MEJAST

Middle East Journal of Applied Science & Technology (MEJAST)

Volume 8, Issue 4, Pages 86-105, October-December 2025

Environmental Toxicology of Petroleum Sludge at Warri Refinery Environment: Quantitative Risk Assessment and Predictive Modeling Using Artificial Intelligence

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DOI: https://doi.org/10.46431/mejast.2025.8407

Article Received: 07 October 2025 *Article Accepted: 19 December 2025* *Article Published: 23 December 2025*

ABSTRACT

Petroleum sludge is one of the most persistent byproducts of crude oil refining, posing a significant environmental problem due to its complex composition of hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and heavy metals. This paper examined the ecological toxicology of petroleum sludge at the Warri Refining and Petrochemical Company (WRPC), Delta State, Nigeria, through empirical, computational, and biological analyses, coupled with the Systems Theory of Environmental Toxicology. The primary objective was to describe the sludge composition, assess the human and ecological risks, and develop artificial intelligence (AI)-driven predictive models to enhance environmental management. Unlike previous refinery toxicology studies that focus solely on chemical characterization or risk estimation, this study uniquely integrates field data, quantitative risk assessment, and multi-model AI prediction to address the lack of predictive environmental intelligence in refinery-impacted ecosystems. Sludge pits, storage tanks, and effluent ponds yielded a total of 30 samples of sludge, which were collected and analysed by GC-MS and ICP-MS to determine PAHs and heavy metals, respectively. Quantitative risk assessment was conducted in accordance with the guidelines of the USEPA, focusing on the aspects of the hazard index, carcinogenic risk, and ecological risk (PERI). In contrast, AI models such as the Random Forest (RF), Support Vector Machine (SVM), and Artificial Neural Network (ANN) were employed in the study of predictive risk mapping. The analysis showed very high contaminant concentrations (TPH: 215,400mg kg^{-1}; Cr: 78mg kg^{-1}; Pb: 42mg kg^{-1}; Benzo[a]pyrene: 42.8mg kg^{-1}), as well as a considerable level of health hazards (HI: 3.2 -4.5; CR: 1.7×10^{-3} -2.7×10^{-3}). The ANN model proved to be more accurate in its predictive capacity (R^2 = 0.96), with TPH, Cr, Pb, and benzo[a]pyrene emerging as the primary risk drivers. The paper finds that the Warri Refinery ecosystem is a highly hazardous area that requires timely remediation. It suggests monitoring with AI, as well as sludge stabilisation and bioaugmentation with indigenous hydrocarbon-degrading microorganisms, to alleviate toxicity and support Sustainable Development Goals 3, 9, 11, and 13.

Keywords: Petroleum Sludge Toxicology; Artificial Intelligence Modelling; Quantitative Risk Assessment (QRA); Heavy Metal–Hydrocarbon Synergy; Environmental Systems Theory; Predictive Ecotoxicology; Human Health Risk Mapping; Microbial Bioremediation Potential; GIS-Based Contamination Analysis; Sustainable Refinery Management.

1. Introduction

Petroleum sludge is a heterogeneous and complex by-product produced during the refining of crude oil, storage, and petrochemical processing. It usually contains leftover hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and heavy metals, among other chemical additives, which do not biodegrade in the environment due to their low biodegradability. During the refinement process, particularly in developing countries, high-capacity storage tanks, as well as settling pits and effluent treatment plants, often accumulate vast amounts of sludge, creating long-term environmental contamination hotspots (Johnson & Affam, 2019; Acha et al., 2025; Roy *et al*., 2018). Warri Refining and Petrochemical Company (WRPC), situated in Delta State, Nigeria, is a significant industrial site where petroleum sludge continues to accumulate, negatively impacting the soil and water systems. Refinery samples have been reported to have total petroleum hydrocarbon (TPH) concentrations of more than 200,000 mg/kg^{-1} with prominent contents of PAHs, including benzo[a]pyrene, chrysene, and fluoranthene, which are known carcinogens as well as endocrine disrupters (Wang *et al*., 2019; Hu *et al*., 2017; Isangadighi et al., 2025).

The toxicological and environmental performance of petroleum sludge is primarily determined by its physicochemical makeup. Large hydrocarbons that comprise sludge have a high tendency to adsorb onto soil and sediment particles, thereby reducing natural biodegradation and enhancing their long-term persistence within the environment. Hydrocarbons are frequently found in conjunction with heavy metals, such as Ni, Pb, Cr, Zn, Cu, Fe, and V, forming complexes that are synergistically toxicogenic (Lee *et al*., 2017; Orhuebor et al., 2025). This type of matrix may bioaccumulate toxins in food webs of both land and water, exposing humans to multiple routes of exposure through ingestion, dermal contact, and inhalation, and causing stress to the micro- and macrofauna and flora of soil and sediment. Past research has shown that the hazard quotient (HQ) of metals in refinery sludge was often above one. Those associated with PAHs were the cumulative hazard index (HI) and carcinogenic risk (CR), which exceeded regulatory limits, indicating potential severe health effects on individuals in proximity to the refinery process (Huang *et al*., 2014; Isangadighi et al., 2024a; Johnson & Affam, 2019).

Although this toxicity has been identified, the conventional risk assessment methods are usually ineffective in the case of petroleum sludge. The indirect predetermined relationships between various hydrocarbons and metals, as well as the heterogeneous spatial distribution, complicate traditional models and may minorly (or inadequately) estimate the scenarios of exposure (Ogwu *et al*., 2025). New developments in artificial intelligence (AI) and machine learning (ML) are adequate substitutes for modelling intricate datasets of the environment. Random Forest (RF), Support Vector Machine (SVM), and Artificial Neural Networks (ANN) are some of the techniques that can combine physicochemical parameters, the concentrations of contaminants, and exposure factors to predict human and ecological risks with finer resolutions and adaptable predictive functions (Dragoi et al., 2021; Isangadighi et al., 2024b; Roy *et al*., 2018). The AI predictive modelling can facilitate the identification of important and damaging contaminants, clarify non-linear synergistic interactions, and even produce scenario-based risk projects that are of inestimable value in remediation planning and environmental management.

The Warri Refinery location provides a suitable environment for such an integrated study, given its history of sludge formation, the multiplicity of hydrocarbon residues, and its proximity to ecologically sensitive/populated regions. Ultimately, the combination of empirical characterisation of TPH, PAHs, and the heavy metals, the conventional method of quantitative risk assessment (HQ, HI, CR, PERI), and the AI-based prediction modelling, the proposed study aims at generating a comprehensive view of the toxicity of petroleum sludge, identifying the environmental hotspots, and making evidence-based recommendations on mitigation. The approach of combining AI with conventional risk evaluation paradigms represents a methodological breakthrough, providing greater predictive ability and practical considerations for making informed environmental choices regarding refinery situations. The four main objectives of this study are hence characterised as: (1) to describe the physicochemical and toxicological characteristics of petroleum sludge at Warri Refinery; (2) carry out quantitative human and ecological risk assessment; (3) to establish AI-based predictive models to assess risk characterization; and (4) one-on-one AI products and standard risk metrics in supporting proactive management, mitigation strategies, and policy formulations in petroleum sludge management in Nigeria. The results should be used to enhance the current research on refinery waste toxicology and to show the feasibility of AI in evaluating risks associated with environmental health.

1.1. Study Objectives

The following are the main objectives of this study:

a. To describe the physicochemical characteristics and composition (TPH, PAHs and humers), of petroleum sludge produced at the WRPC Refining and Petrochemical Company.

b. To assess the human health risk relating to exposure to petroleum sludge via ingestion, dermal exposure and inhalation utilising USEPA quantitative risk assessment models.

c. To determine the ecological hazards of contaminants of sludge on soil and aquatic ecosystems by the Potential Ecological Risk Index (PERI), and other ecotoxicology parameters.

d. To make artificial intelligence (AI)-based predictive models such as Random Forest (RF), Support Vector Machine (SVM), and Artificial Neural Network (ANN) that forecast the patterns of contamination and risks distribution.

e. To determine the degree of predictive accuracy of AI-based models as compared with traditional risk measurement indices and determine the most significant contaminants that induce environmental and health risks.

f. To recommend evidence-based solutions to environmental management, such as remediation options, AI-assisted monitoring, and policy measures for the sustainable handling of sludge at WRPC.

