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Ecological Risk Assessment of Polycyclic Aromatic Hydrocarbons in Eleme Oil Spill Impacted Soils, Rivers State, Nigeria

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ABSTRACT

This study investigated the ecological risk of polycyclic aromatic hydrocarbons (PAHs) in crude oil-impacted soils from Eleme Oil Field, Rivers State, Nigeria. Eight soil samples were collected from impacted sites (A-H) and one control site using a stainless-steel auger at 0-30 cm depth. Sixteen USEPA priority PAHs were analyzed using Gas Chromatography-Flame Ionization Detection (GC-FID). Total PAH concentrations (Σ16 PAHs) varied significantly across the study area, ranging from 5.57 mg/kg to 676.20 mg/kg, with the highest levels recorded in heavily impacted sites. The concentration ranges (mg/kg) were: Naphthalene (0.00-7.04), Acenaphthylene (10.11-11.02), Acenaphthene (10.06-42.00), Fluorene (7.01-54.94), Phenanthrene (72.51-210.07), Anthracene (9.00-87.54), Fluoranthene (7.49-194.77), Pyrene (8.00-106.65), Benzo[a]anthracene (1.07-11.20), Chrysene (13.00-51.90), Benzo[b]fluoranthene (0.01-79.19), Benzo[k]fluoranthene (5.00-199.21), Benzo[a]pyrene (10.60-99.87), Indeno[1,2,3-cd]pyrene (0.93-15.22), Dibenzo[a,h]anthracene (0.33-51.00), and Benzo[g,h,i]perylene (15.00-50.10). No PAHs were detected in the control site. Toxic equivalent quantity (TEQ) values reached critical thresholds at Site F (127.66 mg/kg), Site H (126.11 mg/kg), and Site A (121.31 mg/kg), driven primarily by high concentrations of benzo[a]pyrene and dibenz[a,h]anthracene. Risk quotients (RQ) for individual high molecular weight components exceeded permissible environmental screening levels across all impacted quadrants. Diagnostic ratio analysis confirmed mixed sources: petrogenic (crude oil spills) dominated Sites B and E, while pyrogenic sources (gas flaring, combustion) dominated Sites A, F, and G. The study concludes that Eleme Oil Field is severely contaminated with PAHs, posing serious ecological and public health concerns requiring immediate remediation and continuous monitoring.

Keywords: Ecological risk, polycyclic aromatic hydrocarbons, source apportionment, oil spill, Eleme, Niger Delta

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important class of organic contaminants consisting of two or more fused aromatic rings widely recognized as persistent environmental pollutants[1]. PAHs naturally occur in fossil fuels, including crude oil, and are released into the environment through oil spillage, combustion processes, and industrial effluents. Many PAHs are carcinogenic, mutagenic, and pose serious ecological and human health risks due to their lipophilic nature, environmental persistence, and ability to bioaccumulate[2].

In Nigeria's Niger Delta region, where oil exploration and exploitation have been ongoing for decades, crude oil contamination has introduced significant quantities of PAHs into soils, sediments, surface water, groundwater, and air. This region hosts numerous oil installations, pipelines, flow stations, and associated infrastructure that have periodically leaked or spilled petroleum hydrocarbons into the environment[1,3].

Eleme Local Government Area, Rivers State, is among these oil-producing communities in the lower Niger Delta. It hosts oil fields, flow stations, pipelines, and other petroleum industry assets that have facilitated both conventional and artisanal hydrocarbons release into surrounding soils, sediment and water bodies[4]. Research in other parts of the Niger Delta has documented elevated PAH levels in soils, sediments, and water associated with oil spills, with evidence of toxicological risk to aquatic organisms and human receptors.

Despite extensive oil activities around Eleme, the geochemical nature, distribution patterns, and environmental behavior of PAHs in crude oil ecosystems remain poorly quantified and understood. Local communities in Eleme rely heavily on groundwater and surface water sources for domestic use, fishing, and agriculture. However, periodic oil spills, leaks, illegal refining, and pipeline vandalism can release PAHs that persist in environmental compartments and pose substantial risks to ecosystems and public health.

