product	Failure Rate per 1000km-years	Years
United States	Gas	1.18	1984-1992
United States	Oil	0.56-1.33	1984-1992
Europe	Gas	1.85	1984-1992
Europe	Oil	0.83	1984-1992
Western Europe	Oil	0.43	1991-1995
Western Europe	Gas	0.48	1971-1997
Canada	Oil & Gas	0.35	N/A

Region	Product	Failure Rate per 1000km-years	Years
Hungary	Oil & Gas	4.03	N/A
Nigeria	Oil	6.4	1976-1995
Niger Delta (Nigeria)	Oil	1.14	1999-2005

*Adapted from Achebe et al., 2012 as cited by Shittu, 2014 [60].

From table 1, compared to other regions in the world, there is a high susceptibility for pipeline failure and subsequent spillage of petroleum oil and other associated products in Nigeria and the Niger Delta Region in particular. This trend has not shown any markable reduction even in the past fifteen years. Therefore, there should be a cause for concern for the health and safety of both environmental resources and human health. Furthermore, most of the NDR experiences periodic flooding as it lies on a shallow plain [31]. The environmental fate of crude can be enhanced by the direction of flow of both underground and surface water [21], [45], [61], [62]. The variation of flow of the water table contributes significantly to material transference, including contaminants. The groundwater level is significant during the rainy season, and all water bodies flow southward [33]. This may serve as a substantial threat as oil spills during the rainy season will tend to migrate farther and contaminate very delicate areas within the NDR.

2. Research Methods

2.1. Research Bibliographical Databases

Bibliographical databases such as Google Scholar, Pub Med, and Scopus were reviewed. This review includes relevant articles published between 1976 and 2021. Thus, understanding the risk associated with exploring a complex mixture such as petroleum crude is crucial, as it requires a way to estimate the proportion of toxic components in the air, water, and soil over a while (chemical fate and transport). Such estimates are crucial to ascertaining the short- and long-term hazards of substances in the environment and their possible long-term impacts on ecological resources and human health (environmental modelling).

Several mathematical modelling tools (screening level tools) integrated into computer programs and having default exposure factors have been developed and used to provide technical assistance in risk exposure assessment [63]. These tools are designed to be fast, handy, and convenient. They are usually utilized whenever relevant empirical data from monitoring or exposure-linked data are unavailable and are mainly employed to assess risk at the screening level [64]. The most notable drawback common to these tools is the overestimation of exposure values.

2.2. Environmental Modelling

Environmental modelling of organic compounds is vital in determining chemical behavior in an exposed environment. It is helpful because of the effect created on the ecosystem when these chemical pollutants are transferred from one medium to another depending on the material properties of the medium and environmental variables such as temperature and humidity. Biotic and abiotic substances retain chemical pollutants either by adhering to the surface of the material or by dissolving into the molecular network of the particulate matter [65]. These chemical pollutants are usually transported through fluids in their natural biotic or abiotic medium. Knowledge of environmental chemical partitioning of substances released into the environment is vital as it may be difficult to clean up after being released and may result in severe ecological and health damage [66]. Modelling organic chemicals in the environment is helpful in estimating these behaviors and helps hold polluters responsible for toxic chemicals released. For this study, an environmental modelling screening-level tool, EPI Suite™ was used. EPI Suite™ is a screening-level software model developed by the USEPA [63]. The model could predict the partitioning of chemicals in the environment and thus helps in the environment assessment of the possible effects of chemicals in the environment. Three crude oil chemicals: benzene, toluene and naphthalene were selected.

This can sometimes be misleading, as substances that pose no concern may appear otherwise due to the exaggeratedly high estimation averages. However, this prejudice increases confidence, as substances termed below the threshold value and with no environmental effects will present no concerns [64], [67]. Although several environmental models are accessible, the fugacity model was utilized in this study, as it is easy to use and readily available. Fugacity models estimate substances' propensity to distribute into soil, water, and sediment in the environment (partition). The model utilizes mass balance equations and partition coefficients to predict the partitioning and transport of contaminants [68]. The fugacity model is incorporated into the United States Environmental Protection Agency's (USEPA) screening level computer modelling tool-Estimation Programs Interface (EPI) Suite™ [63]. A Level III fugacity model is integrated into the EPI Suite™, infers both a steady-state condition and homogeneity of all the compartments (soil,

sediment, air, and water); however, the partitions are not in equilibrium.

