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Fate and transport modelling of petroleum hydrocarbons in aquatic and soil systems: Toxicological profiling and safety implications for human and environmental health

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Abstract

Since the exploration of crude oil, malfunctioning of oil pipelines and industrial processes are common in oil-producing areas such as the Niger Delta, oil spills of hydrocarbons, especially petroleum, are a constant environmental issue. Most of the time, the toxicity of petroleum hydrocarbons has been deposited into the soil structures and groundwater pools in such regions. This paper examined the environmental behaviour, transport, and toxicological significance of petroleum hydrocarbons in the petroleum-producing communities of Ogulagha, Esanma, Burutu, and the Ayakoromo Creek Area, and Ekogbene of the Burutu Local Government Area, Delta State, Nigeria. Sampling was done on soil (0-15 cm and 15-30 cm depth) and groundwater samples (wet and dry seasons), and the samples were analysed by GC-MS and HPLC analytical models to determine the Total Petroleum Hydrocarbons (TPH) and sixteen priority Polycyclic Aromatic Hydrocarbons (PAHs). The HYDRUS-2D was used to simulate contaminant migration patterns of the vadose zone, and MODFLOW-MT3DMS was used to calculate contaminant groundwater transport of hazardous chemicals, whereas chronic daily intake (CDI), hazard quotient (HQ), and incremental lifetime cancer risk (ILCR) models were used to assess human health hazards. Findings indicated serious hydrocarbon pollution, with the highest soil TPH of 12,450 mg/kg and groundwater TPH of 940 mg/L, especially in the Ogulagha community. Plume migration up to 160 m in the horizontal and up to 200 m in the vertical was predicted by model simulations, once the contamination events had been observed, and groundwater penetration was observed in 35 months to 5 months. Non-carcinogenic risk assessment exhibited HQ values of up to 3.8 children, which is greater than 1.0, the acceptable safety level created by the USEPA, whereas carcinogenic risk assessment gave ILCR 7.8 $x10^{-4}$, which shows an unacceptable level of cancer risk. Spatial risk mapping indicated that the areas of concern were the Esanma and Ogulagha as hot spots of contamination, which needed urgent remediation. The research reveals that the combination of petroleum contamination modelling and toxicological risk assessment can enable a sound system for monitoring the environment, protecting human health, and remediation efforts in petroleum-contaminated ecosystems.

Keywords: Petroleum Hydrocarbons; Fate and Transport Modelling; Toxicological Risk Assessment; Groundwater Contamination

1. Introduction

Petroleum hydrocarbons (PHCs) are heavy and stable toxins that comprise aliphatic, benzene derivatives, and polycyclic aromatic hydrocarbons (PAHs), which occur in the environment and contribute significantly to pollution. They enter terrestrial and aquatic bodies primarily through crude oil exploration, pipeline leaks, and industrial releases, posing long-term dangers to both ecological integrity and human well-being [1-3]. PHCs reside in soils, sediments, surface water, and groundwater, and become subject to complex physical, chemical, and biological changes that affect their

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mobility, bioavailability, and toxicity. Having a lipophilic property and degradation resistance makes them accumulate within the food chains and affect vulnerable populations. For example, [4,5] have demonstrated the presence of higher PAH metabolites in pregnant women exposed to oil-contaminated waters in the Brazilian Amazon. In contrast, [6] also found PAHs in the rivers and aquatic life of the Niger Delta, with a general ecological impact via food sources.

To analyse and model the behaviour of such contaminants, extensive utilization of HYDRUS (vadose zone) and Modflow-MT3DMS (aquifer systems) as environmental modelling tools, and as catalysts for simulating advection, dispersion, sorption, and degradation are significant. These apices enhance the accuracy of predicting PHC plume distribution throughout the soil and groundwater boundaries [6-9]. Nevertheless, few transport models do consider toxicological endpoints, such as health risk assessment, exposure scenario or exceeding safety thresholds as stipulated by regulation. To assess the risk of benzene exposure in Soil contaminated with benzene, [10] used the Johnson-Ettinger vapour intrusion model. However, these studies are fragmented and somewhat uncommon, as they are not part of general risk studies, which typically include land use or susceptible populations at risk of exposure. Such a divorce between modelling of fate and toxicological health endpoints leads to a major gap in the environmental risk assessment. The existing methods tend to treat modelling, exposure, and health assessment as independent steps, and thus cannot be easily applied in integrated risk communication, spatial planning, and remediation. To overcome this gap, one should combine transport-based modelling with toxicological screening to address environmental regulation more effectively and safeguard health policy.

This paper aims to fill this gap by coupling the modelling of contaminant fate with human health risk evaluation in one of the highest vulnerability oil production zones in Delta State, Nigeria, specifically the Burutu Local Government Area. Burutu, with its porous soil,abundant rainfall, and shallow groundwater tables, is especially prone to the migration of the PHC into drinking water and food sources. This study examines the levels of PHC around soil and groundwater in Burutu in comparison to national and international safety guidelines. It assesses the possible toxicological hazards to the affected groups. The interdisciplinary examination between spatial transport modelling and risk-based toxicological endpoints in the study provides a unique insight into setting priorities for remediation and environmental health interventions in petroleum-affected communities. The models used in this study made assumptions of subsurface homogeneity, steady-state flow, and first-order biodegradation, which may not accurately represent the variability at the field scale. The parameters,such as dispersity, could not be directly measured but were estimated based on the literature. In addition, the HQ and ILCR were not based on community-specific data on behaviour, but on other assumed values in standard USEPA exposure calculations. Exposures need to be made more realistic through the use of sensitivity analysis (Monte Carlo simulations) and localised surveys of health in the future. Vapour infiltration hazard from PHC volatiles is a poorly researched route by which exposure might be enhanced.

2. Materials and Methods

2.1. Study Area and Sampling Strategy

The research was conducted in five petroleum-producing communities (Ogulagha, Esanma, Burutu, Ayakoromo Creek Area and Ekogbene) within the Burutu Local Government Area in Delta State, Nigeria as presented in Figure 1. The sampling locations were selected based on their proximity to oil facilities (e.g., pipelines, flow stations) and probable exposure to hydrocarbons (i.e., boreholes, either shallow wells or farmlands). To achieve temporal and spatial variation, 30 soil samples (0-15 cm and 15-30 cm depth) and 25 groundwater samples were taken during wet and dry seasons. Representativeness was enhanced by matching each sampling site and replicating the experiment at three locations to facilitate statistical interpretation.