The present study sought to evaluate the ecological risk of PAHs in the Eleme Oil Field soil, addressing the following specific objectives: (1) determine the concentration levels of PAHs in soils from selected crude oil impacted sites in Eleme; (2) assess the geochemical distribution and compositional patterns of PAHs across different environmental media; (3) identify probable sources of detected PAHs using molecular diagnostic ratios and geochemical indicators; and (4) evaluate the ecological risk and potential health implications associated with PAH contamination in the study area. Proper understanding of the ecological risk of PAHs on the study site soil will mark a major step towards adequate and prompt remediation of the site, so as to ensure the sustainability of biological organisms and the ecosystem at large.

Materials and Methods

Study area

The study was conducted in Eleme Oil Field, Eleme LGA, Rivers State (latitude 4°45′-4°50′N, longitude 7°05′-7°10′E). The area lies within the Niger Delta Basin, dominated by the Benin Formation (coastal plain sands). The climate is humid tropical with annual rainfall of 2,000–2,500 mm and temperatures of 25-32°C **(Figure 1)**.

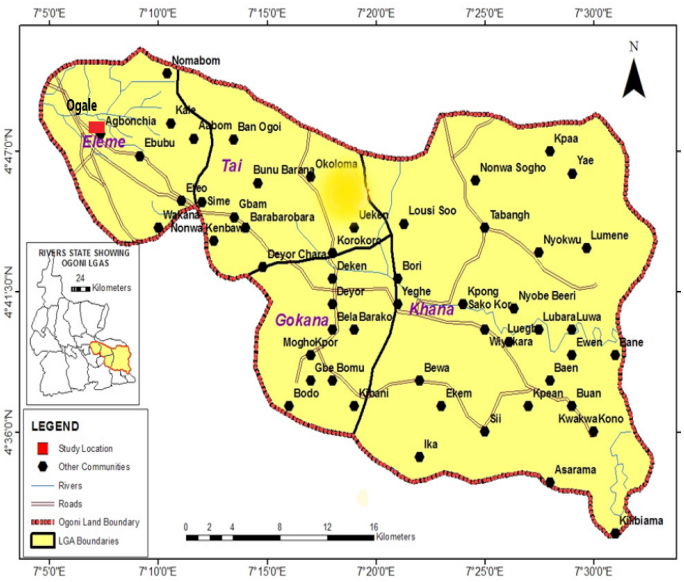

Figure 1: Map of Study Area Showing Sampling Locations.

Sampling and Analysis

Eight soil samples (A-H) were collected from impacted sites and one control site at depths of 0-30 cm using a stainless-steel auger. Samples were stored in pre-cleaned amber glass bottles. Soxhlet extraction (n-hexane: dichloromethane, 1:1 v/v) was performed following USEPA Method 3540C. Sixteen priority PAHs were quantified using Agilent 6890N GC-FID. Detection limits ranged from 0.001-0.005 mg/kg **(Table 1)**.

Source Apportionment

Diagnostic ratios (Yunker et al., 2002; Soclo et al., 2000) were calculated:

HMW/LMW: petrogenic<1.0, pyrogenic >1.0

Phe/Ant: petrogenic<10, pyrogenic >10

Flu/(Flu+Pyr): petrogenic<0.4, pyrogenic >0.5

BaA/(BaA+Chr): petrogenic<0.2, pyrogenic >0.35

Table 1: PAH diagnostic ratios with source interpretation thresholds.

Ratio	Petrogenic Range	Pyrogenic Range	Key Reference
HMW/LMW	<1.0	>1.0	Soclo, et al.[5]
Phe/Ant	<10	>10	Budzinski, et al.
Flu/Pyr	<1.0	>1.0	Yunker, et al.[6]
Flu/(Flu+Pyr)	<0.4	>0.5	Yunker, et al.[6]
BaA/(BaA+Chr)	<0.2	>0.35	Yunker, et al.[6]

Ecological risk assessment

Toxic Equivalent Concentration (TEQ) was calculated using TEFs[7]:

$TEQ = \Sigma (PAH_i \times TEF_i)$

Risk Quotients (RQ) were calculated as: RQ = C□$_a$□ / C□□$_{ree}$□$_i$□□

Where C□ $_{ree}$□$_i$□□ is the USEPA Eco-SSL (100-120 mg/kg for invertebrates; 50-160 mg/kg for plants) **(Table 2)**.

Table 2: Toxic equivalency factors for carcinogenic PAHs[7].