2.3. Niger Delta Region (NDR)

On the Southern tip of Nigeria lies the NDR. It is covered by Equatorial Guinea forests and a renowned "biodiversity hotspot" for regional wildlife. She is bordered on the east by Cameroun and on the South by the Atlantic Ocean. The Niger Delta [56], [69] of land and forests. Geopolitically, there are nine states in the NDR (Figure 1).

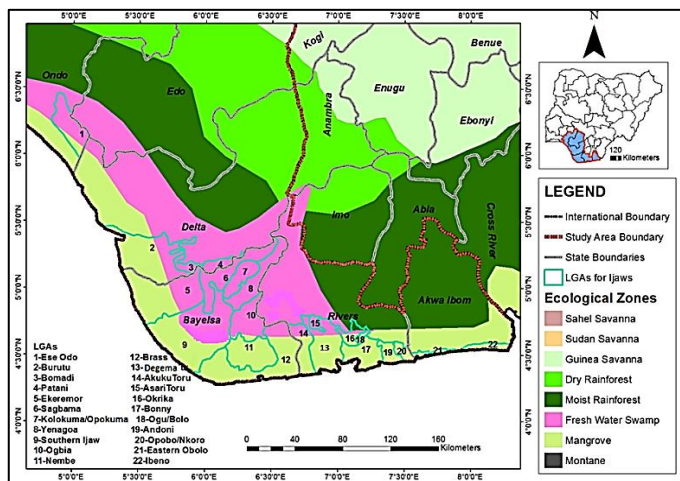


Figure 2. Map of Niger Delta Region (NDR)

The NDR is an oil-rich region located in the South of Nigeria. An estimated one "Exxon Valdez" oil spill enters the NDR ecosystem each year. Over the past one-half of a century, a substantial volume of crude oil has been spilled, representing fifty times the 1989 Exxon Valdez spill in Alaska [70]. This has brought untold hardship to inhabitants of the region, resulting in agitations, crude oil theft/bunkering, and pipeline sabotage.

2.4. Model Justification

EPI Suite™ has been validated independently, using external validation sets. Details of these are available in the Help files. There is also a complete list of references provided to users to assist in examining the employed statistics. EPI Suite™ has been reviewed in several technical journals and panels by the Science Advisory Board (SAB) [71]. The board described the software as sufficiently accurate to be used as a regulatory screening tool, user-friendly, cost-effective, and based on sound scientific work.

For simplification and to compensate for the unavailability of experimental data, the following assumptions were made:

- Based on a legacy of spill episodes in the NDR, a substantial volume of crude oil is expected to be released into the environment.

- The concentration of each of the constituents of interest (benzene, toluene, and naphthalene) in the event of a spill will be less than the detection limit (DL) in water (due to their volatile nature); however, some concentration will be expected to be in the sediment, which presents possible bioaccumulation. Research by Lindén and Pålsson [72] puts the concentration of polyaromatic hydrocarbon (PAH) in Ogoniland (Naphthalene) at 8.0 mg/kg, Benzene 9.0 mg/kg [33] and Toluene 7.2 mg/kg respectively. These chemicals were chosen due to their high toxicity profile.
- The wind speed, river depth, and current velocity for stream and river systems for the study area were assumed to fall within the assigned default values in EPI Suite™.