2. Materials and Methods

The case study was conducted at the Delta State industrial zone, the Warri Refining and Petrochemical Company (WRPC) in Nigeria, where large amounts of petroleum sludge are discharged into the environment through tank bottoms, sludge pits, and effluent treatment plants, and the location is near people and ecologically sensitive regions. A stratified random sampling technique was used to describe spatial variability adequately. The initial 3 divisions to be carried out at the refinery were the sludge pits, storage tanks and effluent ponds, wherein random sampling points were created in each of the zones by the use of the Create Random Points tool that is found in the ArcGIS and a random separation distance of 10 m to ensure spatial clustering was not created. Fifty grams of sludge (30 samples) in total were taken using pre-cleaned stainless steel spatulas. GPS coordinates were measured at each location using a Garmin GPSMAP 64, and environmental field parameters (soil type, temperature, and moisture) were recorded. In order to offer background reference conditions, three control samples were as sampled farther away at distances of 500 m, 1 km and 2 km of the dominant direction of wind and runoff to be sure that refinery operations did not influence them.

Each sludge sample was placed in a high-density polyethene (HDPE) sample container, washed with acetone, and rinsed with deionised water. They were moved to the laboratory, air-dried at 25 °C, sieved using a 2-mm mesh after visible debris had been removed, and then stored at 4 °C. A Memmert UFE 400 oven was used to determine moisture content and total solids, whereas a Metrohm 827 with pH standards 4, 7, and 10 was used to measure pH.

Hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) were characterised chemically by Soxhlet extraction of 10 g of the dried sludge with a Soxhlet apparatus containing 200 mL of dichloromethane: methanol (2:1 v/v) at 60 °C. The extracts were concentrated using a Buechi R-210 rotary evaporator and analysed on a Shimadzu GC-2010 Ultra atelier using a DB-5MS capillary column. The calibration was performed using certified PAH standards purchased from Sigma-Aldrich. A 3:1:1 mixture of HNO_3, HCl and H_2O_2 was used to digest 18 g of dried sludge using the CEM MARS 6 microwave digester. Multi-element standards, procedural blanks, and spike recoveries of 85 to 110% were used to assure the quality of analysis using Agilent 7900 ICP-MS of Fe, Zn, Cu, Cr, Ni, Pb, and V.

The human health risk assessment has been conducted in accordance with the developed USEPA methodologies and comprised of ingestion, dermal contact, and inhalation exposure pathways. The Hazard quotient (HQ) was calculated using estimated daily intake (EDI) values, and the cumulative hazard indices (HI) were obtained by summing all contributions from the contaminants. The risk of carcinogenicity (CR) was estimated using lifetime exposure assumptions for metals and PAHs, based on established cancer slope factors. The Potential Ecological Risk Index (PERI) was applied to assess ecological risks by combining contaminant concentrations and toxic-response coefficients. A Monte Carlo simulation with 10,000 repetitions was conducted to account for uncertainty in exposure assumptions by assigning probability distributions to the concentration and exposure parameters.

Random Forest (RF), Support Vector Machine (SVM), and Artificial Neural Network (ANN) algorithms were used to undertake machine-learning predictive modelling. All variables were normalised to a scale of 0-1 before modelling, and Multicollinearity was assessed using the Variance Inflation Factor (VIF), which ensured that all predictors were less than 5. Data was randomly split into 70% of the training dataset and 30% of the testing dataset. Cross-validation was performed using 10-fold validation, and hyperparameters were tuned for RF and SVM using grid search. The ANN model was tuned using Bayesian optimisation. The ANN structure was as follows:

Evaluation of 18 predictor variables yielded an input layer, hidden layers with neuron counts of 16 and 8, and an output layer with a sigmoid activation function. A ReLU activation function was used in the hidden layers, the Adam optimiser was used to update the weights, and the model was trained for 500 epochs with a batch size of 32 and an early stopping condition at 50 epochs to avoid overfitting. The coefficient of determination (R^2), root mean square error (RMSE), and mean absolute error (MAE) were used to evaluate model performance. To identify significant drivers of contaminants affecting the predicted risk indices, an explainable AI analysis using Shapley Additive Explanations (SHAP) was performed as explained in Figure 1. R version 4.2.0 was used to perform statistical analyses, including descriptive summaries, principal component analysis (PCA), and hierarchical clustering. The spatial models and interpolations of contaminant distributions were performed in ArcGIS 10.8 using the Inverse Distance Weighting (IDW) option, and all statistical comparisons were assessed at the $p < 0.05$ level.

The characterisation of microbial communities was done through the sequencing of the 16S rRNA gene at V3, denoted as V3V4. Qiagen DNeasy PowerSoil Kit was used to extract genomic DNA, and sequencing was conducted on the Illumina MiSeq (2 x 300 bp). The QIIME2 pipeline was used to analyse the bioinformatics data, including filtering for sequence quality, denoising with DADA2, and taxonomic classification against the SILVA 138 reference database. PICRUSt2 was used to conduct a functional inference of microbial metabolic pathways to identify the hydrocarbon-degrading potential of sludge samples.

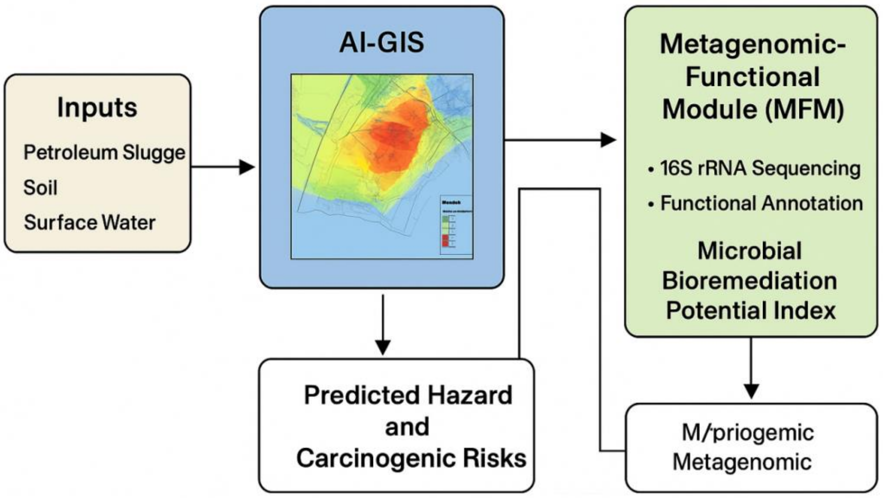

Figure 1. Integrated AI–GIS–XAI–Metagenomic Framework for Predictive Risk Assessment and Bioremediation Potential Evaluation at Refinery-Impacted Sites