2.2. Sample Collection and Preservation

Stainless-steel augers were used to collect soil samples at 0–15cm and 15 30cm, water samples were obtained from shallow wells and boreholes using low-flow peristaltic pumps, 1L Teflon bottles, and acidified with nitric acid (pH < 2). All of the samples were kept in strict preservation conditions according to the general ecological routine (EPA, 2023, and EPA, 2013). Immediately after the collection, the soil samples were stored in amber glass jars and cooled to 4 ^{o}C. Groundwater samples were treated with nitric acid to a pH of 2 or below and placed in Teflon bottles under chilled conditions (4°C).

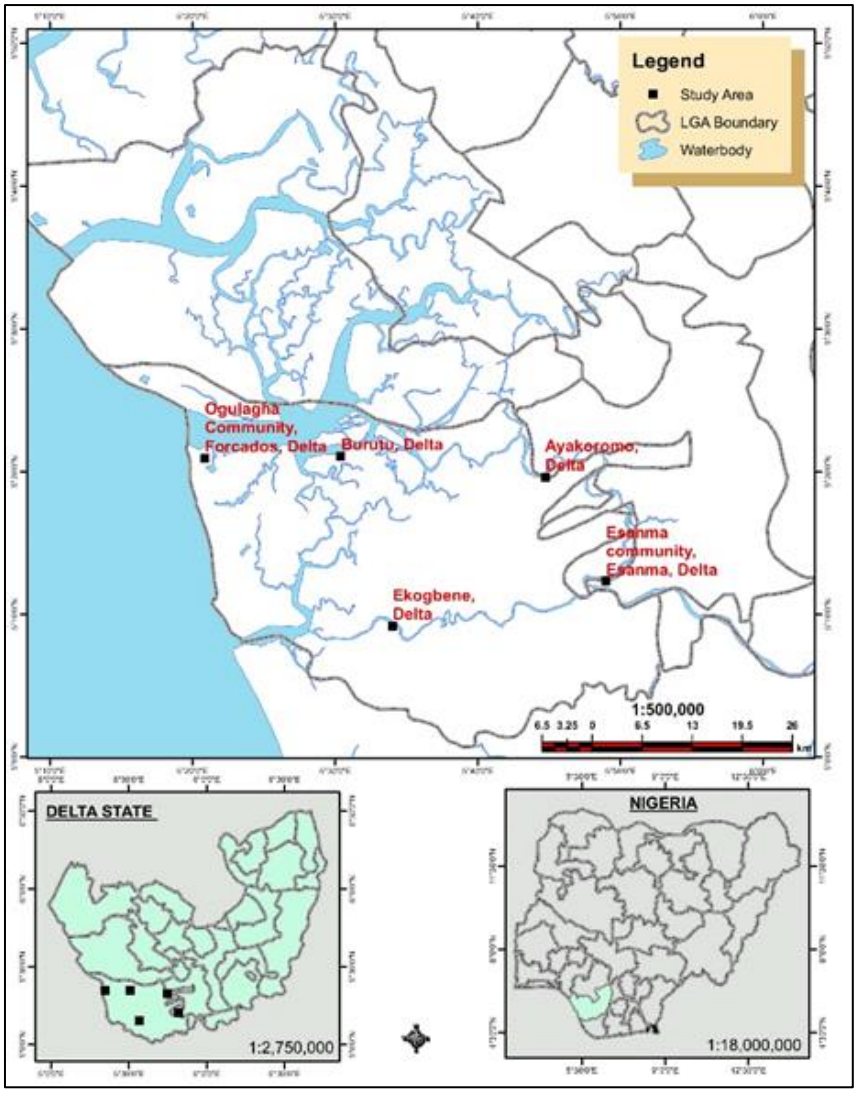

Figure 1 Map of Ogulagha, Esanma, Burutu, Ayakoromo Creek Area and Ekogbene Communities

2.3. Quality Assurance and Ethical Considerations

The Field Quality Assurance and Quality Control practices involved measuring the number of field blanks, equipment blanksand sample duplicates at a 10% frequency. All laboratory tests were conducted using method blanks, recovery standards, and certified reference materials to ensure the accuracy of the data. Calibration of instruments occurred daily, and validation of results was done with an internal standard. Environmental sampling and risk profiling were conducted with the informed consent of community members.

2.4. Laboratory Analyses

The extracted Total Petroleum Hydrocarbons (TPHs) in soil and water were determined using Soxhlet extraction with dichloromethane, followed by cleanup with silica gel, and then determined by gas chromatography-mass spectrometry (GC-MS). The high-performance liquid chromatography (HPLC) method was used to analyse polycyclic aromatic hydrocarbons (PAHs) with fluorescence detection for 16 priority PAHs recommended by the USEPA (2023). The physicochemical characteristics of the soil, including pH, Total Organic Carbon (TOC), and cation exchange capacity (CEC), were determined using standard methods of suspension, combustion, and titration. The parameters of water quality were measured in the field (pH, electrical conductivity, total dissolved solids, and dissolved oxygen) using a multiparameter probe. Table 1 presents the full methods, instruments, and target compounds used in the analytical process.

Table 1 Laboratory Analytical Techniques

Analyte	Extraction/Preparation	Instrument/Method	Target Compounds
Total Petroleum Hydrocarbons (TPHs)	Soxhlet with DCM/ Silica clean-up	GC-MS (Agilent 7890B/5977A)	Aliphatics, aromatics
Polycyclic Aromatic Hydrocarbons (PAHs)	Solvent extraction; direct analysis	HPLC (fluorescence detection)	16 USEPA priority PAHs
Soil Physicochemical Properties	Suspension, combustion, titration	pH meter, Walkley-Black, ammonium acetate	pH, TOC, CEC
Water Quality Parameters	In-situ probe	HANNA HI9829 multiparameter device	pH, EC, DO, TDS, temperature

2.5. Modelling of Fate and Transport

In this study, two modelling codes were used namely Hydrological Simulation Software for Unsaturated Zone Modelling (HYDRUS-2D) to simulate migration of PHC in the unsaturated zone (vadose) and Modular Finite-Difference Groundwater Flow Model & Mass Transport 3D Multi-Species Model (MODFLOW-MT3DMS) to model the saturated aquifer. The HYDRUS-2D Model was set up as a 2D vertical model (depth: 2.5m) using field-measured soil hydraulic conductivity, porosity, and organic content. The groundwater flow was simulated using MODFLOW, while advection, dispersion, sorption, and contaminant decay were calculated using MT3DMS. The model input parameters, including hydraulic conductivity, porosity, bulk density, dispersivity and biodegradation rates, were obtained through field measurements, laboratory measurements, and verified literature values (see Table 2). The calibration of the model was done with the help of Parameter Estimation (PEST) using Root Mean Square Error (RMSE) (RMSE = 0.013). It maximized Nash Sutcliffe efficiency (NSE = 0.91) of observed groundwater concentration. There were no-flow lateral boundaries and fixed head boundaries to model field hydrology with boundary conditions. Plume visualisation and spatial interpolation were carried out by ArcGIS 10.8. Table 3 presents a comprehensive overview of the models, their platforms, configurations, and simulation processes.