2.5. Estimation of Organic Carbon Partitioning Coefficient (K_{oc})

To estimate the K_{oc} for each of the components of interest (Equation 2). Results obtained were used as input into the EPI Suite™ fugacity model. The range of values for soil organic matter (OM) percentage concentration was sourced from works of literature. For all the land use types (forest vegetation, grass vegetation, continuously cultivated lands), the OM% in the NDR ranges from 2.21% to 3.81 % [73]. Also, the Soil-water distribution coefficient (K_d) was used to compute K_{oc} values (Equation 2). It is important to note that K_d is usually empirically determined site-specific values. Hence, simulated or actual groundwater is utilized [74]. The soil-water distribution coefficient (K_d) values were computed from the octanol-water partition coefficient (K_{ow}) (Equation 1) [75]. The values for K_{ow} were varied based on different analytical methods (absorption spectrometry, radiochemical, gas-liquid chromatography, high-pressure liquid chromatography, and recommended values) as presented by Sangster [76]. K_{ow} values were assigned at the researchers' discretion. K_d values were also calculated (Equation 1).

$$K_d = 0.39 + 0.67 \times K_{ow} \quad (1)$$

For instance, the log K_{ow} value for Benzene absorption spectrometry was obtained to be 2.04 [76].

$$\text{But, } K_{ow} = 10^{(2.04)} \quad (2)$$

Therefore, $K_d = 0.39 + 0.67 \times 109.6 = 73.8$ (Table 2)

Corresponding values for K_{oc} were computed (Equation 3)

$$K_{oc} = \frac{K_d}{OM\%} \times 100\% \quad (3)$$

Where;
 K_{oc} is the Organic carbon partition coefficient
 K_d , the soil-water distribution/partition coefficient
 OM, Organic matter/fraction (percent)

Table 2. Assigned %OM and calculated K_d values for BTN.

Distribution coefficient (K_d) [*]			
% Organic Matter	Benzene	Toluene	Naphthalene
2.2	73.8	217	686
2.5	88.7	293	1680
3.17	90.8	360.2	1888.7
3.49	90.8	385.9	1535.3

* K_d values employed here may be overestimated. Empirical K_d values may vary greatly for a particular contaminant.

Table 3. EPI Suite™ Entry Data for BTN

Name of Chemical	CAS Number	SMILES Notation
Benzene	000071-43-2	c(cccc1)c1
Toluene (Benzene, methyl-)	000108-88-3	c(cccc1)(c1)c
Naphthalene	000091-20-3	c(c(ccc1)ccc2)(c1)c2

