

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

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Abstract

Background:

Over the years, the issue of 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 spilled crude oil can provide essential knowledge required to deal with the complexity associated with the fate of volatile petroleum chemicals in the environment.

Objective:

This paper explores environmental fate of toxic volatile organics from oil spill in the Niger Delta Region of Nigeria.

Methods:

A critical analysis of available literatures/data from PubMed, Scopus, ResearchGate, Google Scholar, Jstor, including expert working group reports and environmental modeling using a screening tool (USEPA EPI Suite™) was carried out to determine the environmental partitioning of Benzene, Toluene and Naphthalene (BTN) respectively. The organic-carbon partitioning coefficient (K_{oc}) was computed as a function of soil-water distribution coefficient (K_d) and percentage organic matter (%OM). This was utilized to determine the distribution of BTN in the environment and the possible risk posed on delicate ecological resources from crude oil pollution due to exploration and production activities within the Niger Delta Region (NDR), Nigeria.

Results:

Results from literature implicated sabotage and operational failures from pipelines as primary causes of crude oil spillages. Generation of a fugacity model using EPI Suite™ revealed that the behavior of BTN is greatly influenced by K_{oc} values. The default Molecular Connectivity Index (MCI) showed that benzene and toluene will partition more into the water compartment while naphthalene will partition into the soil compartment. However, user-entered values showed all three chemicals partitioning more into the soil compartment. Aquatic toxicology estimation using Ecological Structural Activity Relationship (ECOSAR) revealed all chemicals not to be toxic even at over-estimated K_{oc} values.

Conclusion:

This research established the usefulness of screening level environmental modelling tools in assessing environmental risk and hence helpful in developing site-specific models for monitoring chemicals in the environment which can assist governments, policy makers and industries in the design of appropriate regional disaster management plans.

Introduction

Societal growing concern and man's yearning for development, have fuelled his quest to explore his environment in order to harness its vast but limited resources over the past hundreds of years (Raimi *et al.*, 2019; Raimi *et al.*, 2019; Okoyen *et al.*, 2020). In the current global pandemic situation caused by COVID-19, the pressure on the environment has increased with an intensified release of waste (Raimi *et al.*, 2020; Samson *et al.*, 2020; Raimi and Raimi, 2020; Morufu *et al.*, 2021; Raimi *et al.*, 2021; Morufu *et al.*, 2021). Sadly, much attention was not paid to the environmental impact of the processes carried out (Raimi *et al.*, 2019; Omidiji and Raimi, 2019; Raimi *et al.*, 2019; Raimi *et al.*, 2020; Olalekan *et al.*, 2020; Adedoyin *et al.*, 2020; Olalekan *et al.*, 2020; Ajayi *et al.*, 2020). 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 major source of energy that drives the economy of industrialized and developing nations (Premoboere and Raimi, 2018; Ebuete *et al.*, 2019; Sueiman *et al.*, 2019). However, its exploration and exploitation have been accompanied by alarming degree of environmental degradation, hence threatening the health and wellbeing of humans and other vital environmental resources (Raimi *et al.*, 2019; Olalekan *et al.*, 2019; Raimi *et al.*, 2019; Okoyen *et al.*, 2020). It is indubitable that crude oil and gas has contributed immensely to societal development, however, its exploration, exploitation and trade have contributed its own quota in the current global environmental challenges (Premoboere and Raimi, 2018; Olalekan *et al.*, 2020).

Before the 1960's, little attention was paid on the effects of crude oil spillages. However, three notable incidence sparked international attention namely: 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 an increase in environmental research, and the adoption of several national and international control practices such as the Oil Pollution Act of 1990. Despite these controls, environmental hazards, petroleum contamination remains a prevalent issue (Albers, 2002; Premoboere and Raimi, 2018). This awareness has contributed to development in the field of environmental toxicology. The field of environmental toxicology is an element of environmental science and environmental studies, which covers several aspects including; protection of water, soil, fisheries and wildlife management, protection of endangered species, habitat and ecosystem conservation etc. (Albers, 2002; Raimi and Sabinus, 2017; Raimi *et al.*, 2017; Raimi and Sabinus, 2017; Olalekan *et al.*, 2018; Sawyerr *et al.*, 2018; Raimi, 2019; Olalekan *et al.*, 2018; Raimi *et al.*, 2019; Olalekan *et al.*, 2019; Raimi *et al.*, 2019; Okoyen *et al.*, 2020).