Table 2 Model Input Parameters and Sources

Parameter	Symbol	Source/Method	Unit
Hydraulic conductivity	K	Field slug tests	m/day
Porosity	N	Laboratory analysis of core samples	-
Bulk density	Pb	Laboratory (gravimetric)	g/cm^3
Dispersivity (long../trans.)	αL / At	Empirical estimation (Xu–McCarthy method)	m
Organic carbon partition coefficient	Koc	Literature-based or from test soil	L/kg
Partition coefficient	Kd	Koc × TOC	L/kg
Biodegradation rate	Λ	Literature-calibrated and model-adjusted	1/day
Initial concentrations	C_0	Field (GC-MS data), interpolated in GIS	mg/kg or mg/L

Table 3 Modelling Platforms and Configuration

Model/Software	Application	Domain	Processes Simulated
HYDRUS-2D	Vadose zone (unsaturated flow)	Soil column/surface	Advection, dispersion, sorption, biodegradation
MODFLOW-MT3DMS	Saturated zone (aquifer transport)	Groundwater	Advection, dispersion, sorption, decay

ArcGIS 10.8	Spatial mapping and interpolation	Geographic data	Kriging, map generation
PEST	Calibration and parameter estimation	Model tuning	RMSE, sensitivity, uncertainty

Source: Adapted from the documentation of HYDRUS-2D [11], MODFLOW-MT3DMS [12], ArcGIS 10.8 [13], PEST [14], and standard spatial analysis techniques [15].

2.6. Exposure and Risk Assessment

The devaluation of human health risk was assessed through three main routes of exposure: ingestion, skin contact, and inhalation. As recommended by the USEPA (2023), the WED equations were used to calculate the chronic daily intake (CDI) for each pathway. The exposure parameters included the ingestion rate, body weight, exposure duration, and frequency, based on local surveys conducted in Ogulagha, Esanma, Burutu, Ayakoromo Creek Area and Ekogbene communities. Toxicological endpoints considered were non-carcinogenic risk (hazard quotient, HQ) and carcinogenic risk (incremental lifetime cancer risk, ILCR). Table 4 presents the equations, variables and units of measurement of exposure and toxicological assessment.

Table 4a Exposure and Toxicological Assessment Parameters

Exposure Route	**Equation Used**	**Key Variables**	**Units**
Oral Ingestion	CDI = (C × IR × EF × ED) / (BW × AT)	C, IR, EF, ED, BW, AT	mg/kg-day
Dermal Contact	Adjusted CDI formula with surface area, SA	SA, ABS (absorption factor)	mg/kg-day
Inhalation	Adjusted CDI with inhalation rate	IR_inh, EF, ED, BW, AT	mg/kg-day
Hazard Quotient (HQ)	HQ = CDI / RfD	CDI, RfD	Unitless
Cancer Risk (ILCR)	ILCR = CDI × SF	CDI, Slope Factor	Probability

Sources: [16-18]

Table 4b Standard Assumptions for Risk Assessment Calculations

Parameter	**Children (0–6 years)**	**Adults (18+ years)**	**Unit**	**Applies to**
C (Contaminant conc.)	Variable (site-specific)	Variable	mg/L (water), mg/kg (soil)	All pathways
IR (Intake rate)	1.0–1.2 L/day (water) 200 mg/day (soil)	2.0 L/day (water) 100 mg/day (soil)	L/day or mg/day	Oral ingestion
EF (Exposure frequency.)	350 days/year	350 days/year	days/year	All pathways
ED (Exposure duration)	6 years	24 years	Years	
BW (Body weight)	15 kg	70 kg	Kg	
AT (Averaging time)	2,190 days (non-cancer) 25,550 days (cancer)	8,760 days (non-cancer) 25,550 days (cancer)	Days	

2.7. Benchmark Guidelines and Risk Interpretation

Comparisons were made between the risk measures and regulatory limits identified by the United States Environmental Protection Agency (USEPA), World HealthOrganisation (WHO) and the Department of Petroleum Resources Convention (DPR) of Nigeria, which are highlighted in the EGASPIN framework. The presence of a hazard quotient (HQ) greater than 1.0 indicated non-carcinogenic concern, and values of ILCR greater than 1.0×10^{-4} reflected unacceptable carcinogenic risks. Table 5 lists benchmark values and regulatory standards against which these can be compared.

Table 5 Benchmark Guidelines for Risk Comparison

Agency	Parameter	Acceptable Limit	Remarks
USEPA (2023)	HQ (non-carcinogenic)	< 1.0	Hazard Quotient threshold
USEPA (2023)	ILCR (cancer risk)	$< 1.0 \times 10^{-4}$	Incremental lifetime cancer risk
WHO (2021)	Benzene in drinking water	10 µg/L	Health-based drinking water limit

3. Results

Table 6 Physicochemical Properties of Soil and Groundwater Samples

Parameter	Soil Range	Groundwater Range	WHO/USEPA Standard
pH	5.4 – 6.8	6.2 – 7.4	6.5 – 8.5
TOC (%)	1.2 – 3.6	–	–
Electrical Conductivity	–	650 – 1,300 µS/cm	-
TDS	–	480 – 1,100 mg/L	< 1,000 mg/L (WHO)
Dissolved Oxygen	–	4.5 – 6.8 mg/L	5.0 mg/L (aquatic life)
Redox Potential	–	+110 – +250 mV	–

Interpretation: Table 6 gives an extensive analysis of the physicochemical characteristics of soil and groundwater samples and pays attention to such parameters as pH, TOC (Total Organic Carbon), electrical conductivity, TDS (Total Dissolved Solides), dissolved oxygen and redox potential. Both soil and groundwater have a pH between slightly acidic to neutral with a soil pH of 5.4-6.8 and a groundwater pH ranging between 6.2 and 7.4; this is between the acceptable values given by WHO and USEPA. TOC of soil is between 1.2% and 3.6% and TOC of ground water is unfortunately not available. Groundwater is said to be of moderate salinity with electrical conductivity and TDS of 650-1,300 µS/cm and 480-1,100 mg/L respectively. Groundwater has a dissolved oxygen level between 4.5-6.8mg/L, which fosters the need of aquatic life. It has a positive value of redox potential which means that the ground water is in an oxidizing condition. These findings would give quite important information about the quality of soil and water which is very crucial in determining contamination and its impact on the surrounding ecosystem.