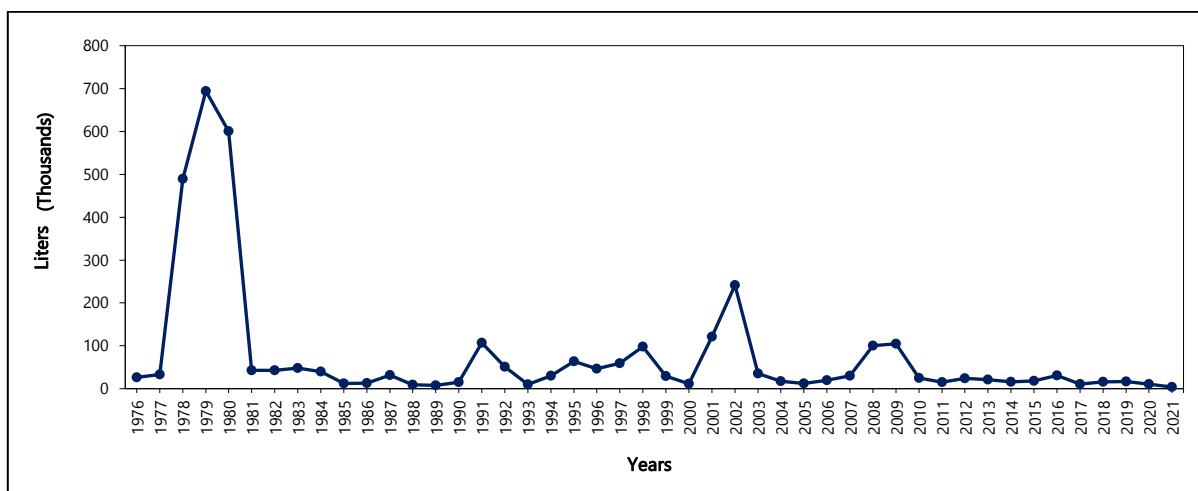


Figure 3. Volume of Spilled Oil in the Niger Delta, 1976- May, 2021

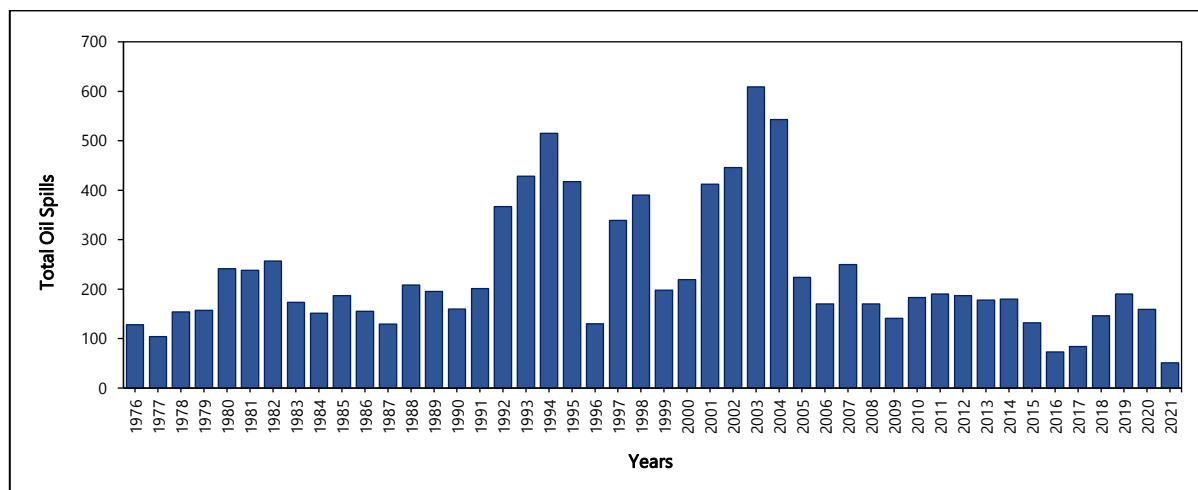


Figure 4. Number of Oil Spills in the Niger Delta from 1976 - May 2021

3. Result and Discussions

3.1. Oil Spills

A careful examination of kinds of literature and data from several sources about the spill of crude in the Niger Delta, revealed an average of over 229.5 spill incidents to have occurred annually in the past 46 years, with a total of over

3.5 million barrels spilled into the various media (land, water, swamp).

This value is debatable as there have been conflicting results regarding the number and amount of crude spilled into the environment by the major oil industry key players. It is believed to be higher than the recorded values. Figures 3 and 4 show the trend of oil spill incidents in the region under review (volume and number of spills). Data from oil

spill episodes in the Niger Delta has been described as consistently unreliable. For instance, in 2014, a total of 204 spills was reported by Shell Petroleum Development Company of Nigeria Limited (SPDC), whereas ENI (Italian oil giants) reported 349 to have occurred in the same year. Both companies admitted that over 550 spills have occurred in the Niger Delta the previous year. Contrasting this to the just 10 spills occurring in the whole of Europe annually from 1971 to 2011, the Niger Delta situation ought to have been declared as a national environmental emergency. The implication of this is that people in the region live in pollution daily. Claims by the oil company operators put the volume of crude spill in this period to be about 5 million liters; however, this figure is most likely to be significantly higher, owing to the poor reporting of incidence in the country [77]. Globally, the pollution profile of Nigeria ranks amongst the worst in comparison with other oil-production nations. Over 63 million liters of crude have been spilled into the Niger Delta environment between the 1970s and 2006, as reported by UNDP, with only about 30% recovered. These spills occur daily and have been on for over six decades. Hence, it will be suitable to infer significant environmental damage and a worrisome public and environmental health impact in the region [78]–[80].

This is indicative that the MNOC is not showing the needed concern for the effect of spilled crude in the environment. There were also results indicating no recoverable oil on-site, even when approximately 19 barrels were spilled. The only rational explanation will be poor response time/logistics or negligence. These results reveal that a significant amount of oil is being spilled into

the environment, hence, justifying this study to ascertain the partitioning of carcinogenic volatile organics to predict their potential hazards on delicate environmental resources.