PAH Congener	TEF Value
Benzo[a]pyrene (BaP)	1
Dibenzo[a,h]anthracene (DahA)	1
Benz[a]anthracene (BaA)	0.1
Benzo[b]fluoranthene (BbF)	0.1
Benzo[k]fluoranthene (BkF)	0.1
Indeno[1,2,3-cd]pyrene (IcdP)	0.1
Chrysene (Chr)	0.01

Risk Quotient (RQ) Method

The risk quotient was calculated by comparing measured PAH concentrations with established ecological screening values (USEPA Eco-SSLs):

RQ = C□$_a$□ / C□ $_{ree}$□$_i$□□

Where C□$_a$□ is the measured PAH concentration (mg/kg) and C□ $_{ree}$□$_i$□□ is the ecological screening value (mg/kg). Risk categories were classified as: RQ < 1 (low risk), 1 ≤ RQ ≤ 10 (moderate risk), and RQ > 10 (high risk)[8].

Results and Discussion

PAH Concentrations

Total PAH concentrations (Σ16 PAHs) varied significantly across sites, ranging from 5.57 to 676.20 mg/kg. No PAHs were detected in the control site.

Table 3: Representation ofPolycyclic Aromatic Hydrocarbon Concentrations at Eleme Sites (mg/kg).

Site	ΣPAHs (mg/kg)	Dominant PAHs	HMW/ LMW	Source
A	619.48	BkF (199.21), BaP (91.86)	3.4	Pyrogenic
B	573	Phe (210.07), Ant (137.54)	0.42	Petrogenic
C	5.57	BaA (5.57)	∞	Pyrogenic
D	42.06	Pyr (12.17), BaA (9.29)	∞	Pyrogenic
E	503	Phe (170.07), Ant (87.54)	0.48	Petrogenic
F	676.2	BkF (178.42), BaP (99.87)	2.82	Pyrogenic
G	398	Flt (194.77), Pyr (50.01)	6.96	Pyrogenic
H	511.15	Phe (157.66), DahA (51.00)	0.97	Mixed

BkF = Benzo[k]fluoranthene, BaP = Benzo[a]pyrene, Phe = Phenanthrene, Ant = Anthracene, BaA = Benz[a]anthracene, Pyr = Pyrene, Flt = Fluoranthene, DahA = Dibenzo[a,h]anthracene

Comparison with Regulatory Standards

Table 4: Comparison with International Soil Quality Guidelines (mg/kg).

Compound	Site A	Site F	Site H	CCME (2010)	USEPA RSL	Netherlands
BaP	91.86	99.87	74.01	0.6	0.00015	5
BaA	11.2	ND	1.07	0.6	-	5
BkF	199.21	178.42	5	-	-	25
DahA	ND	ND	51	0.1	-	5

All impacted sites except C and D exceded international guidelines by factors ranging from 10 to over 600,000.

Source apportionment

Table 5: Diagnostic Ratio Analysis Summary.

Site	HMW/ LMW	Phe/Ant	Flu/ (Flu+Pyr)	BaA/ (BaA+Chr)	Source
A	3.4	1.65	0.33	0.186	Pyrogenic
B	0.42	1.53	0.11	0.183	Petrogenic
E	0.48	1.94	0.1	0.211	Petrogenic
F	2.82	1.49	0.5	0	Pyrogenic
G	6.96	0	0.8	0.435	Pyrogenic
H	0.97	17.52	0.73	0.026	Mixed

The Eleme oil fields separated into distinct clusters: petrogenic (Sites B, E) indicating crude oil contamination, and pyrogenic (Sites A, F, G) indicating combustion-derived PAHs from gas flaring. Site H showed mixed sources.

Ecological risk assessment

Table 6: TEQ Values (mg/kg BaP-equivalent).

Site	TEQ	Risk Level
A	121.31	Extreme
B	2.63	Moderate
C	0.56	Low
D	2.54	Moderate
E	2.74	Moderate
F	127.66	Extreme
G	25.65	High
H	126.11	Extreme

Sites A, F, and H exhibited TEQ values exceeding 100 mg/kg, among the highest ever reported globally, exceeding Canadian residential guidelines (0.6 ppm) by 200-fold.

Table 7: Risk Quotients for Soil Biota.