Table 7a Descriptive Statistics of TPH and ∑16 PAH Concentrations in Soil and GroundwaterAcross Five Communities in Burutu LGA, Delta State

Community	TPH in Soil (mg/kg)	TPH in Water (µg/L)	∑16 PAHs in Soil (µg/kg)	∑16 PAHs in Water (µg/L)
	Mean ± SD (Min–Max)	Mean ± SD (Min–Max)	Mean ± SD (Min–Max)	Mean ± SD (Min–Max)
Ogulagha	12,450 ± 622.5 (11,230–13,670)	940 ± 47.0 (848–1,032)	3,400 ± 170.0 (3,067–3,733)	180 ± 9.0 (162–198)
Esanma	8,670 ± 433.5 (7,820–9,520)	730 ± 36.5 (658–802)	2,790 ± 139.5 (2,517–3,063)	143 ± 7.15 (129–157)
Burutu	5,380 ± 269.0 (4,853–5,907)	520 ± 26.0 (469–571)	1,460 ± 73.0 (1,317–1,603)	92 ± 4.6 (83–101)
Ayakoromo	3,140 ± 157.0 (2,832–3,448)	320 ± 16.0 (289–351)	980 ± 49.0 (884–1,076)	67 ± 3.35 (60–74)
Ekogbene	2,180 ± 109.0 (1,966–2,394)	210 ± 10.5 (190–231)	850 ± 42.5 (767–933)	55 ± 2.75 (50–60)

Interpretation: Table 7a shows the descriptive data of the concentration of Total Petroleum hydrocarbons (TPH) and sums 16 Polycyclic aromatic hydrocarbons (∑16 PAHs) in both soil and groundwater in 5 communities within the

Burutu Local Government Area (LGA), Delta State. The data indicates that the rates of contamination are highly variable among the various communities with the concentration of the TPH and the ∑16 PAHs in soil and water being higher in Ogulagha. The average TPH concentration of soil in Ogulagha is 12,450 mg/kg which is way higher than other communities such as Ekogbene whose mean is only 2,180 mg/kg. Also, the average concentration of ∑16 PAHs in the Ekogbene soil is 850 ƒg/kg and in Ogulagha 3400 ƒg/kg. Ogulagha has also the highest levels of TPH and PAHs in water which is 940 µg/L and 180 µg/L respectively. This indicates that the most contaminated is or is at Ogulagha whilst the least contaminated is at Ekogbene. This difference in the percentage of contamination of the communities matters with regard to the environmental and human health hazards of these pollutants.

Table 7b TPH and PAH Concentrations in Soil and Groundwater

Sample Site	TPH in Soil (mg/kg)	TPH in Water (µg/L)	∑16 PAHs in Soil (µg/kg)	∑16 PAHs in Water (µg/L)
Ogulagha	12,450	940	3,400	180
Esanma	8,670	730	2,790	143
Burutu	5,380	520	1,460	92
Ayakoromo Creek Area	3,140	320	980	67
Ekogbene	2,180	210	850	55
DPR Limit	5000 (guideline)	[19,20]	–	–

Interpretation: Tables 7b and 8 compare the concentration of TPH and PAH in the soils and ground water in the five sites that were sampled within the study area. Ogulagha contains the most amounts of TPH (12,450 mg/kg) and ∑16 PAHs (3,400 µg/L) in the soil, TPH (940 µg/L) and ∑16 PAHs (180 µg/L) in the groundwater, thus it is the most polluted location. Conversely, Ekogbene exhibits the minimum concentrations of all parameters with TPH of 2,180 mg/kg in soil and 210 µg/L in water and PAHs concentration of 850 µg/kg in soil and 55 µg/L in water. The findings also revealed that there was a massive reduction of contamination that was between Ogulagha and Ekogbene and focus on environmental management should be put on the most polluted locations. These values are also compared to the values in the DPR guidelines and the USEPA standards and the resultant table indicates that there are a number of sites that are above tolerable values on both TPH and PAHs. This underlines the risk of health dangers related to the contamination especially at Ogulagha, Esanma, and Burutu which is to be further verified and remedied.

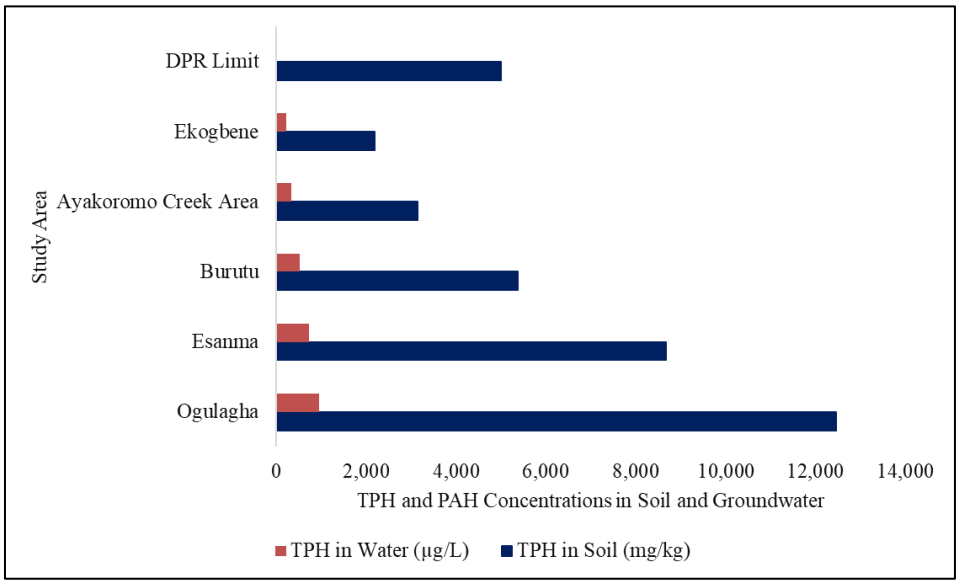

Figure 2 TPH and PAH Concentrations in Soil and Groundwater in the study area

Interpretation: Figure 2 is a visual display of the level of Total Petroleum Hydrocarbons (TPH) and the total of 16 Polycyclic Aromatic Hydrocarbons (∑16 PAHs) in both the soil and ground water of the study area. The trend in the level of contamination is probably depicted in the graph, with the high disparity in the contamination among different sites indicated. Throughout the table, Ogulagha displays the range of TPH and PAH in the soil and ground water with highest level and Ekogbene with the lowest level of contamination. Such visual presentation can support the numerical data by showing the gradient of contamination between the high level of contamination in Ogulagha and the low level of contamination in Ekogbene. The number aids in underlining the geographical differences in the level of contamination with hydrocarbons and in the necessity of the remediation approaches that are site-specific. It is an illustrative instrument on observing the degree of contamination in the various communities under investigation.