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, disproportionate exploitation of the region's environmental resources began. These exploration and exploitation of crude petroleum, has become the mainstay of the nation's economy. The impact of the oil boom gradually created a shift of focus by the Nigerian government from Agriculture to crude oil exploration, which created more wealth for the country and more environmental and socio-economic crisis for the NDR. (Akpomuvie, and Orhioghene 2011; Bakare and Fawehinmi, 2011; Dokpesi, 2004). Claims by the MNOCs suggest that most spillages in the NDR is as a result of vandalization/sabotage. However, there have been counter accusation by the public, 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 spilled, which have been either ignored or poorly managed by the oil companies. These spills, have contaminated vast number of lands, damaging farmlands, affecting fisheries and causing food scarcity and suffering of the people. 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 (Osuji *et al*, 2006; UNEP,2011; Olalekan *et al.*, 2018; Olalekan *et al.*, 2020). 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 also in remediation of contaminated sites.

Environmental Fate of crude oil

When oil is spilt into the environment, it undergoes weathering process. During the weathering process, some of the hydrocarbons are dissolved in water, while others are adsorbed into the soil and the rest volatilizes. Compared to aliphatic and polyaromatic hydrocarbons, monoaromatic hydrocarbon in crude oil dissolves more in water. This is as a result of their low organic carbon partition coefficients (K_{oc}). Conversely, they have the tendency to distribute into groundwater. Polyaromatic hydrocarbon on the other hand has low solubility in water, hence, will partition more into soil and sediment compartment. However, crude oil in general has a low solubility in water (Barakat *et al*, 2001; Potter and Simons, 1998; Irwin *et al*, 1997).

Toxicity of Petroleum Hydrocarbons

The toxicity of petroleum hydrocarbons increases with the quantity of low boiling compounds (Hayes, 1992) and in ascending order of alkanes, alkenes and aromatics (Clements *et al*, 2009). BTEX, which is an acronym for benzene, toluene, ethyl benzene and xylene isomers are more toxic to the environment than other hydrocarbons. They are the common aromatic compounds of crude oil which are most soluble and most mobile and have greater influence on its physical and chemical properties (Wang *et al*, 2006). BTEX is significant for posing health risks when they seep 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 (Wang *et al.*, 2006; Todd *et al*, 1999). Researcher in the field of toxicology, have paid more attention to volatile organic compounds (VOCs) such as BTEX, because of the health risk associated with them (San Sabastian *et al.*, 2001). A wholesome environment, is the bedrock for existence of life. Life expectation in an environment with poor environmental values is usually low. Air and water borne diseases which is usually associated with chemical pollution in the environment, waste disposal etc. is a global environmental health issue (Raimi *et al.*, 2018; Suleiman *et al.*, 2019; Raimi *et al.*, 2020; Gift and Olalekan, 2020; Gift *et al.*, 2020; Morufu *et al.*, 2021). Acidic groundwater pollution attributed to oil and gas related activities in the Niger Delta region have been predicted to have the tendency to affect human health, depending on the dosage and inherent health status, thereby affecting productivity (Morufu and Clinton, 2017; Raimi and Sabinus, 2017; Olalekan *et al.*, 2018; Raimi *et al.*,2018; Raimi, 2019; Odipe *et al.*, 2019)

Oil Spillages in Nigeria

Nwilo and Badejo (2005), 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). Majority of oil spills in Nigeria, occur in the NDR with devastating effects, such as: fire out breaks, drinking water contamination, fish kills etc (Morufu and Clinton, 2017; Raimi and Sabinus, 2017; Olalekan *et al.*, 2018; Raimi, 2019; Olalekan *et al.*, 2019; Olalekan *et al.*, 2020; Raimi *et al.*, 2021). The spill of oil and accompanying environmental degradation is still on the rise in the Niger Delta (Raimi *et al.*, 2019; Okoyen *et al.*, 2020). 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 accurately predicting the volume of oil that have been spilled into the environment over the decades (Mba *et al*, 2019). At the moment, completely 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 the occurrence of spill incidences and the poor control and response time. Terrestrial and marine resources are usually affected whenever oil spills are not properly recovered, as they spread over a large area. Marine habitat, farm lands are the most affected, consequently threatening existence of organism in the affected area (Akpan, 2012; Plessl *et al*. 2017). Apart from crude oil spills, environmental contamination also stems from midstream operations, such refining of petroleum products. Ademiluyi *et al*, (2009), Ademiluyi and Braide, (2012) in their 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 key volatile components in crude petroleum) being discharged with industrial wastewater into the environment.