3.2. Environmental Fate of Volatile Organics

The environmental partitioning of chemical substances is affected by several factors, of which the physical and chemical properties are fundamental. To estimate the partitioning of the chemicals, EPA's EPI Suite™ was utilized. Fugacity model for two sources K_{oc} was employed (default MCI-based and user-entered K_{oc}). The fugacity model was chosen as the basis for assessing the chemicals of interest as it presents a clearer picture of how each component in the substances will be distributed in the environment. Table 4 shows a descriptive statistic of BTN.

Table 4. Descriptive Statistics: % Organic Matter, Benzene, Toluene, Naphthalene

Variable	Mean	SE Mean	Std. Dev	Median
%Organic Matter	3.04	0.30	0.66	3.17
K_d (Benzene)	82.6	4.7	10.5	88.7
K_d (Toluene)	368	61.4	137	360
K_d (Naphthalene)	1460	205	458	1540

The default Level III fugacity model with MCI based soil K_{oc} and user-entered values are shown in Tables 5 and 6.

Figure 5 and 6 shows a representation of the fugacity models (MCI-based and user-entered K_{oc}), which shows how each chemical distributes in the environment.

Table 5. Default Level III Fugacity Model EPI Suite™ (MCI based Soil K_{oc})

Chemical	Mass Amounts (%)			Half-Life (Hrs)			Emissions (Kg/hours)
	C_6H_6	C_7H_8	$C_{10}H_8$	C_6H_6	C_7H_8	$C_{10}H_8$	
Air	31.8	19	0.89	209	43	11.9	1000
Water	41.1	41.2	11.5	900	360	900	1000
Soil	26.7	39.4	86.6	1800	720	1800	1000
Sediment	0.37	0.44	0.998	8100	3240	8100	0
Persistent Time (hours)	197	153	873				

Table 6. Level III Fugacity Model EPI Suite™ (User-entered K_{oc})

Chemical	Mass Amounts (%)			Half-Life (Hrs)			Emissions (Kg/hours)
	C_6H_6	C_7H_8	$C_{10}H_8$	C_6H_6	C_7H_8	$C_{10}H_8$	
Air	8.53	4.7	0.57	209	43	11.9	1000
Water	13.5	14.8	7.77	900	360	900	1000
Soil	75.9	75.2	71	1800	720	1800	1000
Sediment	2.08	5.3	20.7	8100	3240	8100	0
Persistent Time (hours)	599	420	1210				