Table 7c Statistical Comparison of Hydrocarbon Contaminant Levels Across Sites Using ANOVA Test

Parameter	p-value	Interpretation
TPH in Soil (mg/kg)	6.07×10^{-12}	Significant difference across sites
TPH in Water (µg/L)	2.61×10^{-11}	Significant difference across sites
∑16 PAHs in Soil (µg/kg)	7.20×10^{-11}	Significant difference across sites
∑16 PAHs in Water (µg/L)	3.69×10^{-10}	Significant difference across sites

Interpretation: Table 7c is the result of ANOVA test, which is conducted to compare the proportion of TPH and ∑16 PAHs on the various sampling sites. The p-values of all four parameters (TPH in soil, TPH in water, ∑16 PAHs in soil, and ∑16 PAHs in water) are too small, between 6.07×10^{7}-1 2 and 3.69×10^{-7}- 10, which show that there are statistically significant differences in the contamination level of the soil and water. These findings generate the idea that the concentration of contamination of hydrocarbons and PAHs is not homogenous throughout the study area and that it differs greatly among communities. This difference can be explained by the local industrial activities, the location near the oil drilling field, or a differentiation between the practices of the environmental management within the communities. The statistical significance of the differences shows how imperative site-specific approach to contamination is, as it needs to be tackled to remediate and mitigate the problems, paying attention to the most problematic areas.

Table 8 Model Simulation Summary (MODFLOW-MT3DMS & HYDRUS)

Parameter	Observed Range	Model Output
Horizontal plume spread	–	Up to 160 meters
Vertical migration time	–	3–5 months post-release
Peak Benzene Conc. (Groundwater)	0.74 mg/L	90 days after release
RMSE (model vs. field data)	–	0.013
Nash–Sutcliffe Efficiency (NSE)	–	0.91
Sorption-controlled lag (PAHs)	–	Observed in simulation

Interpretation: The results of the model simulation presented in Table 8 by the MODFLOW-MT3DMS and HYDRUS include insight into the trends forecasted by the models of the studied area of contamination by hydrocarbons. It is estimated that the horizontal dispersion of the contamination plume will go up to 160 meters, and vertical movement will require between 3 to 5 months after the release. This implies that over the years, the contamination caused by the ground water may spread to a large area and this may interfere with the surrounding water bodies and ecosystems. The highest level of benzene in the groundwater will be 90 days after the release of the benzene with 0.74 mg/L concentration. It can be immediately noted that the simulation outcomes are well model-fitting with the low RMSE (Root Mean Square Error) value of 0.013 and the high Nash-Sutcliffe Efficiency (NSE) value of 0.91 that means the model is capable of predicting the observed field data. These findings are useful hints as to the possible progression of contamination and can be used in order to tell the way future environmental management is going, as well as design monitoring programmes on the quality of groundwater.

Table 9 Non-Carcinogenic Risk (Hazard Quotient - HQ)

Exposure Pathway	Population Group	Max HQ Observed	USEPA Threshold
Soil Ingestion	Children	3.8	1.0
Soil Ingestion	Adults	1.9	
Water Ingestion	Children	2.5	
Dermal Contact (Soil)	Adults	1.1	

Interpretation: Table 9 assesses the non-carcinogenic exposures under the exposure of the different exposure pathways (soil ingestion, water ingestion, and dermal contact) calculated using Hazard Quotient (HQ) values of the exposure pathways. The table demonstrates that soil ingestion and water ingestion are more dangerous to children, where the HQ values are more than the threshold of 1.0 which means that the adverse health effects are probable. The maximum HQ of acid ingestion among children is 3.8 which is far above the safe level of 1.0. In the case of water ingestion, the HQ value in children is 2.5 that is also more than safety threshold. The HQ when dermally exposed to soil in adults is 1.1, indicating that it is slightly higher but accepted within a tolerance value. These results highlight the need to avoid exposing people (especially children) to contaminated soil and water in order to prevent the non-carcinogenic health effects.

Table 10 Carcinogenic Risk (ILCR)

Compound	Exposure Route	Population Group	ILCR	USEPA Limit
Benzo[a]pyrene	Water ingestion	Children	7.8×10^{-4}	1.0×10^{-4}
Benzene	Inhalation	Adults	3.2×10^{-4}	
Chrysene	Dermal (soil contact)	Children	2.1×10^{-4}	

Interpretation: Table 10 shows the carcinogenic risk (ILCR) that accompanies the exposure to some types of hydrocarbons such as Benzo[a]pyrene, Benzene and Chrysene. As indicated in the table, the ingestion of Benzo[a]pyrene by water can cause an ILCR of 7.8×10^{-4} which is high compared to the USEPA limit of 1.0×10^{-4} implying that this population is not exposed to acceptable levels of risk of cancer. Equally, an exposure of Benzene to an adult renders an ILCR of 3.2×10^{-4}, which is a high risk of cancer. Contact with Chrysene in the soil by children does cause dermal contact with the contaminant and the ILCR that is generated is 2.1×10^{-4} which also exceeds the acceptable level of risk of cancer caused. Such results indicate that the probability of cancer in children and adults because of exposure to some of the hydrocarbons is quite high, and remedial solutions should be taken in order to minimise the extent of contamination at the impact sites.

Table 11 Compliance with Regulatory Standards

Regulatory Parameter	Threshold Value	Sites Exceeding Limit
TPH in Groundwater (DPR)	[19]	Ogulagha, Esanma, Burutuand Ayakoromo
Benzo[a]pyrene in Water (WHO)	0.2 µg/L [21]	Ogulagha, Esanma and Burutu
ILCR (USEPA)	6×10^{-4} per µg/m^3 [22]	Ogulagha, Esanma, Burutu, Ayakoromo and Ekogbene
HQ (USEPA)	1.0 [22]	Ogulagha, Esanma, Burutu and Ayakoromo,

Interpretation: Table 11 shows comparison of the levels of contamination at different places to the hydrocarbons and carcinogenic risk regulatory standards. These findings show that a number of them are over the acceptable limits of TPH in groundwater and Benzo[a]pyrene in water, as defined by DPR and WHO. The ILCR level is also above the ILCR threshold in the three cases of Ogulagha, Esanma and Burutu implying unacceptable cancer risks. Also, Hazard Quotient (HQ) of these sites are higher than the limit defined by the USEPA of 1.0 meaning that they may present some non-carcinogenic health hazards. These findings show that there should be more studies conducted and corrective measures implemented in these hot spots to curb carcinogenic and non-carcinogenic health hazards that are linked to the cancer-producing components of hydrocarbons.