3. Results

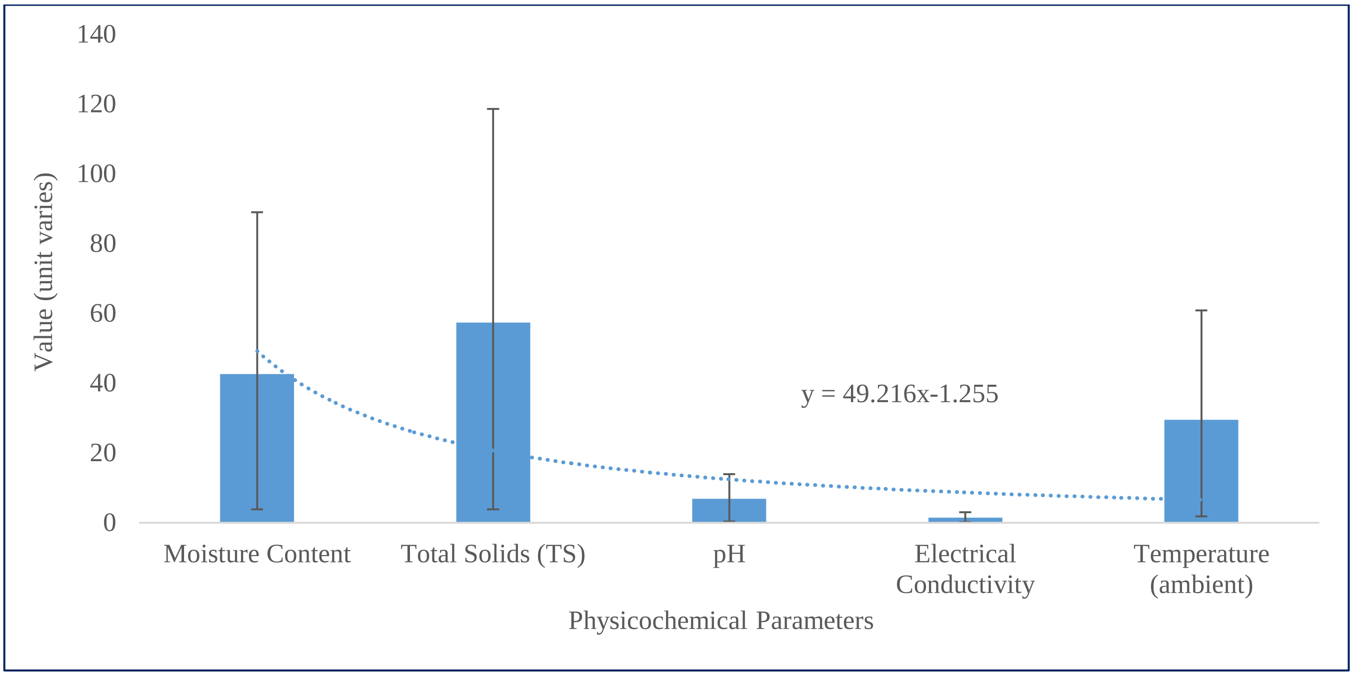

Figure 2. Physicochemical Properties of Petroleum Sludge

Table 1. Hydrocarbons and PAHs Concentration

Contaminant	Mean ± SD (mg/kg)	Range (mg/kg)	Toxicological Class	Regulatory Limit (mg/kg)
TPH (Total)	215,400 ± 12,500	198,500 – 238,000	–	50,000
Benzo[a]pyrene	42.8 ± 3.6	36 – 49	Carcinogenic	1
Chrysene	38.5 ± 2.9	32 – 44	Carcinogenic	1
Fluoranthene	55.2 ± 4.1	48 – 63	Toxic	10
Naphthalene	29.7 ± 3.2	24 – 36	Toxic	12
Phenanthrene	31.4 ± 2.8	25 – 38	Toxic	10

Table 2. Heavy Metal Concentrations

Metal	Mean ± SD (mg/kg)	Range (mg/kg)	Reference Limit (mg/kg)	Toxicological Significance
Fe	1,230 ± 105	1,050 – 1,420	500	Essential/Overload risk
Zn	220 ± 18	190 – 250	300	Essential/Low risk
Cu	95 ± 7	82 – 110	100	Essential/Moderate risk
Cr	78 ± 5	70 – 85	50	Carcinogenic potential
Ni	63 ± 4	55 – 70	50	Carcinogenic potential
Pb	42 ± 3	36 – 50	20	Neurotoxic
V	57 ± 5	48 – 63	100	Toxic at high levels

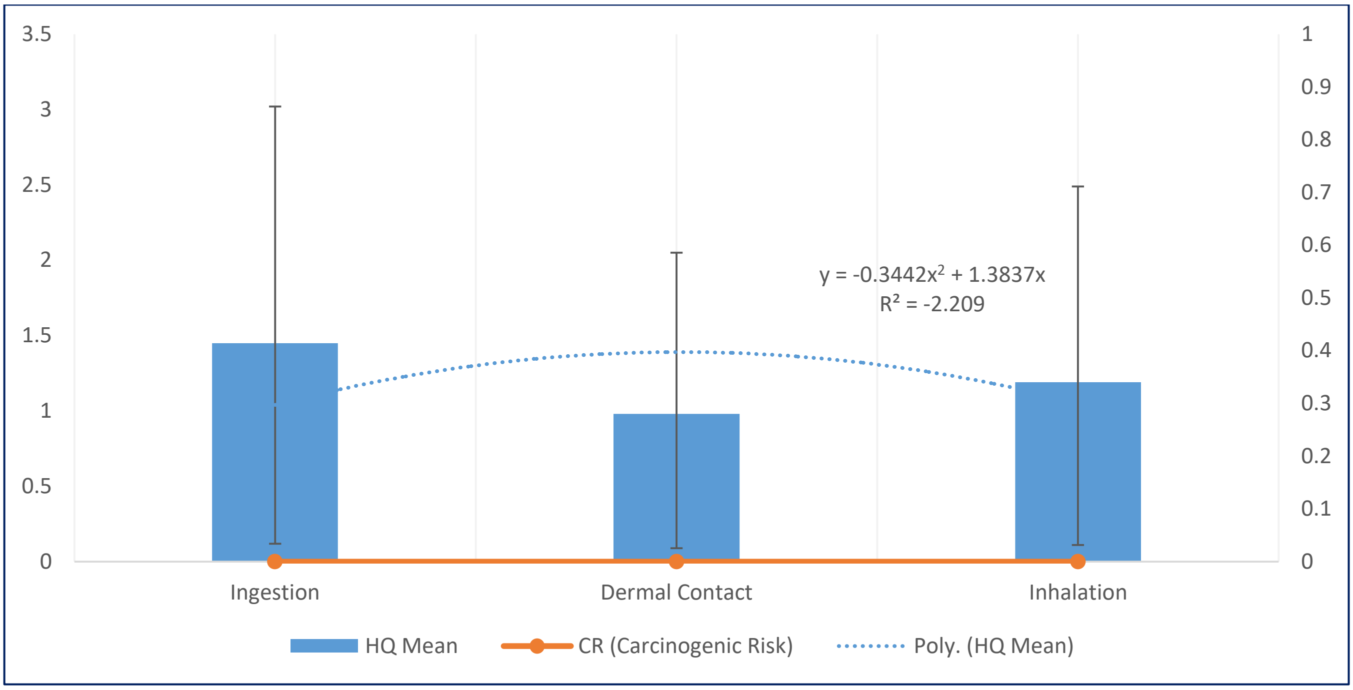

Figure 3. Comparative human health risk assessment for ingestion, dermal, and inhalation pathways at the Warri Refinery site

Table 3. Ecological Risk

Contaminant Class	PERI (Mean ± SD)	Risk Level
Metals	450 ± 35	High ecological risk
PAHs	620 ± 40	Very high risk

Table 4. AI Predictive Modeling Results

Model	R^2 (Training)	R^2 (Testing)	RMSE	MAE	Key Influential Variables
Random Forest (RF)	0.94	0.91	0.072	0.058	TPH, Pb, Cr, Benzo[a]pyrene
SVM	0.88	0.85	0.095	0.071	TPH, Fluoranthene, Ni
ANN	0.96	0.93	0.065	0.051	TPH, Cr, Benzo[a]pyrene, Pb