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 year since 2006 while Nigerian National Oil Spill Detection and Response Agency (NOSDRA) confirmed 327 oil spill cases. The inconsistency of these reports display laxity in harmonising data by regulatory bodies or failure to disclose many oil spill incidents.

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. It is bordered on the east by Cameroon and on the South by the Atlantic Ocean. The Niger Delta Region occupies about 12% of the total surface area of Nigeria translating to approximately 112,110 square kilometres, with an estimated 28 million inhabitants, going by the 2006 population census (Myers *et al*, 2000; Wizer and Wali, 2020). Within the NDR is the faunal zone where mangrove swamps and large reserves of oil are situated on a sizable expanse of land and forests. Geopolitically, there are nine states in the NDR (Figure 1)

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, which represents fifty times the 1989 Exxon Valdez spill in Alaska (Obot *et al*, 2006). This has brought untold hardship to inhabitants of the region, resulting in agitations, crude oil theft/bunkering and pipeline sabotage.

Niger Delta: Causes of Oil spills

Spillages occur either from natural causes such as a natural disaster or due to production activities, poor control of oil well, sabotage, poor loading and offloading practices. As stated by Badejo and Nwilo (2004), half of the oil spillages in the NDR is attributed to poor assets quality (corrosion), less than two percent due to production failure/crude transfer operations and twenty-eight percent to sabotage (Kadafa, 2012; Nwilo and Badejo, 2001, 2004; Wizer and Wali, 2020). Figure 2, shows the oil spill data from January 2013 – to May 2021, showing the causes of oil spill in the region under review.

Adapted from

If the data presented on the SPDC website is anything to go by (as there are counter claims by affected community that spills are results of corroded pipelines), Figure 2 shows sabotage/theft to be the major cause of spill of crude in the Niger Delta, followed by spills due to operations, in a total of 1142 spills.

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 severe oil spills are assumed to occur less frequently (Eckle *et al*, 2012). For purposes of risk assessment, the probability and severity of environmental pollution on specific areas from hydrocarbons is logically determined by the quantity of spillage of every discharge, the probability 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 serve as potential hazards for the ecosystem and are by themselves 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, in order to design a suitable remediation and/or disaster management response approach. Table 1., gives a comparison of 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	Year
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
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.

From the table 1, it is clear that 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. There should therefore be a cause for concern for health and safety of both environmental resources and human health. Furthermore, majority of the NDR experiences periodic flooding as it lies on a very low plain (Odubo and Raimi, 2019). The environmental fate of crude can be enhanced by the direction of flow of both underground and surface water (Morufu and Clinton, 2017; Raimi and Sabinus, 2017; Olalekan *et al.*, 2018; Olalekan *et al.*, 2020). The variation of flow of the water table contributes significantly in material transference including contaminants. During the rainy season, the level of ground water is significant and all water bodies flow southward (UNEP, 2011). This may serve as a significant threat as oil spill during the rainy season will have the tendency to migrate farther, and hence may contaminate very delicate areas within the NDR.

Environmental Modelling

Environmental modelling of organic compounds is vital in determining chemical behaviour in an exposed environment. It is useful because of the effect created on the ecosystem when these chemical pollutants are transferred from one medium to another depending on material properties of individual medium and on environmental variables such as temperature and humidity. The way chemical pollutants are retained by biotic and abiotic substances are either by adhering to the surface of the material or by dissolving into the molecular network of the particulate matter (Chiou, 2003). 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 serious environmental and health damage (Adeolu *et al.*, 2018). Modelling of organic chemicals in the environment is useful in estimating these behaviours and help in holding polluters responsible for toxic chemicals release. 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. The model has the ability to 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.