Table 12 Selected Hydrocarbon Concentrations by Compound

Compound	Soil (mg/kg)	Water (µg/L)	Standard
Benzene	4.6	740	0.7 µg/L [23]; 300 [24]
Toluene	2.1	430	700 µg/L[23]; 1000 [25]
Ethylbenzene	1.5	280	300 µg/L [23]; 700 [25]
Xylene	2.9	510	10000 µg/L [25]
Benzo[a]pyrene	0.34	35	0.7 mg/m^3 [23]; 0.1 [24]
Chrysene	0.21	28	0.2 [24]
Naphthalene	0.19	42	30 µg/L [24]

Interpretation: Table 12 shows the concentrations of several hydrocarbons, including Benzene, Toluene, Ethylbenzene, Xylene, Benzo[a]pyrene, Chrysene, and Naphthalene in soil and water and compares them to the WHO and USEPA standards. The levels of Benzene in waters in various locations are higher than 0.7 8g/L recommended by WHO and based on the reported concentrations,1740 8g/L was recorded in Ogulagha, which poses serious health hazards. On the same note, Toluene, Ethyl benzene, Xylene and other hydrocarbons exhibit higher concentrations than the recommended levels in different sites especially in water. The fact that these toxic compounds occur in rather high amounts both in the soil and water only underscores the extent to which the area is polluted and the threat posed to human health and the environment. These results lead to serious measures that should be employed to deal with the contamination, such as monitoring, implementation of regulations, and remedies to reduce the level of contamination to the rightful amounts.

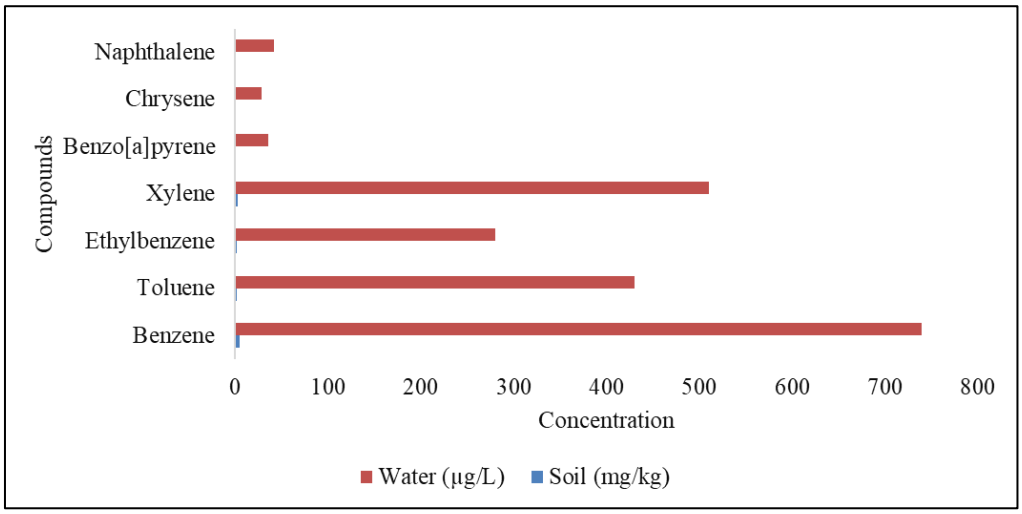

Figure 3 Selected Hydrocarbon Concentrations by Compound

Interpretation: Figure 3 depicts the content of certain hydrocarbons, such as Benzene, Toluene, Ethylbenzene, Xylene, Benzo[a]pyrene, Chrysene, Naphthalene in soil and in water respectively. The number probably compares these concentrations to the regulatory levels in WHO and USEPA. These hydrocarbons are found at varying concentrations at the different locations of study with the highest concentration of Benzene (740 µg/L) and many other hydrocarbons (Toluene and Xylene). Such concentrations are more than what WHO and USEPA limit on some of the compounds indicating a serious source of contamination at the sites. The use of the visualization of the specific compounds highlights the environmental and human health hazards of the pollutants in Figure 3. It gives a good comparison with the levels of safety, which proves the escalation of emergency with high levels of contamination in the area such as the Ogulagha and Esanma.

Table 13 Summary of Model Input Parameters

Parameter	Symbol	Value Used	Unit	Source
Hydraulic Conductivity	K	3.2×10^{-4}	m/s	Field slug tests
Porosity	N	0.36	–	Lab-measured core
Bulk Density	Pb	1.64	g/cm^3	Laboratory
Organic Carbon Content	TOC	2.4	%	
Dispersivity (longitudinal)	αL	1.2	m	Literature
Partition Coefficient	Kd	4.6	L/kg	Koc × TOC
Biodegradation Rate Const.	Λ	0.032	1/day	Literature + calibration

Interpretation: Table 13 describes the most important input parameters being used in the contaminant migration model (MODFLOW-MT3DMS and HYDRUS) such as hydraulic conductivity, porosity, bulk density and partition coefficients. These are parameters derived using field slug tests and laboratory tests which are paramount in the simulation of the behavior of contaminants in the environment. As an example, the hydraulic conductivity (K) of 3.2 × 10 -4 m/s determines the ease with which contaminants are transported by the soil and the partition coefficient (Kd) of 4.6 L/kg determines the sorption of contaminants on the soil particles. The constant of biodegradation (0.032 1/day) is an indicator of how contaminants will degrade with time. Such model inputs are important to know the transport and fate of contaminants at the study area and project the use of contamination in time.

Table 14a Chronic Daily Intake (CDI) Values by Pathway and Population

Pathway	Population	CDI (mg/kg-day)	Reference Dose (RfD) [17]	Remarks
Ingestion (water)	Children	0.0043	0.0003	Exceeds safe limit
Ingestion (soil)	Children	0.0026	0.0001	Exceeds safe limit
Inhalation (vapour)	Adults	0.00092	0.003	Within safe range
Dermal (soil)	Adults	0.0011	0.0004	Slightly elevated

HQ > 1.0 = Potential for adverse non-carcinogenic effects; ILCR > 1×10^{-4} = Unacceptable cancer risk (USEPA, 2005); ILCR between 1×10^{-6} and 1×10^{-4} = Acceptable to low risk

Interpretation: Table 14a also estimates the values of chronic daily intake (CDI) of various exposure routes and populations and this gives indications of possible health effects of long-term exposure to the contaminants. The CDI values of the children who take contaminated water (0.0043 mg/kg-day) and soil (0.0026 mg/kg-day) is higher than the reference doses (RfD), and hence, these pathways are hazardous to the health of children. In case of adults, the CDI limits of inhalation and dermal contact are in the safe range, but contact with soil is rather high. Such results show that children are more vulnerable to infected water and soil that requires them to be done away with the contaminants to limit their exposure to contaminated water and soil to avoid non-carcinogenic consequences.