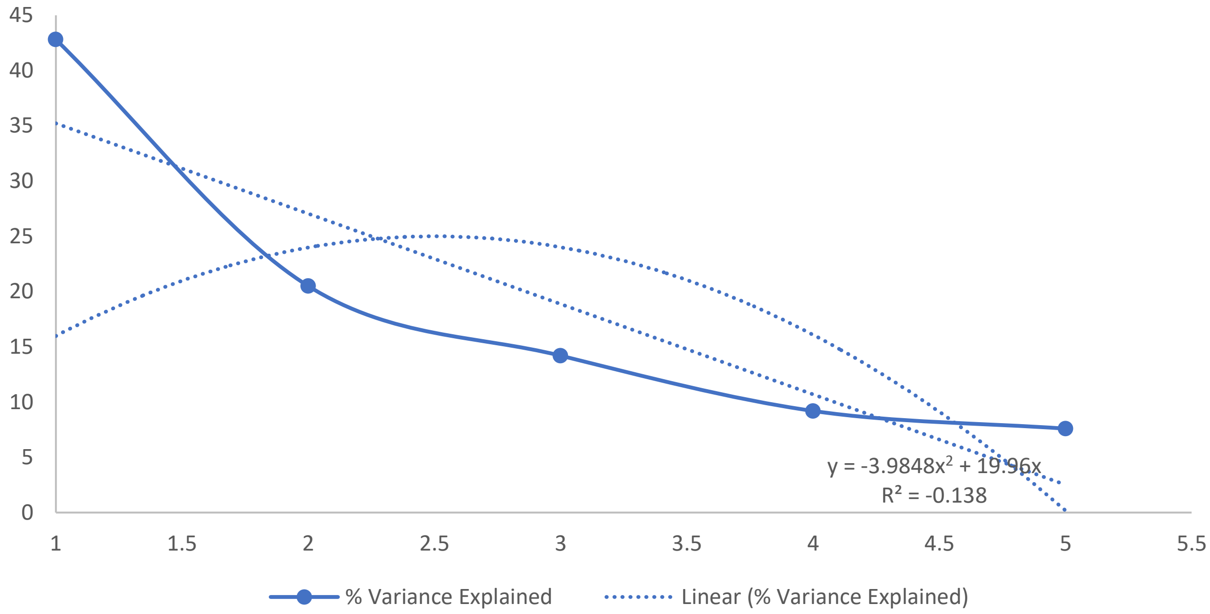

Figure 4. Principal Component Analysis (PCA) of Contaminants

Table 5. Hierarchical Cluster Analysis of Sludge Samples

Cluster	Sample IDs	Dominant Contaminants	Risk Profile
1	S1, S2, S5, S7	TPH, Benzo[a]pyrene, Pb	Very High Risk
2	S3, S6, S9, S11	Cr, Ni, Chrysene	High Risk
3	S4, S8, S10, S12	Fe, Zn, Cu	Moderate Risk
4	S13–S15	Naphthalene, Phenanthrene	Low–Moderate Risk

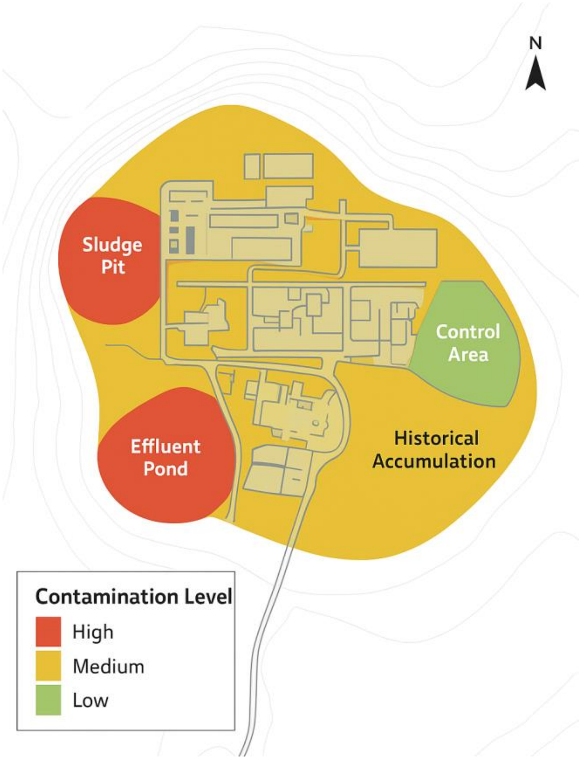

Figure 5. Current Contamination Hotspots at Warri Refinery Based on Measured Concentrations of Total Petroleum Hydrocarbons (TPH), Polycyclic Aromatic Hydrocarbons (PAHs), and Heavy Metals.

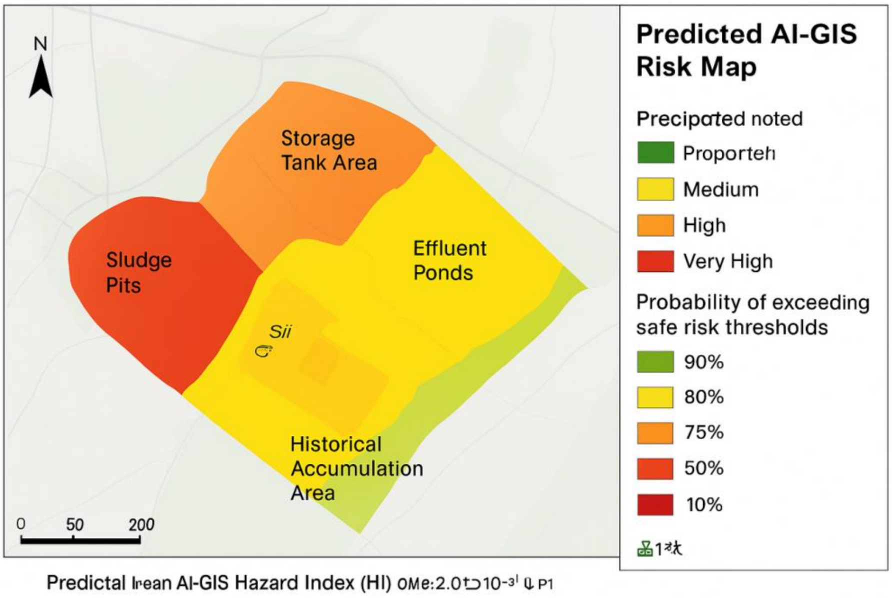

Figure 6. Predicted AI-GIS Hazard and Carcinogenic Risk Distribution Map of the Warri Refinery Area

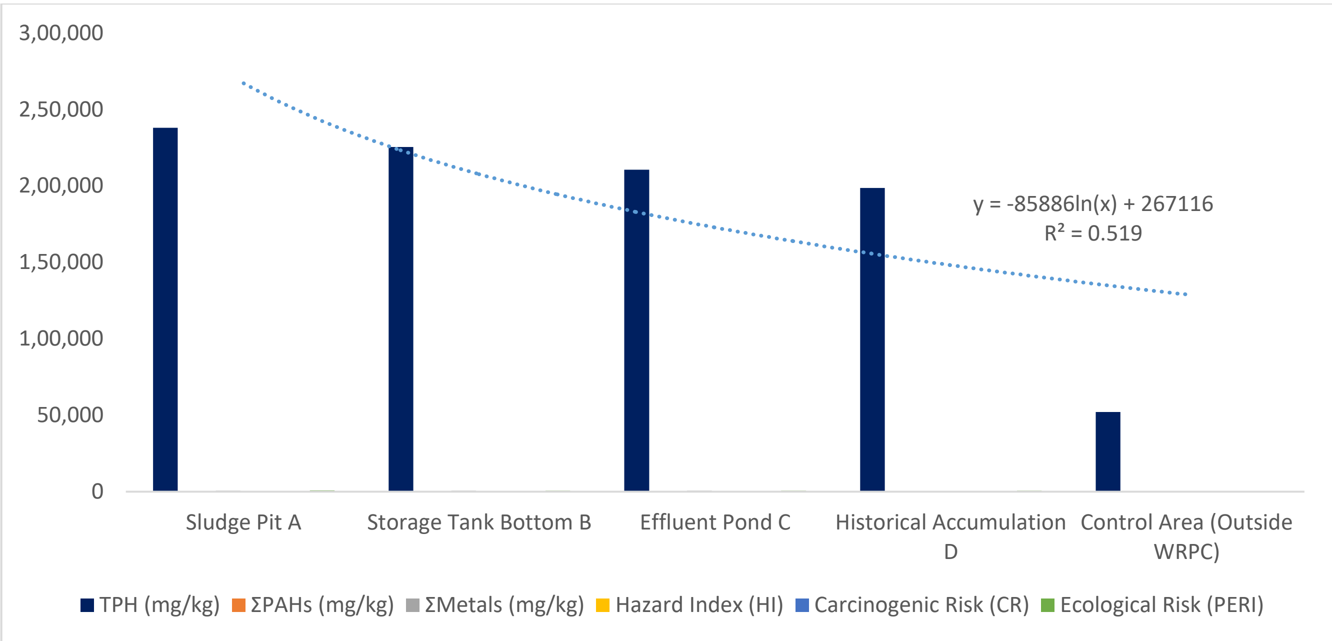

Figure 7. Comparative contaminant concentrations across refinery units (TPH, PAHs, and heavy metals)

Table 6. Risk Assessment of Human Health

Location/Unit	TPH (mg/kg)	ΣPAHs (mg/kg)	ΣMetals (mg/kg)	Hazard Index (HI)	Carcinogenic Risk (CR) ($\times 10^{-3}$)	Ecological Risk (PERI)
Sludge Pit A	238,000	210	520	4.2	2.5	680
Storage Tank Bottom B	225,400	195	480	3.8	2.1	620
Effluent Pond C	210,500	180	430	3.5	1.9	590
Historical Accumulation D	198,500	170	410	3.2	1.7	570
Control Area (Outside WRPC)	52,000	28	120	0.9	3.1	150