Methods

Bibliographical databases such as Google Scholar, ResearchGate, Pub Med, Jstor and Scopus were reviewed. This review includes relevant articles published between 1976 and 2021. Thus, understanding the risk associated with the exploration of a complex mixture such as petroleum crude is crucial, as it requires a way to estimate the proportion of toxic components that can be in the air, water and soil over a period of time (chemical fate and transport). Such estimates are key to ascertaining the short- and long-term hazards of substances in the environment and its possible long-term impacts on ecological resources and/or human health (environmental modelling). Several mathematical modelling tools (screening level tools) integrated into computer programmes and having default exposure factors have been developed and used to provide technical assistance in risk exposure assessment (USEPA, 2012). These tools are designed to be fast, handy and convenient. They are usually utilized whenever suitable empirical data from monitoring or exposure linked data are unavailable and mostly employed in assessing risk at the screening level (US EPA, 2010). The most notable drawback common to these tools is the overestimation of exposure values.

This can sometime be misleading, as substances that pose no concern, may appear otherwise due to the exaggeratedly high estimation averages. However, this prejudice increases the confidence level, as substances termed to be below the threshold value and with no environmental effects, will present no concerns (US EPA, 2010). Although, several environmental models are accessible, the fugacity model was utilised in this study, as it is easy to use and readily available. Fugacity models estimates the propensity of substances to distribute into soil, water and sediment in the environment (partition). The model utilises mass balance equations and partition coefficient to predict the partitioning and transport of contaminants (Mackay, 1979). The fugacity model is incorporated into the United States Environmental Protection Agency's (USEPA) screening level computer modelling tool-Estimation Programs Interface (EPI) Suite™ (USEPA, 2012). A Level III fugacity model is integrated into the EPI Suite™, infers both a steady state condition and homogeneity of all the compartment (soil, sediment, air and water), however, the partitions are not in equilibrium.

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 the examination of the employed statistics. EPI Suite™ have been reviewed in several technical journals and also panel reviewed by the Science Advisory Board (SAB)^[1]. 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.

Assumptions:

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

- A substantial volume of crude oil is expected to be released into the environment, based on legacy of spill episodes in the NDR.
- The concentration of each of the constituents of interest (benzene, toluene and naphthalene) in an 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 (2013) puts the concentration of polyaromatic hydrocarbon (PAH) in Ogoniland^[2] (Naphthalene) at 8.0 mg/kg, Benzene 9.0 mg/kg (UNEP, 2011) 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 study area were assumed to fall within the assigned default values in EPI Suite™.

Estimation of Organic carbon partitioning coefficient (K_{oc})

To estimate the K_{oc} for each of the component of interest, equation 2 was used. Results obtained was used as input into EPI Suite™ fugacity model. Range of values for soil organic matter (OM) percentage concentration was sourced from literatures. For all the land use type (forest vegetation, grass vegetation, continuous cultivated lands), the OM% in the NDR ranges from 2.21 to 3.81 % (Oguike and Mbagwu, 2009). Also, Soil-water distribution coefficient (K_d)^[3] was used to compute K_{oc} values, using equation 2. It is important to note that K_d are usually empirically determined site specific values. Hence, simulated or actual ground water is utilized (USEPA, 1999). The soil-water distribution coefficient (K_d) values was computed from the octanol-water partition coefficient (K_{ow}) using equation 1 (Andersen *et al.*,2005). 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 (1989). K_{ow} values were assigned at the researchers' discretion. K_d values were also calculated using equation 1.

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

For instance, $\log K_{ow}$ value for Benzene absorption spectrometry was obtained to be 2.04 (Sangster, 1989),

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

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

Corresponding values for K_{oc} were computed using 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

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
3.81	68.9	583.9	1500.3

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

Results

Oil Spills

A careful examination of literatures 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 occurs annually in the past 46 years with a total of over 3.5 million barrels spilled into the various media (land, water, swamp etc.). This value is debatable as there have been conflicting results as regard the number and/or amount of crude that is spilled into the environment by the major oil industry key players. It is believed to be higher than the recorded values. Figure 3 and 4 shows 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 one that is described as consistently unreliable. For instance, in 2014, a total of 204 spills was reported by 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 puts 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 the poor reporting of incidence in the country (Amnesty International. 2016). 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 literally occur on a daily bases, and have been on for over six decades. Hence, it will be right to infer that there is significant damage to the environment and a worrisome public and environmental health impact in the region. (USEIA, 2014; UNDP,2016; Udoh,2018).