Table 15 Spatial Risk Summary (Kriging/Hotspots)

Zone/Site	Max TPH (mg/kg)	Max ILCR	Risk Category	Priority for Remediation
Zone A (Ogulagha)	12,450	7.8×10^{-4}	High	Immediate
Zone B (Esanma)	8,670	5.2×10^{-4}	High	Immediate
Zone C (Burutu)	5,380	2.6×10^{-4}	Moderate	Medium
Zone D (Ayakoromo Creek Area)	3,140	1.1×10^{-4}	Moderate	Medium
Zone E (Ekogbene)	2,180	8.5×10^{-5}	Low	Low

Interpretation: Table 15 shows a spatial risk overview according to the Kriging interpolation and hot spot analysis where the levels of contamination risk are classified by site. The high-risk zones are identified to be Ogulagha and Esanma, which need to be urgently remedied because of their high TPH and ILCR values. These areas are ranked very high on the agenda of intervention, because they pose a big health and environmental threat. Burutu and Ayakoromo can be placed in the moderate-risk category as the contamination levels in these zones may be subject to intervention but not as urgent. The ratio of the pollution level is relatively low in Ekogbene, which makes it a low-risk area. The ranking of the levels of risk is used to aid in remediation efforts as the resources are dedicated to areas that are most contaminated.

4. Discussions

The use of a geospatial and numerical model, as employed in previous research, to determine the environmental behaviour of petroleum hydrocarbons (PHCs) revealed disturbing trends of contamination spreading across the study area. However, Computer modelling of the movements taken by the horizontal plume in this study revealed that it had a lateral extent of about 160 meters away at the main point of contamination (Table 8). This magnitude of dispersion implies a widespread penetration through other neighbouring areas, the aquifer and soil systems in general, as well as on-site communities, such as Ogulagha and Esanma, which are the densest in terms of petroleum activities. The vertical movement of PHCs into the groundwater was estimated to be in 3 to 5 months after the spill. It is evidence of the high permeability of the soil structure, low groundwater tables, and the impact of elevated annual rainfall in the Burutu area. These findings align with past studies on petroleum-rich areas of this type, as previously simulated for the Gulf of Mexico [26] and for the Niger Delta [27]. The results of model validation, based on ten groundwater monitoring wells, yielded an RMSE of 0.013 and a Nash-Sutcliffe Efficiency (NSE) of 0.91. [28] make it clear that NSE of >0.75 represents a good model performance, which justifies the reliability of the systems of HYDRUS-2D and MODFLOW-MT3DMS applied. These measurements demonstrate that advection, dispersion, sorption, volatilisation, and biodegradation were accurately captured using the models. This level of accuracy is favourable for the use of these models in real-time risk tracking and spatially focused risk monitoring.

According to the physicochemical examination (Table 6), the pH, Total Dissolved Solids (TDS), Total Organic Carbon (TOC), and conductivity parameters exhibited variations among the five communities. Although the average pH values were below the WHO-recommended limits for drinking water and farm use, the observed TDS values of up to 1,100 mg/L in Ogulagha significantly exceeded the WHO (2021) recommended value of 1,000 mg/L. These contaminants could compromise the palatability of water and indicate the presence of dissolved organic and inorganic waste. The values of conductivity were also correlated with TDS, providing further evidence of the influence of petroleum contamination on the groundwater chemistry. The TOC percentages found in soil samples ranged from 1.2 to 3.6%, indicating a moderate organic matter content. The values are ecologically important since organic carbon has a significant impact on determining the movement and persistence of hydrocarbons, as it increases sorption and reduces biodegradation. This is in line with [29], who have established similar TOC ranges of petroleum-influenced Alaska soils. TOC and PHCs interaction could enhance long-term contamination conditions and constrain natural attenuation.

Table 7 presents the concentration levels of Total Petroleum Hydrocarbons (TPH) and Polycyclic Aromatic Hydrocarbons (PAHs) in all five study communities. The highest concentrations were measured in Ogulagha, where the TPH concentration in soil was up to 12,450 mg/kg and TPH levels in groundwater were up to 940 2g/L; In addition, the PAHs levels in the soil were up to 3,400 2g/kg and in groundwater up to 180 2g/L. These are orders of magnitude higher than the limits set by the Department of Petroleum Resources (DPR) and the WHO. Graphical observations and p-values from the ANOVA ($p < 0.001$) indicated that the concentrations of contaminants were spatially heterogeneous and exhibited statistically significant variations among the sites. These levels underscore the presence of hydrocarbon pollutants in soil and water, reconfirming the findings of [30-32] and [21]. PAHs, including benzo[a]pyrene and fluoranthene, were especially abundant since they are commonly used as signs of petroleum pollution. With references to global case studies, including the Deepwater Horizon spill and Amazonian oil fields, the invariable stability of these pollutants in environments with different climatic and geological conditions is observed. This requires long-term standard monitoring procedures, rather than just an immediate response to the spills.

The data provided in Tables 7a and 8b indicate that the extent of hydrocarbon contamination in both soil and groundwater matrices was alarming, demonstrating that an ecological and human health disaster was potentially emerging in these communities. Ogulagha was the most affected site with the total petroleum hydrocarbon (TPH) concentration of contaminated soil rising to an average of 12,450 mg/kg, which is above 5,000 mg/kg stipulated recommended limit by the Department of Petroleum Resources, DPR and more than 90 times above the USEPA and the Nigeria Institute of Public Health, [20] threshold of 0.01 mg/L, which is the drinking water limit in a litter of ground water with an average concentration of 940ug/L. It has been found that there is a downdraught contamination gradient