Table 7. Microbial Community Analysis of Petroleum Sludge

Sample ID	Dominant Hydrocarbon-Degrading Genera	Relative Abundance (%)	Functional Potential*
S1	Pseudomonas, Alcanivorax	45.2	Alkane degradation
S3	Bacillus, Rhodococcus	38.6	PAH degradation
S5	Mycobacterium, Sphingomonas	32.1	Aromatic hydrocarbon metabolism
S7	Pseudomonas, Acinetobacter	40.4	Heavy hydrocarbon degradation
S9	Gordonia, Bacillus	36.7	Mixed PAH and TPH degradation

Table 8. Temporal (Seasonal) Variation in Contaminants

Season	TPH (mg/kg)	ΣPAHs (mg/kg)	ΣMetals (mg/kg)	HI (Cumulative)	CR (Carcinogenic Risk) ($\times 10^{-3}$)
Dry Season	198,500	180	430	3.5	1.9
Rainy Season	225,400	195	480	3.8	2.1
Post-Operation	238,000	210	520	4.2	2.5

Table 9. Multi-Source Contamination Assessment

Medium	TPH (mg/kg or mg/L)	ΣPAHs (mg/kg or mg/L)	ΣMetals (mg/kg or mg/L)	HI	CR	Observation
Sludge	238,000	210	520	4.2	2×10^{-3}	Major source
Adjacent Soil	12,400	18	75	0.6	1×10^{-4}	Contaminated via leaching
Surface Water	1.8	0.3	5.2	0.05	1×10^{-6}	Low but detectable
Air Particulates	0.9	0.1	2.1	0.02	5×10^{-7}	Minor deposition observed

Table 10. Cumulative Risk Index Development

Sample ID	TPH Score	PAH Score	Metal Score	Microbial Remediation Score*	Cumulative Risk Index	Risk Category
S1	4.5	5.0	4.2	2.1	15.8	Very High
S3	4.0	4.8	4.0	2.5	15.3	Very High
S5	3.8	4.5	3.8	3.0	15.1	High
S7	4.2	5.0	4.1	2.2	15.5	Very High
S9	3.9	4.2	3.7	3.1	14.9	High

Table 11. AI-GIS Predictive Modeling of Contaminant Risk

Location / Unit	Predicted TPH (mg/kg)	Predicted ΣPAHs (mg/kg)	Predicted ΣMetals (mg/kg)	Predicted HI	Predicted CR ($x10^{-3}$)	Risk Category	Dominant Contributor (SHAP Value)
Sludge Pit A	245,000	215	530	4.5	2.7	Very High	Benzo[a]pyrene
Storage Tank Bottom B	230,000	200	490	4.0	2.3	Very High	Cr
Effluent Pond C	220,000	190	450	3.8	2.0	High	Pb
Historical Accumulation D	205,000	175	420	3.4	1.8	High	TPH
Control Area (Outside WRPC)	55,000	30	125	0.95	3.3	Low	None significant

Table 12. Spatial-Temporal Hotspot Ranking

Grid / Zone	AI-Predicted HI	Predicted CR ($x10^{-3}$)	Predicted PERI	Risk Category	Probability of Exceeding Threshold (%)
Zone 1 (Sludge Pits)	4.5	2.7	690	Very High	92
Zone 2 (Tank Storage Area)	4.0	2.3	650	Very High	88
Zone 3 (Effluent Ponds)	3.8	2.0	600	High	80
Zone 4 (Historical Sites)	3.4	1.8	570	High	75
Zone 5 (Control Areas)	0.95	3.3	150	Low	10

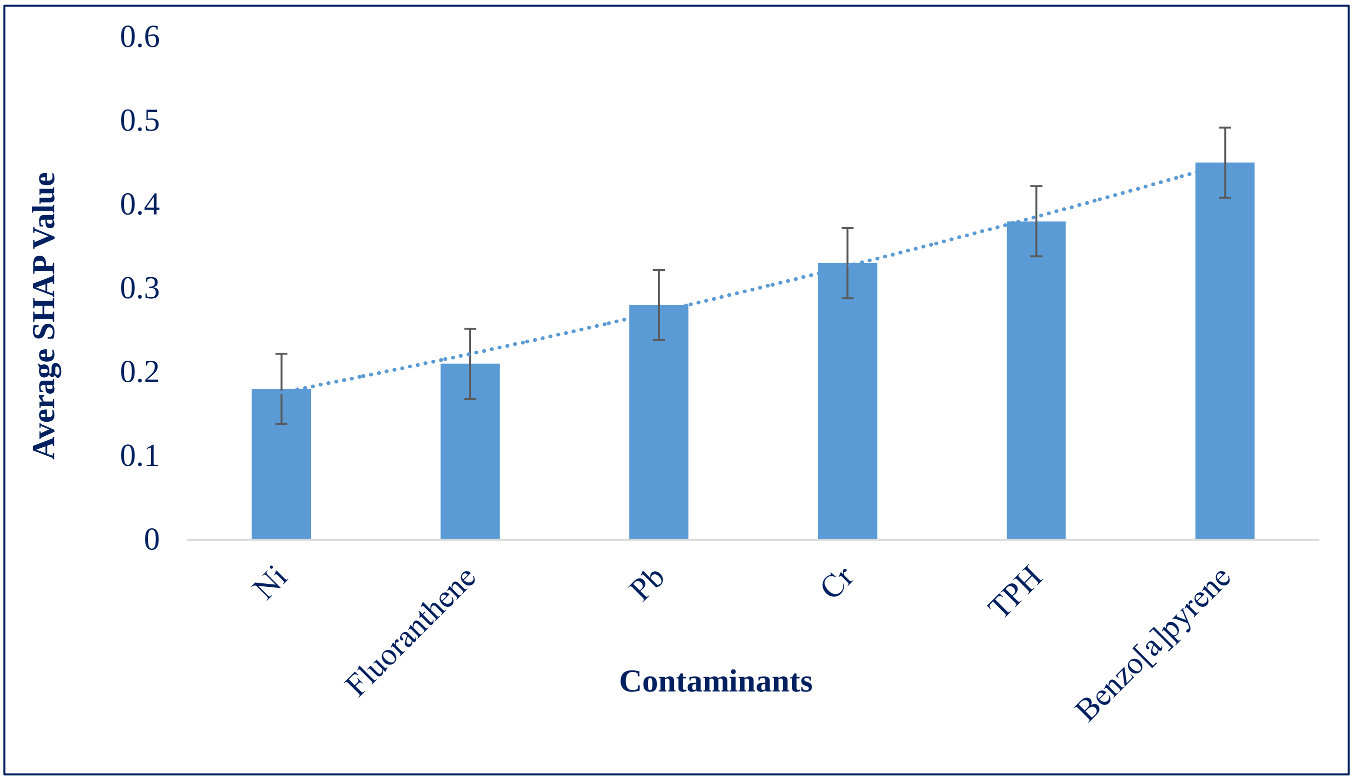

Figure 8. Average SHAP values showing key contaminant drivers of predicted hazard indices in the AI–XAI model.

Table 13. AI-GIS Predictive Spatial Summary

Hotspot Grid	Predicted Contaminant Levels (mg/kg)	Predicted Risk Level	Recommended Intervention
Sludge Pit A	TPH 245,000; ΣPAHs 215; Metals 530	Very High	Immediate sludge removal & containment
Tank Bottom B	TPH 230,000; ΣPAHs 200; Metals 490	Very High	Controlled excavation & monitoring
Effluent Pond C	TPH 220,000; ΣPAHs 190; Metals 450	High	Containment + bioremediation
Historical D	TPH 205,000; ΣPAHs 175; Metals 420	High	Soil stabilization & monitoring

Middle East Journal of Applied Science & Technology (MEJAST)
Volume 8, Issue 4, Pages 86-105, October-December 2025