This is indicative that the MNOC are 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 as much as approximately 19 barrels of crude was spilled. The only rational explanation will be poor response time/logistics or negligence. These results reveal that a significant amount of crude is being spilled into the environment, hence, justifying this study to ascertain the partitioning of carcinogenic volatile organics in the environment to predict their potential hazards on delicate environmental resources.

Environmental Fate of Volatile Organics

The environmental partitioning of chemical substances is affected by several factors, of which the physical and chemical properties are very important. In order 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 assessment of the chemicals of interest as it presents a clearer picture of how each component in the substances will distributed in the environment. Table 4 presents a descriptive statistic of BTN.

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

Variable	Mean	SE Mean	StDev	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

Results obtained for the default Level III fugacity model with MCI based soil K_{oc} and the user-entered values are shown in Table 5 and 6 respectively.

Table 5: Default Level III Fugacity model EPI Suite™ (MCI based soil K_{oc})

Chemical	Mass Amounts (%)			Half-Life (Hrs)			Emissions (Kg/hr)
	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(hr)	197	153	873				

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

Chemical	Mass Amounts (%)			Half-Life (Hrs)			Emissions (Kg/hr)
	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(hr)	599	420	1210				

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

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 overall aquatic community. The lethal concentration that will kill 50% of the organism (LC_{50}) is used to predict for fish and daphnid, while effective concentration that will kill 50% of the organism (EC_{50}) is used to predict for green algae. The model also calculates chronic values (Chv) for earthworms (Mayo-Bean *et al.*, 2012). Table 7 gives a summary toxicity prediction of BTN.

Table 7: Ecotoxicity prediction

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

Bioconcentration/Bioaccumulation and Biodegradation

The bioaccumulation/bioconcentration of substances is the build-up of toxic chemicals in living organisms, which may have subsequent toxic 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} (Gruiz *et al*, 2015). **Table 8** gives the bioaccumulation and biodegradation of the chemicals under review.

Table 8: Bioaccumulation and Biodegradation probability

Chemical	BCF (L/kg wet weight)		$logK_{ow}$		BIOWWIN5 (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

Discussion

Results from Table 2 for K_d of Benzene, Toluene and Naphthalene using Minitab shows there is partial concentration of data around the mean, which is indicative of 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, there is a well-defined trend from the results 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 is most likely due to overestimation of the K_{ow} and consequently 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, increases the tendency for the chemicals to partition more into soil and sediment compartments. Similar results were gotten by Helen *et al* (2008). 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, with regards to sampling for BTN, more attention should be paid on the water compartment for Benzene and Toluene as more of the chemicals will remain in water. However, concern should be drawn to the sediment compartment for Naphthalene. The MCI gave an indication that sample collection should be focused on the water compartment for Benzene and Toluene, but on the soil compartment for Naphthalene.

The figure (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 being subtracted more from the water compartment-mass balance. If this scenario does occur in real life, it creates the possibility for plant uptake of the chemicals along with 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 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 behaviour of chemicals in the environment.

Table 7, reveals the chemicals will not be toxic on surrogate species at 96 and/or 48 hours respectively (estimated ECOSAR values are higher). However, 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 also support the prediction for the BCF criteria ($BCF \text{ not } \geq 4$). This is also collaborated by the criteria set in Annex D^[1] of the Stockholm convention. Results in Table 8, indicates that Benzene and Toluene are readily biodegradable (MITI non regression probability ≥ 0.5 -BIOWWIN 5), whereas Naphthalene will tend to persist more in the environment (BIOWWIN 5, < 0.5). There is no change between the BCF and $\log K_{ow}$ values for both models.

Environmental Persistence

According to the criteria for persistent chemicals contained in "Annex D" of the "Stockholm Convention", a chemical is categorised 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 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).

Conclusion

Judging from all reviewed literatures, online data, this research work has revealed that exploration activities in the NDR have resulted in significant degradation of environmental resources. Agitation and vandalization/sabotage of petroleum installations is as result of dissatisfaction of the outright disregard for human right by MNOCs and government's complacency in addressing issues of serious environmental degradation in the area. Oil spill in the NDR stems from several sources. However, reports from MNOCs claim that sabotage and operational activities is the major causes. This can clearly be seen as result of poor disaster management plan and response time on the part of the government agencies (Raimi et al., 2021) and 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} and have significant effects of 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), indication that the chemical is less soluble in water. Model prediction for the user defined model indicated that all chemicals (BTN) will partition more into the soil compartment (Fig. 6). This is clearly 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.