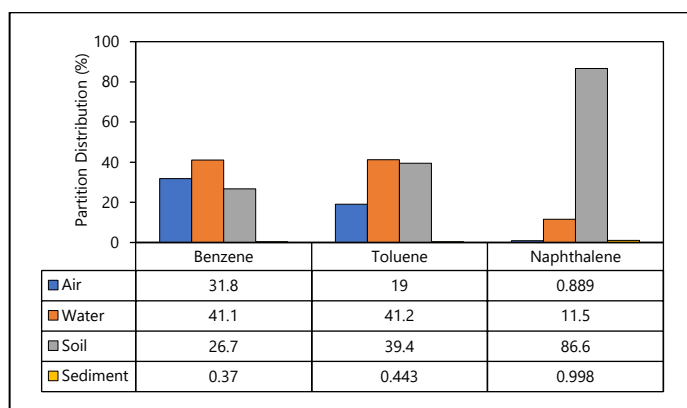


Figure 5. Environmental Distribution of BTN for MCI-based Soil K_{oc}

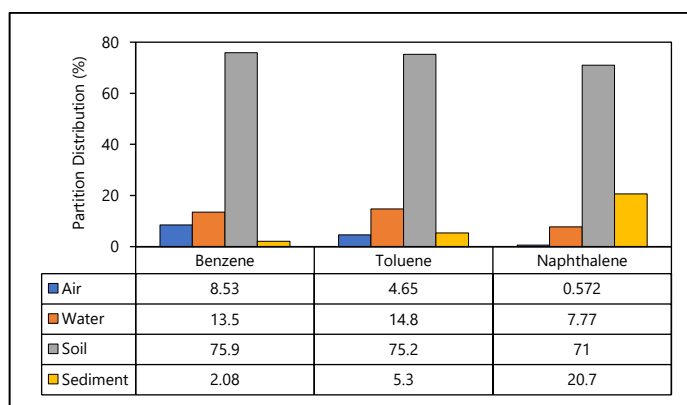


Figure 6. Environmental Distribution of BTN for User-entered Soil K_{oc}

3.3. Aquatic Ecotoxicology-ECOSAR

Predicting the toxicology of chemicals in water was carried out using the ECOSAR model. Using three stand-in species: fish (freshwater, daphnid) planktonic crustaceans, and green algae, ECOSAR predicts the possible toxicity of chemicals on the overall aquatic community. The lethal concentration that will kill 50% of the organism (LC50) is used to predict fish and daphnid, while the effective concentration that will kill 50% of the organism (EC50) is used to predict green algae. The model also calculates chronic values (Chv) for earthworms [67]. Table 7 gives a summary toxicity prediction of BTN.

3.4. Bioconcentration/Bioaccumulation & Biodegradation

The bioaccumulation/bioconcentration of substances builds up toxic chemicals in living organisms, which may have subsequent poisonous effects on higher predators and humans and may lead to biomagnification through the food chain. The determination of the susceptibility for an organic substance to bioaccumulate is usually carried out using the K_{ow} [81]. Table 8 gives the bioaccumulation and biodegradation of the chemicals under review.

Results from Table 2 for K_d of Benzene, Toluene and Naphthalene using Minitab show there is partial concentration of data around the mean, indicating the minimum variation between the data set. For Naphthalene, the standard deviation appears to be more significant, indicating the importance of acquiring as much data as possible for research work that involves comparison between models. A comparison of the concentration results for chemicals in water computed from Table 5 and 6 shows a decrease in concentration for all three chemicals. This implies fewer chemicals (BTN) in water (River or lake) in the event of crude oil spill. However, this also indicates more of the contaminants will be in the sediment and soil, which creates the potential for possible environmental persistence. Also, with more of the chemical in the sediments, there will be increased ingestion potential for mud-dwelling organisms such as crabs, catfish etc. and consequently a tendency for biomagnification through the food chain.

Generally, the results show a well-defined trend that the weaker the K_{oc} values, the weaker the sorption ability on soil for each chemical and vice versa. The much larger values obtained for the user-entered K_{oc} values are most likely due to overestimating the K_{ow} and K_d values. A critical observation of the results for both MCI and user-entered models shows a clear trend that higher K_{oc} values, increase the tendency for the chemicals to partition more into soil and sediment compartments. Similar results were gotten by [82], their study revealed that very strong K_{oc} values is an indication that contaminants will stick more to soil organics and most likely persist in the environment. However, this may result in such chemicals not being bioavailable.

From Figure 5, components for benzene and Toluene are predicted to partition into the water and soil compartment. Naphthalene shows a larger partition into the soil compartment (86.6%), which suggests minimum biodegradability. In the MCI model (Table 6), although the mass amount in the sediment compartment tends to increase from Benzene to Naphthalene, the half-life and persistent time of Toluene is less than that for Benzene, indicating that while a chemical may be present in a smaller amount, it can be more persistent. Except for the air compartment, the half-lives for Benzene and Naphthalene are identical.

Furthermore, regarding sampling for BTN, more attention should be paid to the water compartment for Benzene and Toluene as more of the chemicals will remain in the water. However, the concern should be drawn to the sediment compartment for Naphthalene. The MCI indicated that sample collection should be focused on the water compartment for Benzene and Toluene, but on the soil compartment for Naphthalene.