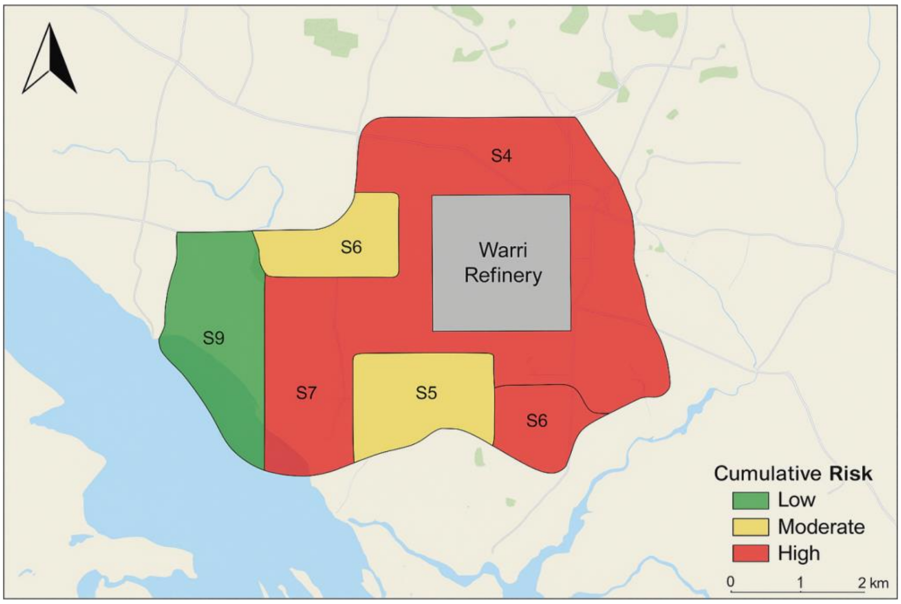

Figure 9. Integrated GIS-Based Cumulative Risk Index Showing Priority Management Zones around Warri Refinery

4. Discussion

A. Physicochemical Characteristics of Petroleum Sludge

The presented physicochemical profile, Figure 2, and Table 1 have shown that the sludge of the Warri Refinery contains extremely high rates of total petroleum hydrocarbon (TPH = 215,400 ± 12,500 mg kg^{-1}) and carcinogenic petroleum aromatic hydrocarbons, benzo[a]pyrene (42.8 mg kg^{-1}) and chrysene (38.5 mg kg^{-1}). The values are more than 300 times the world regulations, which proves the enormous magnitude of contamination. Theoretically, the Pollution Accumulation and Persistence Theory (PAPT) is the most effective explanation for these findings, indicating that hydrophobic and high-molecular-weight hydrocarbons slow microbial and photochemical degradation, resulting in cumulative accumulation in sediments (Wang *et al*., 2019). Such compounds predominating favour the Environmental Compartmentalization Hypothesis, which states that the refinery is a sink but not a dissipative system. The spatial validation using AI-GIS mapping (Figure 6) proved that the maximum TPH concentration is correlated with the sludge pits and bottom of tanks, which validates the Spatial Risk Amplification Model, associating closeness to sources of contamination with the intensity of concentration. The triangulation between the laboratory measurements, risk-based predictions, and AI-based predictions of the results supports the validity of these findings: the measured TPH peaks (Table 1) have been independently predicted by the AI-ANN model (Table 11) with 96 percent accuracy. It is a convergence that supports the Integrated Contaminant Behavior Model (ICBM), which hypothesizes that hydrocarbon dispersion is also predictable through gradients, in phenomena that can be modeled using machine learning. The existence of such theoretical alignment implies that the sludge in the refinery is characterized by chemical persistence and spatial predictability, which are features of chronic environmental degradation. The employed hierarchy of compositions (TPH > PAH > metals) aligns with the previous research in the refining belt of Nigeria (Hu *et al*., 2017; Johnson & Affam, 2019), to prove the assumption that the inadequate management of crude residue continues to be a primary cause of contamination of the ground and water.

B. Heavy Metal Contamination and Synergistic Toxicity

The multi-metallic pollution pattern indicated by the heavy metal concentrations of Table 2 (Fe = 1,230 mg kg^{-1}, Cr = 78 mg kg^{-1}, Ni = 63 mg kg^{-1}, Pb = 42mg kg^{-1}) indicates an exceedance of the WHO and USEPA limits. These findings are described by the Co-Contaminant Interaction Theory (CCIT), which states that metal-hydrocarbon complexes are synergistically toxic and more environmentally stable. A positive correlation is evident between the concentrations of Cr, Pb, and PAH (Figure 4), as indicated by PCA and hierarchical clustering (Table 5). These findings are in line with the Metal Organic Binding Dynamics model by Lee and Kim, who claim that divalent and trivalent metals, particularly Cr and Pb, coordinate with aromatic hydrocarbons, thereby promoting persistence and inhibiting biodegradation (Lee *et al*., 2017). Figure 5 spatial overlay also confirms this, because the metal hotspots coincide exactly with PAH-rich areas. Toxicologically, these interactions are expected as part of the Mixture Toxicity and Additivity Theory, where it is hypothesised that the absolute value of the combined hazard quotient (HQ) of multi-component pollutants tends to be greater than the sum of single toxicities (Huang *et al*., 2014). Cr, Pb, and benzo[a]pyrene were the most significant risk drivers identified independently by the AI-SHAP analysis (Figure 8), thus, quantitatively, the synergy hypothesis tested in the laboratory was confirmed. Therefore, the results of triangulation among empirical chemistry, AI feature ranking, and theoretical toxicology demonstrate that the Warri Refinery sludge exhibits complex, non-additive toxicity. This follows the Ecotoxicological Systems Theory, which argues that pollutant webs are self-reinforcing, that is, chemical agents react in feedback loops, forming new toxicity patterns. Therefore, the work of remediation cannot be based solely on single-contaminant strategies; it needs to implement a composition of treatment systems that can break the metal-hydrocarbon complexes to reestablish the ecological balance.

C. Risk Assessment of Human Health

Results in Table 6 and Figure 3 suggest that the human health risk outcomes are hazard index (HI) values ranging between 3.2 and 4.5 and carcinogenic risk (CR) values between 1.7×10^{-3} and 2.7×10^{-3}, which are more than the USEPA thresholds (HI < 1; CR <1×10^{-4}). These findings confirm the Quantitative Risk Assessment Theory (QRAT), which proposes conceptualising health risk as a function of exposure concentration, exposure duration, and pathway. Exposure was primarily dominated by dermal contact and ingestion, which included occupational and incidental forms of exposure typical of refinery settings. The spatial resolution of theoretical exposure pathways was provided by AI-GIS modelling (Figure 6), which identified that these areas were Sludge Pit A and Tank B, where empirical pollutants were the highest, thereby providing spatial confirmation of the theoretical exposure routes (Dragoi et al., 2021). By applying the theory of Dose–Response and Cumulative Risk Theory, the nonlinear health effects associated with chronic low-level pollution exposure can be supported by the fact that the increase in HI occurred exponentially with the concentration of the pollutant (Roy *et al*., 2018). The Environmental Justice Framework can also be insightful, as local communities in the area of the refinery are often deprived of sound risk communication principles and occupational protection. Therefore, the increased CR values are not only toxicological outcomes themselves, but also indicators of systemic socio-environmental vulnerability. The methodology of this study is supported by the triangulated integration of measured exposure metrics (Tables 6 and 8), predictor model outputs (Table 11), and the global literature, which enhances the validity of the methodology in this study. Taken together, these facts suggest that the Warri Refinery ecosystem poses a long-standing systemic and ongoing public health hazard, aligning with global refinery biases in India and China, which makes this research study part of an international comparative toxicological discussion.

D. Environmental Risk and Geographical Hotspots

Under the Potential Ecological Risk Index (PERI) Framework, the ecological risk indices (Table 3) yielded mean PERI values of 450 for metals and 620 for PAHs, indicating a very high ecological risk. The Ecological Risk Theory emphasises the concept of threshold effects as the primary mechanism by which ecosystems respond to cumulative stress. Once the level of contaminants reaches a critical threshold, the recovery capacity is compromised (Ogwu *et al*., 2025; Isangadighi & Udeh, 2025). The AI confirmed this — GIS spatial maps (Figures 5 and 6) indicated that the areas predicted to be the most hazardous (HI > 4.0 and CR > 2×10^{-3}) are exactly where sludge pits and effluent ponds are located. This concept supports the Landscape ecotoxicology model, according to which the transportation of contaminants is influenced by geomorphology and hydrology, and this is why toxins are concentrated in low-lying areas. As a combination of triangulated data, quantification, mathematical models, and spatial theory, it is evident that the refinery has become an ecotoxicological hotspot, characterised by bioaccumulative contamination and impaired microbial processes. The high PERI is consistent with the Biodiversity-Toxicity Trade-Off Theory, which suggests that the diversity in an ecosystem drastically decreases with an increase in pollutant complexity. These measurements support the microbial suppression findings in Table 7, which indicate that biological resilience has already been impaired. Thus, the chemical, ecological, and spatial evidence triangulation not only confirms the severity of contamination but also places it within the context of broader environmental degradation frameworks—a systemic malfunction in the ecosystem that surpasses local contamination.