Possible toxicity ranking of the chemicals (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 effect on higher mammals at these concentrations in the event of a spill. This is acknowledged by Clements et al., (2009). They stated that the release of hydrocarbons to surface and subsurface soil undergoes rapid weathering, hence losing the toxic and bioavailable components. 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 LC_{50} and EC_{50} prediction for the species (user-entered model) revealed a LC_{50} 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 (EC_{50}) for BTN. Similarly, for the default MCI model, a 79%,70% and 89% LC_{50} (96 hours) was predicted for fish,63%,50%,82% for daphnid (LC_{50} -48 hours) and 50%,45%,85% EC_{50} 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 seem 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 as it gave an over estimation of the actual effects of the chemicals than what is contained in literatures and the EPI Suite™ model. Hence, experimentation should be given precedence in future attempt of models' comparison. Results analysed has 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 accuracy of the model will likely improve with the availability of more experimentally determined values. Thus, the current scenario of a worsening trend in environmental pollution in the Niger Delta require 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 channels of communication are required between academia, policy makers, and society to ensure that timely, science-based information on the potential threats posed by toxic volatile organics from oil spill in the Niger Delta is made available to policy makers and other stakeholders.

Recommendation

Pollution is a global problem that knows no borders as contaminants are found in every continent even in the most remote areas, and are readily transported from one country to another. While, thousands of different toxic volatile organics from oil spill and naturally existing elements with possible 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 literatures, it can be deduced that oil spillages in the NDR affects not only the environment including threats to soil health but its impacts go far beyond the soil dimension and soil contaminants can have irreparable consequences on human and ecosystem health, loss of ecosystem services, and has cause huge financial/economic losses and social inequities for both the indigenous Niger Deltans, MNOCs and the federal government, all of which jeopardise the achievement of the 2030 Agenda on Sustainable Development (Morufu *et al.*, 2021). It is therefore recommended that a multi-dimensional disaster management technique be employed. This approach should encompass both proactive and reactive response to disasters, including, rehabilitation/remediation of affected spill sites. An effective disaster management system is one which integrates legislative decisions and operational actions. For it to be holistic it will also incorporate non-governmental institutions, advocacy groups and regional/community-based organizations.

Further Studies

In the course of this research work, several areas have been identified for further research work. These include:

- Geographic Information systems (GIS) mapping of oil wells within the NDR to evaluate hazard prone environmental resources.
- Development of a site/regional specific model for the prediction of toxic chemicals from crude oil in the NDR.
- Modelling and investigation of the toxicity of higher molecular weight aromatic hydrocarbons in crude oil.

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Footnotes

[1] A 2007 “Quality Review Draft” can be accessed on the USEPA website on: http://www.epa.gov/sab/panels/epi_suite_review_panel.htm.

[3] K_d values employed here may be overestimated. Empirical K_d values may vary greatly for a particular contaminant.

[4] Stockholm Convention, Annex D. Available at: <http://chm.pops.int/Home/tabid/2121/Default.aspx>.

Declarations

Competing Interests: The authors declare no competing interests.