Figure 6 above corresponds to Table 7 and presents the distribution of BTN for the user-entered values in the environment. Compared to the default model, there is a significant migration of mass amount into the soil compartment for all chemicals. This high value is clearly due to the non-empirical data used in the determination of K_{oc} values. As the mass distributes more into the soil compartment, it is subtracted more from the water compartment-mass balance. If this scenario occurs in real

life, it creates the possibility for plant uptake of the chemicals and nutrients with possible harmful effects on mammals within the area of interest. As with the default model, the half-life for each of the chemicals remained unchanged. However, there is a 32.8%, 36.2%, and 72.1% increase in the persistent time for BTN, respectively. This further establishes the effect of K_{oc} values on the partitioning behavior of chemicals in the environment.

Table 7. Table Title (Volume of Spilled Oil in the Niger Delta, 1976- May 2021).

ECOSAR Class	Organisms	Endpoint (Time)	Prediction(ppm)		
			C ₆ H ₆	C ₇ H ₈	C ₁₀ H ₈
Neutral Organics	Fish	LC ₅₀ (96-hr)	65.1	24.8	9.4
Neutral Organics	Daphnid	LC ₅₀ (48-hr)	36.9	14.8	5.9
Neutral Organics	Green Algae	EC ₅₀ (96-hr)	27.5	13.5	6.9

Table 8. Bioaccumulation and Biodegradation Probability

Chemical	BCF (L/kg wet weight)		log K _{ow}		BIOOWIN5 (MITI)	
	MCI	User	MCI	User	MCI	User
C ₆ H ₆	11.8	11.8	2.13	2.13	0.73	0.53
C ₇ H ₈	29.4	29.4	2.73	2.73	0.52	0.52
C ₁₀ H ₈	69.9	69.9	3.3	3.3	0.40	0.45

Table 7 reveals the chemicals will not be toxic on surrogate species at 96 and 48 hours, respectively (estimated ECOSAR values are higher). However, the effect may be anticipated in mud-dwelling organisms.

Based on the criteria provided by REACH, none of the chemicals will bioaccumulate (BCF < 2000). Also, the log K_{ow} values obtained for both models support the prediction for the BCF criteria (BCF not ≥ 4). This is also collaborated by the requirements set in Annex D of the Stockholm convention. Results in Table 8 indicate that Benzene and Toluene are readily biodegradable (MITI non-regression probability ≥ 0.5- BIOOWIN 5), whereas Naphthalene will tend to persist more in the environment (BIOOWIN 5, < 0.5). There is no change between the BCF and log K_{ow} values for both models.

3.5. Environmental Persistence

According to the criteria for persistent chemicals contained in "Annex D" of the "Stockholm Convention", a chemical is categorized as "persistent" if there is evidence that the half-life in the water compartment is >2 months or if the half-life in the soil compartment is >6 months. None of the chemicals can be categorized as a POP. This is because their persistent times in the water and soil compartment ranged from 15 to 37.5 days for the water compartment and 30 to 75 days for the soil compartment respectively (Table 5 and 6).

4. Conclusion and Recommendation

4.1. Conclusion

Judging from all reviewed kinds of literature, online data, this research work has revealed that exploration activities in the NDR have resulted in significant degradation of environmental resources. Agitation and sabotage of petroleum installations result from the dissatisfaction of the outright disregard for human rights by MNOCs and the government's complacency in addressing issues of severe environmental degradation in the area. Oil spill in the NDR stems from several sources. However, reports from MNOCs claim that sabotage and operational activities are the major causes. This can result from poor disaster management plans and response time from government agencies (Raimi et al., 2021), the MNOCs, and the non-implementation of statutory laws.

For the fugacity modelling, results showed that several physiochemical factors, including K_{oc} and K_{ow} , significantly affect the disposition of chemical substances in the environment. Prediction from the default model shows the chemicals under investigation will partition more into the air component (except for naphthalene, which will partition more into the soil compartment), indicating that the chemical is less soluble in water. Model prediction for the user-defined model indicated that all chemicals (BTN) would partition more into the soil

compartment (Figure 6). This is due to the overestimated soil K_{oc} values for the user-entered model (95%, 98%, and 97% increase respectively, compared to the default MCI values) for BTN, which is a function of their K_d and K_{ow} values. K_d values are site-specific and usually experimentally determined. This shows the importance of K_{oc} values. Changing the K_{oc} values can be used to obtain site-specific values.