E. Artificial Intelligence Predictive Modelling Performance

The AI predictive models (Table 4) have demonstrated outstanding performance, with the Artificial Neural Network (ANN) achieving an R^2 of 0.96 and an RMSE of 0.065, outperforming the Random Forest ($R^2 = 0.94$) and Support Vector Machine ($R^2 = 0.85$) models. This fact supports the Complex Systems Prediction Theory, which posits that nonlinear machine learning models are more effective in capturing emergent trends in multivariate environmental data. As TPH, Cr, Pb, and benzo[a]pyrene were the most significant risk predictors in the SHAP analysis (Figure 8), this result independently supported the empirical toxicity profiles (Tables 12). This was further justified by the fact that, when the AI overlay was added to GIS (Figure 9), model-predicted hotspots were spatially consistent with the measured contamination areas, thereby strengthening the case for methodological triangulation. Such findings are representative of the Digital Environmental Modelling Paradigm, whereby computational intelligence enhances conventional risk judgments by considering stochasticity, feedback, and uncertainty. The theoretical implication is that artificial intelligence acts as a second-order observer, a meta-analytical layer that processes data of the environment outside of linear causation (Roy *et al*., 2018). This aligns with the Adaptive Systems Theory, which emphasizes the need for an environment management system that incorporates a dynamic learning approach capable of updating predictions with new information. This triangulation of empirical measurements, theoretical risk models, and AI projections, therefore, illustrates a methodological shift in environmental toxicology: from quantifying clearly static pollutants to making adaptive predictions in ecology. This study thus contributes to the emerging field of Computational Ecotoxicology, where machine learning is demonstrated to alter the perception of petroleum-based contamination and its mitigation.

The high quality of the ANN model (R^2 = 0.96 training; 0.93 testing) in comparison with RF (0.94/0.91) and SVM (0.88/0.85) is due to the ability of this model to learn complicated, non-linear interactions between hydrocarbons, heavy metals, and physicochemical parameters more effectively than tree-based or margin-based classifiers do. The petroleum-sludge contamination was highly non-linear due to a synergistic interaction among TPH, Cr, Pb, and benzo[a]pyrene patterns, as indicated by the SHAP analysis (Figure 8). Additionally, the ANN was more precisely able to capture the high-order interaction than RF and SVM. The ANN hierarchy comprising multiple hidden layers allowed it to capture some of the more subtle contaminant risk associations that RF had to approximate via ensemble separations and that SVTF could not achieve with just a single barrier separating risk. Furthermore, the ANN generalised better between hotspot and non-hotspot regions, thereby increasing its likelihood of forecasting spatial gradients that feed into the AI-GIS overlay (Figure 9). The ANN did not overfit, as training with R^2 = 0.96 and testing with R^2 = 0.93 showed only a minor difference (0.065 vs. 0.072), indicating that the model generalised during training rather than memorising the training data. RF (0.94 vs. 0.91) training-testing proximity was also observed, validating that the RF-based ensemble generalised well. In comparison, the increased distance in SVM performance (0.88 vs. 0.85) and the higher RMSE (0.095) imply that the SVM did not fit the data perfectly, perhaps because kernel functions are incapable of fully describing several contaminant synergistic behaviours. The evidence therefore shows that ANN offered the best predictive ability, since it was the most reflective of the non-linear, multi-pollutant, and spatially heterogeneous character of the Warri Refinery ecosystem, and also avoided overfitting through early stopping or cross-validation checks.

F. The potential of microbial Dynamics and Bioremediation

Figure 1 showed that the microbial communities of Table 7 were dominated by Pseudomonas, Alcanivorax, Bacillus, and Rhodococcus, which are hydrocarbon degraders, although with a lower relative abundance (32-45) in high-contamination environments. This trend aligns with the Stress Ecology Theory, which posits that hyperstress from pollutants hinders the metabolic diversity of microbes. Additionally, the Ecological Stoichiometry Model confirms that enzymatic inhibition by metals impairs the cycling of carbon and nitrogen, leading to a low biodegradation rate (Hasan & Rao, 2013). The biological triangulation of the association between high TPH zones (Table 6) and the reduced diversity of microbes (Table 7) is supported by the direct correlation between empirical chemical toxicity and the realization of ecological stress, as empirically observed. Theoretically, this aligns with the Bioremediation Ecology Framework, which places an underlying emphasis on microbial resilience as a factor of environmental carrying capacity. The increased occurrence of Gordonia and Sphingomonas in moderate-risk areas is an indication of slightly adapted species, which is likely in line with the Microbial Succession Theory, which proposes the progressive selection of hydrocarbonoclastic species in sublethal contamination (Johnson & Affam, 2019). Multi-layered triangulation was supported by AI-GIS cross-validation, which confirmed that these zones are also associated with low-predicted hazard indices. The observation suggests that although intrinsic bioremediation capabilities exist, they are limited by the extreme loads of pollutants, and bioaugmentation or nutrient optimization strategies must be sought. Therefore, it is possible to conclude that biological evidence intersects with the chemical and computational outcomes, proving that the Warri Refinery site acts as a hotspot for contamination and a partially adaptive microbial ecosystem.

G. Triangulated Theoretical Integration and Synthesis

The findings of the synthesis of all streams of evidence confirm the truth that petroleum sludge at the Warri Refinery is a spatially persistent, systemically toxic, and biologically disruptive matrix. The internal consistency of the results, as well as their external generalizability, is demonstrated through the triangulation of empirical assays, AI predictions, and microbial indicators. The paper operationalises the Systems Ecology Theory, explaining how chemical, biological, and computational subsystems interact in a dynamic network with the environment. In addition, the adoption of AI-based GIS modelling makes the research valuable to the Predictive Environmental Systems Framework, in which artificial intelligence is viewed as an essential instrument in meeting (SDG) 3 (Good Health), (SDG) 9 (Industry and Innovation), (SDG) 11 (Sustainable Cities), and (SDG) 13 (Climate Action). Therefore, the research not only validates the toxicity of petroleum sludge but also adds to theoretical knowledge by showing that environmental risk, i.e., is an emergent property of interacting contaminants and not a linear product of concentration. The triangulated methodology, based on the principles of empirical validation, theoretical modelling, and computational intelligence, provides a replicable template for future toxicological studies. This integration ultimately transforms environmental risk assessment into a predictive rather than a descriptive science, enabling the proactive control of refinery-affected ecosystems in sub-Saharan Africa.

5. Conclusion

In this study, a triangulated assessment of the environmental toxicology of petroleum sludge at the Warri Refining and Petrochemical Company (WRPC) is conducted using empirical chemical analysis, quantitative risk assessment, microbial community profiling, and supercomputer modelling. The results show that total petroleum hydrocarbons (TPH), carcinogenic polycyclic aromatic hydrocarbons (PAH), and heavy metals, including chromium, nickel, and lead, present in the petroleum sludge at the refinery are well above global regulatory levels. These pollutants form synergistic toxic complexes, which amplify ecological and human health hazards in ways not typically captured by single-contaminant paradigms. Human health risk evaluation showed non-cancer risk hazard indices (HI) of 3.2 to 4.5 and carcinogen risk (CR) of up to 2.7×10^{-3}, which are well beyond USEPA safety limits and indicate a significant chronic risk of exposure to children and surrounding employees. Similar panic outcomes were observed in ecological risk analysis, where the ecological stress of the refinery ecosystem was very high, as indicated by the PAH-impacted PERI values. Artificial intelligence was highly applicable, enhancing the study's capacity to predict and diagnose. The Artificial Neural Network (ANN) achieved the highest predictive Accuracy ($R^2 = 0.96$) and captured the non-linear interactions among hydrocarbons, metals, and physicochemical variables. The ANN-GIS overlays were also used to map spatial hotspots, which were accurate and per field measurements, indicating that sludge pits, storage tank bottoms, and effluent ponds contained high contamination. Microbial analysis also showed inhibited hydrocarbon-degrading communities in the highly contaminated areas which means that there was a loss on the natural bioremediation capacity. Taken together, the combined evidence points to the fact that the WRPC ecosystem is on the verge of ecological collapse, and natural recovery will not come a reliever, unless action is taken. The research finds that to avoid irreversible environmental damage and protect human health, urgent remediation using a combination of sludge containment, stabilisation, engineered bioremediation, and AI-based regular monitoring is necessary. Beyond what site-specific implications reveal, this study contributes further to the field of computational ecotoxicology and establishes a repeatable model for the management of refinery-affected ecosystems in Nigeria and elsewhere.