Figures

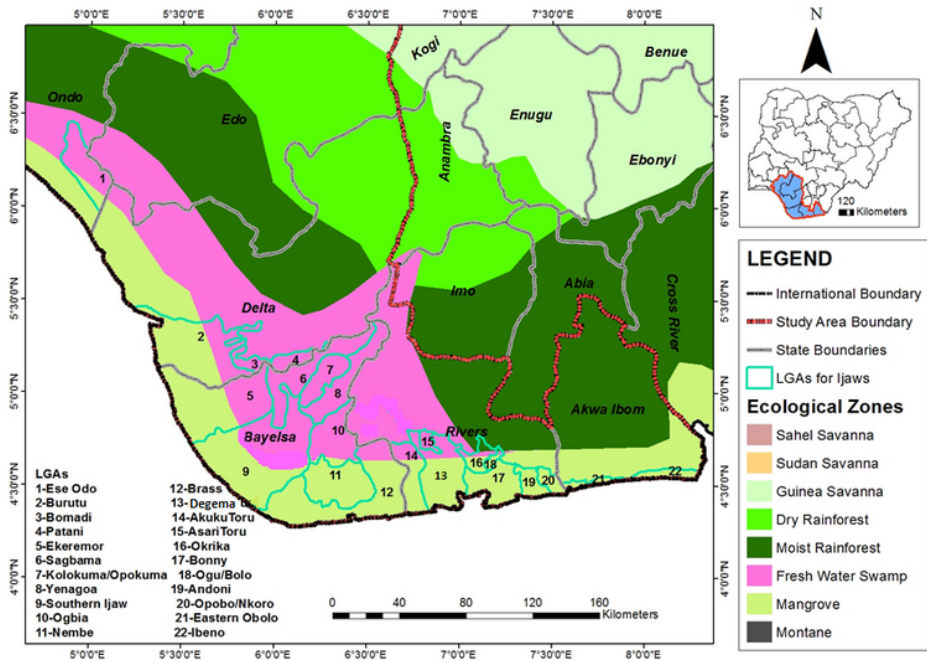


Figure 1
Map of Niger Delta Region (NDR)

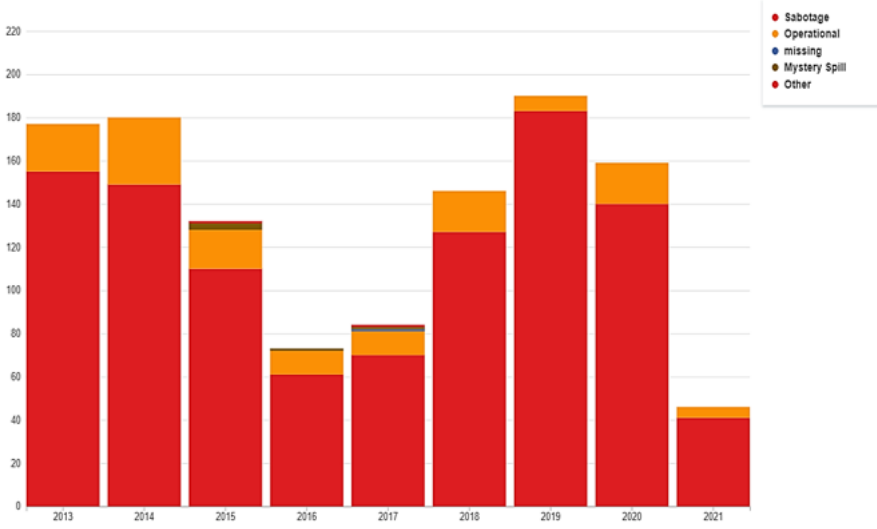


Figure 2
Annual oil spill incidences by cause for 2013-2021 (SPDC, 2021)