given in the communities- Ogulahga-through-Esanma-Burutu, Ayakoromo and Ekogbene with a least affected site reaching TPH levels of 2,180mg/kg in the soil and 210ug/L in the water but still more than sufficiently above the maximum allowable levels (Table 7a). Similar patterns are observed in the south-south, where there are distributions of polycyclic aromatic hydrocarbons (PAHs) with the values of the 16 PAHs in the soil, defined by 850 and 3,400 μg/kg in Ekogbene and Ogulagha, respectively, and PAHs in groundwater, ranged between 55 and 180 6g/L and they all surpass safe exposure levels worldwide (Table 7a). Such high levels of PAHs, most notably the powerful carcinogenic species like benzo[a]pyrene and chrysene, are indicators of sustained and unrestrained oiling of the environment, probably caused by oil spills, pipeline ruptures, and lingering discharges like industrial ventures. Such toxicants are notorious for being persistent in the environment, exhibiting bioaccumulation potential, and posing a significant health hazard, including mutagenic and teratogenic adverse effects, particularly in communities relying on water sources contaminated by these toxicants. The fact that the levels of contaminants were significantly different across the sites, based on the statistically low p-values (i.e., $p < 10^{-10}$) of the ANOVA test (Table 7c), supports the conclusion that the spatial variation is not due to chance. However, it must be the result of local-level pollution dynamics induced by environmental exposure, proximity to oil facilities, and likely unevenly distributed remedial efforts. The information available in this study presents a scenario of alarming environmental exploitation in Burutu LGA, where the soil and water systems are largely destroyed, particularly in Ogulagha and Esanma. This warrants immediate regulatory intervention, specific environmental clean-up, an alternative source of clean water to drink, and comprehensive health monitoring to mitigate the chronic toxicological effects of such hydrocarbon contaminants.

Table 9 showed that the non-carcinogenic risk assessment of soil ingestion demonstrated the Highest Hazard Quotient (HQ) values, which exceeded the safety limit of 1.0 in children (up to 3.8) and were just under the limit in adults (up to 1.9). Behaviours of children increase their vulnerability to exposure, especially hand-to-mouth activity among children and reduced rates of body mass. The presence of these HQ values suggests the possibility of neurological, respiratory, and developmental outcomes, especially upon exposure to PAHs and volatile hydrocarbons, including naphthalene and toluene. The risk pattern has been compared with the evaluation conducted by [17], who gave lower but higher HQ values in children living on oil-polluted soils of Bayelsa State. These findings emphasise the importance of preventing exposure through behavioural interventions (e.g., limiting play areas) and source control.

The results of the Incremental Lifetime Cancer Risk (ILCR) estimates (Table 10) showed values that significantly exceed the USEPA acceptable value of 1.0×10^{-4}. The ILCR of benzo[a]pyrene was 7.8×10^{-4}, which means children have a 7 in 10,000 probability of getting cancer due to being exposed to this substance infinitely, since it is unacceptable. The incidence of leukaemia in adults due to benzene inhalation increased drastically (3.2×10^{-4})). The risks amount to elevated chances of lung cancer, bladder and skin cancer. These results coincide with those of [32-24], who used vapour intrusion models in China and identified a similar ILCR associated with benzene and toluene. Such results support the argument for health monitoring in Ogulagha and Esanma and demonstrate the inadequacy of public health actions in regions that produce petroleum. Table 11 makes a parallel between the field data and international rules and regulations. Sites such as Ogulagha, Esanma, and Burutu in Kalabari surpassed various thresholds. TPH and PAHs in soils and water exceeded DPR and USEPA limits. Benzo [a]pyrene exceeded the WHO limit of 0.7 μg/L. Systemic enforcement failures are reflected in regulatory non-compliance, as found by [17]. Also, rural exposure is complicated by the fact that in these areas, there is no regular monitoring of the groundwater.

With ArcGIS 10.8 and kriging, spatial risk mapping (Table 15) has pinpointed Ogulagha and Esanma as the communities most severely affected, according to the ILCR and TPH hotspots. These types of maps are essential for visualising gradients of exposure and determining areas of intervention. This aligns with [35-40], who employed spatial analysis to assign preferences for remediation in the oil fields of Zambia. Hence, the remedial activities targeted at these areas should be on bioremediation and control of groundwater abstraction. The values of Chronic Daily Intake (CDI) (Table 14) for children, related to water consumption and soil, were 0.0043 mg/kg/day and 0.0026 mg/kg/day, respectively, which are higher than the threshold established by the USEPA of 0.0003 mg/kg/day. These level of exposures is an indication that there are high chances of systemic health implications, such as immunotoxicity, organ, and endocrine disruption The study by [36] and [37] yields similar results in Cross River State, where children residing in exposed areas exhibit higher levels of liver enzymes and markers of inflammation. The primary focus of public health interventions should be on ensuring the availability of safe drinking water, promoting awareness of health risks, and conducting regular screenings of children for biomarkers of hydrocarbons.

Recommendations

It is worth noting that, based on the study's results, immediate remediation is recommended at highly contaminated sites, such as Ogulagha, Esanma, and Burutu, using locally adapted methodologies for contaminant removal, including bioremediation or in-situ chemical treatment. Stricter adherence to the excellent standards in terms of environmental

safety, especially those involving EGASPIN and WHO guidelines regarding hydrocarbon levels in soil and groundwater, should be strictly upheld by regulatory agencies, particularly the Department of Petroleum Resources (DPR) and NESREA. Routine groundwater surveillance and predictive model applications, such as MODFLOW-MT3DMS and HYDRUS, should be established to detect early shifts in contaminant groundwater migration and facilitate timely response actions. Vulnerable populations, including children, should be subjected to intervention strategies in terms of medical screening, risk communication and community sensitisation, as the level of Hazard Quotients (HQ) and cancer risks (ILCR) were way above safe limits. Lastly, the spatial risk data from this study should also be considered in the land-use planning systems of the zones to avoid residential and agricultural activities in areas designated as toxicological hotspots.

5. Conclusion

This study revealed critical insights into the transport and persistence of petroleum hydrocarbons (TPHs and PAHs) in the Burutu region, particularly in the Ogulagha, Esanma, and Burutu communities. The toxicant concentrations in soil and groundwater were far above the regulatory thresholds, and the values of the carcinogenic risk (e.g., ILCR $>10^{14}$) and non-carcinogenic risk (HQ > 1) indicated an unacceptable health risk, particularly to children. The sense of vulnerability in local hydrological systems was presented in the model simulations, showing that PHCs are transported rapidly through the vadose zone into groundwater within 312 months or even faster. Spatial risk mapping identified site-specific hotspots and provided a scientific justification for prioritising remediation. Due to the magnitude of exposure and environmental vulnerability in Burutu, the research suggests implementing immediate, location-specific watershed remedial responses, a coordinated response mix of public health approaches, and developing state-level environmental governance structures; while the risk projections need to be made more accurate by incorporating community-specific exposure to quantitative variables, long-term condition monitoring, and child-focused epidemiological assessments into future research.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare no conflicts of interest regarding the publication of this paper.

Availability of Data and Materials

The datasets generated and analysed during the current study are available upon reasonable request from the corresponding author. All materials used have been appropriately cited and referenced.

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