The chemical's possible toxicity ranking (based on the two EPI Suite™ models) from least to most toxic follows $C6H6 < C7H8 < C10H8$. This indicates that naphthalene will tend to be more persistent in the environment. However, BTN may generally not cause instant toxic effects on higher mammals at these concentrations in the event of a spill. This is acknowledged by Clements et al., stated that the release of hydrocarbons to surface and subsurface soil undergoes rapid weathering, hence losing the toxic and bioavailable components [38]. Results also indicate that neither of the chemicals will bioaccumulate nor bioconcentrate. Estimation of possible toxicity effects on surrogate species (fish, daphnid, and green algae) was carried out with ECOSAR model (Table 7). ECOSAR LC50 and EC50 prediction for the species (user-entered model) revealed a LC50 of 98%, 95%, 93% higher than the estimated concentration for fish at 96 hours, 96%, 91%, 88% higher for daphnid (at 48 hours) and 94%, 90%, 90% for green algae (EC50) for BTN. Similarly, for the default MCI model, a 79%, 70% and 89% LC50 (96 hours) was predicted for fish, 63%, 50%, 82% for daphnid (LC50-48 hours) and 50%, 45%, 85% EC50 at 96 hours for green algae.

With the lower concentration of the chemicals in the freshwater system, it can be deduced that even at very high estimated K_{oc} values, toxic effects will not be expected for all chemicals. However, while the user-entered model predicts a defined trend of a concentration increase from benzene to naphthalene (suggesting naphthalene to exist in higher concentration), the default model seems erratic (suggesting benzene to be more concentrated in freshwater). Furthermore, experimental database prediction using EPI Suite™ puts the solubility of benzene and naphthalene as 1790 mg/L and 31 mg/L respectively, which shows benzene to be more soluble and hence should pose more toxicity threat in water. Results obtained with the user-entered values suggest that the methodology proposed for estimating K_{oc} values from other sources other than from experimentation was not entirely successful. It gave an overestimation of the actual effects of the chemicals than what is contained in literature and the EPI Suite™ model. Hence, experimentation should be given precedence in future attempts of models' comparison. The results analyzed have further established the usefulness of EPI Suite™ and its application and effectiveness in creating site-specific models even for non-

empirical values. This also indicates that the model's accuracy will likely improve with the availability of more experimentally determined values. Thus, the current scenario of a worsening trend in the environmental pollution in the Niger Delta requires greater political, business, and social commitment to seek alternative solutions to the use of highly toxic contaminants and increased investment in research, prevention, and remediation. In addition, clear communication channels are required between academia, policymakers, and society to ensure that timely, science-based information on the potential threats posed by toxic volatile organics from oil spills in the Niger Delta is made available to policymakers' other stakeholders.

4.2. Recommendation

Pollution is a global problem that knows no borders as contaminants are found in every continent, even in their most remote areas, and are readily transported from one country to another. In comparison, thousands of different toxic volatile organics from oil spills and naturally existing elements with potential toxicity have been released into the Niger Delta milieu through human activities since ancient times. These contaminants tend to have residence times in the environment in the order of hundreds to thousands of years and are distributed throughout the planet. Indeed, based on the findings from reviewed works of literature, it can be deduced that oil spillages in the NDR affect not only the environment, including threats to soil health, but its impacts go far beyond the soil dimension.

Soil contaminants can have irreparable consequences on human and ecosystem health, loss of ecosystem services, and has caused substantial financial/economic losses and social inequities for both the indigenous Niger Deltans, MNOCs, and the federal government, all of which jeopardize the achievement of the 2030 Agenda on Sustainable Development [83]. It is therefore recommended that a multi-dimensional disaster management technique be employed. This approach should encompass proactive and reactive responses to disasters, including rehabilitation or remediation of affected spill sites. An effective disaster management system integrates legislative decisions and operational actions. It will also incorporate non-governmental institutions, advocacy groups, and regional/community-based organizations to be holistic.

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