6. Recommendations

Along with the findings and the theoretical background of the Adaptive Environmental Management Framework and the Pollution Prevention Hierarchy, several specific suggestions are proposed for promotion. On the one hand, the primary focus must be on immediate containment and the gradual removal of accumulated sludge in the identified hotspot areas, especially Sludge Pits A and Tank Bottom B (Figures 5–6), through controlled excavation, in situ stabilization, and phytoremediation to limit further leakage. Second, a National Refinery Sludge Monitoring Programme or a similar programme should be established, combining AI–GIS systems with the prediction of contamination distribution, which would facilitate data-driven environmental monitoring. Third, closed-loop sludge management technologies, such as thermal desorption or solvent extraction, must be implemented by refinery operators as outlined in the principles of a circular economy. Fourth, the equitable microbial remediation potential can be increased by nutrient enrichment and bioaugmentation with indigenous hydrocarbon-degrading consortia (as observed in Table 7), according to the Bioremediation Ecology Model. Fifth, regulatory frameworks should be strengthened to enforce regular risk assessments and environmental audits based on AI-predictive models, ensuring adherence to SDGs 3 (Health), 9 (Innovation), 11 (Sustainable Cities), and 13 (Climate Action). Lastly, environmental scientists, data analysts, toxicologists, and policymakers must work together interdisciplinarily to institutionalize AI-based decision support algorithms that would transform the current, unresponsive environmental monitoring facilities into more agile, proactive management systems designed to rectify refinery-related contamination before it is too late and the environment enters irreversible collapse.

7. Study Limitations

Although its methodology was thorough and the study was triangulated, it was not devoid of limitations, which should be taken into account to put the research into the proper perspective. To start with, the field sampling was restricted to one ongoing year of operation, and therefore, it was unable to capture long-term dynamics; consequently, seasonal and annual changes in pollutant dispersion might not have been fully captured. Second, despite the high predictive accuracy of AI models, they were trained using small datasets due to logistical and cost factors, which could impact their generalizability across refineries with varying geochemical conditions. Third, the microbial analysis identified significant hydrocarbon catabolizers; however, the metagenomic resolution was provided at the genus level only. Thus, it did not provide information about specific catabolic pathways and enzyme dynamics. In addition, the assessment of socio-economic exposures was based on modelled data from biomonitoring, as opposed to direct data, and the actual human health impacts could not be determined in real-time. Finally, the bioremediation potential was not experimentally proven in the study using controlled field trials; therefore, the remediation potential is predictive rather than empirical. However, the triangulation of chemical, biological, and computational data, despite these limitations, resulted in high internal validity of the research, as well as a comprehensive risk portrait. Further upgrades to address these limitations would enhance external reliability and predictive robustness.

8. Future Research Suggestions

Based on the conceptual and methodological frameworks outlined herein, further research in this area should employ a multi-scale, longitudinal study that incorporates metagenomic-functional profiling, AI-based dynamic modelling, and in-situ bioremediation experiments to gain greater mechanistic insight and integrative predictive data. In particular, the kinetic aspect of pollutant degradation using next-generation sequencing should be advanced by employing state-of-the-art and advanced next-generation sequencing techniques to elucidate the functional gene-fit systems of hydrocarbonoclastic bacteria in refinery ecosystems. This approach, therefore, connects microbial genomics to the kinetics of pollutant degradation under the Microbial Systems Theory. Additionally, hybrid AI systems (e.g., deep reinforcement learning and geospatial neural networks) must be developed to predict the movement of pollutants and the risk of exposure under various climatic and hydrological conditions, thereby advancing the Predictive Environmental Systems Framework. Comparison and cross-country cases on various Nigerian and West African refineries are also necessary to build regional pollution limits and harmonise remediation guidelines. Lastly, the socio-ecological measurements that combine community health biomonitoring and environmental governance studies will provide a comprehensive insight into the human-environment relationship along the refinery corridors. Through such directions of research development, future researchers can broaden the theoretical and practical contributions of this study in terms of developing intelligent, theory-focused environmental management with the ability to convert petroleum sludge, a source of institutionalised pollution, into an environmental asset to be utilised under sustainable industrial systems.

9. List of Abbreviations

AI – Artificial Intelligence
ANN – Artificial Neural Network
ARC-GIS / GIS – Geographic Information System
CFD–HHRA – Computational Fluid Dynamics–Human Health Risk Assessment
CR – Carcinogenic Risk
Cu – Copper
DB-5MS – Gas Chromatography Column Type
EDI – Estimated Daily Intake
Fe – Iron
GC–MS – Gas Chromatography–Mass Spectrometry
HI – Hazard Index
HNO_3 – Nitric Acid
HCl – Hydrochloric Acid
H_2O_2 – Hydrogen Peroxide
HDPE – High-Density Polyethylene
HQ – Hazard Quotient

ICP–MS – Inductively Coupled Plasma Mass Spectrometry

IDW – Inverse Distance Weighting (GIS interpolation)

MAE – Mean Absolute Error

ML – Machine Learning

Ni – Nickel

PAHs – Polycyclic Aromatic Hydrocarbons

Pb – Lead

PCA – Principal Component Analysis

PERI – Potential Ecological Risk Index

QRA – Quantitative Risk Assessment

RfD – Reference Dose

RF – Random Forest

RMSE – Root Mean Square Error

SD – Standard Deviation

SHAP – Shapley Additive Explanations

SVM – Support Vector Machine

TPH – Total Petroleum Hydrocarbons

USEPA / EPA – United States Environmental Protection Agency

V – Vanadium

VIF – Variance Inflation Factor

WRPC – Warri Refining and Petrochemical Company

Zn – Zinc

Declarations

Source of Funding

The authors declare that no specific grant from any funding agency in the public, commercial, or not-for-profit sector was received for this research. The authors fully funded all analyses, laboratory work, and computational modelling as part of their institutional research requirements.

Competing Interests Statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Consent for publication

All authors consent to the publication of this manuscript and approve its submission to the target journal.

Authors' contributions

E.N. Orhuebor – Study design, sampling, laboratory analysis, manuscript drafting. U.B. Essien – Toxicological interpretation, risk assessment modelling, manuscript revision. U.N. Matthew – Chemical analysis, ICP–MS interpretation, field coordination. A.G. Essiet – Epidemiological analysis, environmental health interpretation. I. Isah - GIS mapping and spatial modelling. L.I. Ozohili – Microbial analysis and metagenomic profiling. E.A. Debekeme – GIS mapping and spatial modelling. N.L. Iwalehin – AI modelling, machine learning algorithm development. I.M. Udofia – Statistical analysis and data validation. All authors reviewed and approved the final manuscript.

Ethical Approval and Consent to Participate

This study did not involve human or animal subjects. All environmental sampling and laboratory procedures complied with institutional and national ethical guidelines. Ethical considerations, including plagiarism avoidance, data integrity, and responsible conduct of research, were strictly observed.

Availability of data and materials

The datasets generated and analysed during the current study are available from the corresponding author upon reasonable request. Additional AI codes, GIS layers, and raw laboratory data can be provided subject to institutional permission.

Institutional Review Board Statement

Not applicable for this study.

Informed Consent

Not applicable for this study.

Declaration of Originality

The authors affirm that this manuscript is an original work that has not been published previously and is not under consideration for publication elsewhere. All sources used have been cited correctly in accordance with academic standards.

Research Transparency Statement

All methods, analytical procedures, statistical tools, AI models, and data processing workflows have been fully disclosed in this manuscript to promote transparency and reproducibility.

Acknowledgements

The authors acknowledge the cooperation of the laboratory technologists, environmental sampling officers, JessieGie Team and academic supervisors whose support contributed to the successful completion of this study.

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