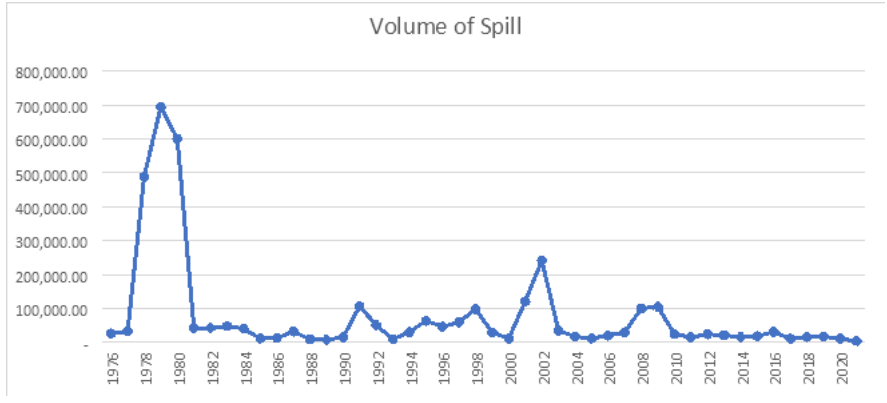


Figure 3

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

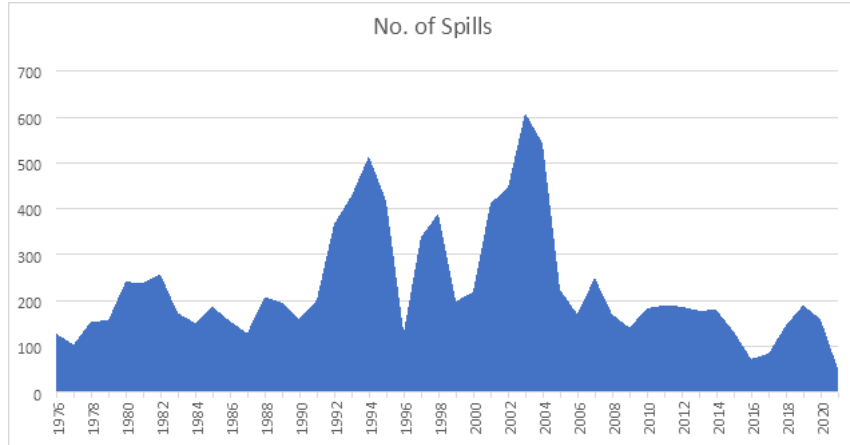


Figure 4

Number of Oil Spills in the Niger Delta from 1976 - May,2021

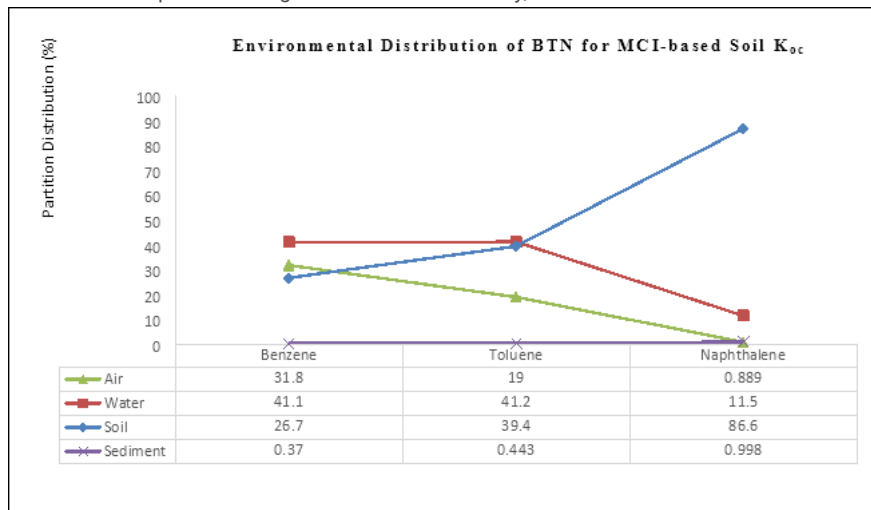


Figure 5

Environmental Distribution of BTN for MCI-based Soil Koc

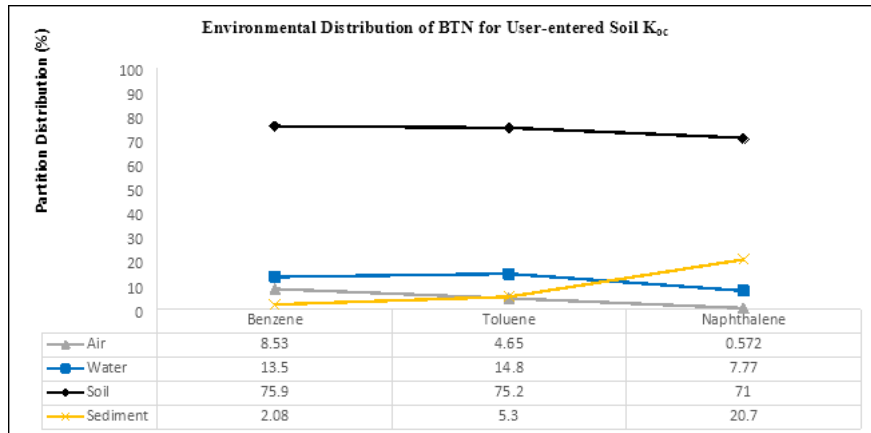


Figure 6

Environmental Distribution of BTN for User-entered Soil Koc

Supplementary Files

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- OILSPILLDATA2011202119762010.xlsx