Site	ΣPAHs (mg/kg)	RQ (Invertebrate)	RQ (Plant)	Classification
A	619.48	5.16-6.19	3.87-12.39	High Risk
B	573	4.78-5.73	3.58-11.46	High Risk
F	676.2	5.64-6.76	4.23-13.52	High Risk
G	398	3.32-3.98	2.49-7.96	High Risk
H	511.15	4.26-5.11	3.19-10.22	High Risk

Sites A, B, E, F, G, and H showed RQ values exceeding 3.0, indicating severe impairment of soil ecological function.

Discussion

Magnitude and spatial distribution of PAH contamination

The total PAH concentrations (Σ16 PAHs) recorded in this study, ranging from 5.57 mg/kg to 676.20 mg/kg, represent one of the most severe cases of PAH contamination documented in the Niger Delta and globally. These values substantially exceed those reported by Howard, et al. in the Ogoni region (0.5–45 mg/kg) and Luke, et al. in the Warri area (2-120 mg/kg), indicating that Eleme Oil Field has experienced either more frequent, voluminous, or recent hydrocarbon inputs.

The spatial heterogeneity observed across the eight sampling sites is attributable to multiple factors: proximity to point sources such as flow stations and pipelines; local topographical features influencing oil transport and infiltration; differential rates of natural attenuation governed by soil properties; and historical land use practices. The complete absence of PAHs in the control

site confirms the anthropogenic origin of contamination and validates the analytical protocols employed[4].

The extreme concentrations at Sites A (619.48 mg/kg), F (676.20 mg/kg), and H (511.15 mg/kg) classify these locations as contamination hotspots requiring immediate remediation. Comparatively, Sites C (5.57 mg/kg) and D (42.06 mg/kg) exhibited lower contamination, likely due to their relative distance from active petroleum infrastructure or more favorable conditions for natural attenuation.

Congener-specific distribution and environmental fate

The dominance of high molecular weight (HMW) PAHs (4-6 rings) at Sites A, F, and G-particularly Benzo[k] fluoranthene (199.21 mg/kg), Benzo[a]pyrene (99.87 mg/kg), and Indeno[1,2,3-cd] pyrene (15.22 mg/kg)-is environmentally significant. These compounds exhibit low water solubility, high hydrophobicity, and strong affinity for soil organic matter, resulting in prolonged environmental persistence with half-lives ranging from months to decades[2].

The presence of Benzo[a]pyrene (BaP) at concentrations exceeding 99 mg/kg represents a critical public health concern. BaP, classified by the International Agency for Research on Cancer (IARC) as a Group 1 carcinogen, exceeds the USEPA Regional Screening Level for residential soil (0.00015 mg/kg) by factors of 600,000–660,000. This comparison underscores the unacceptable risk to local communities that depend on these lands for subsistence agriculture and domestic water supply.

Conversely, the dominance of low molecular weight (LMW) PAHs at Sites B and E-with phenanthrene reaching 210.07 mg/kg-indicates a petrogenic signature characteristic of fresh or lightly weathered crude oil. LMW PAHs are generally more volatile, water-soluble, and susceptible to biodegradation than their HMW counterparts. However, their elevated concentrations suggest either recent spill events or continuous inputs overwhelming natural attenuation processes[5].

Source apportionment and its environmental implications

Diagnostic ratio analysis provides compelling evidence for dual-source contamination in the Eleme Oil Field, with significant implications for remediation strategy and regulatory enforcement.

Petrogenic Sources (Sites B and E): The HMW/LMW ratios of 0.42 and 0.48, combined with Flu/(Flu+Pyr) values below 0.11 and Phe/Ant ratios below 2.0, unequivocally indicate crude oil inputs. These signatures are consistent with direct releases from pipeline leaks, wellhead failures, or artisanal refining activities. The dominance of phenanthrene and anthracene at these sites further supports this interpretation, as these compounds are abundant in crude oil and typically persist under anaerobic conditions[5].

Pyrogenic Sources (Sites A, F, and G): HMW/LMW ratios of 3.40, 2.82, and 6.96 respectively indicate combustion-derived PAHs, with the BaA/(BaA+Chr) ratio at Site G (0.435) providing particularly strong diagnostic evidence[6]. The most plausible source is gas flaring-a pervasive feature of oil production in the Niger Delta for decades-which releases PAHs as incomplete combustion products that deposit onto surrounding soils via atmospheric transport[1]. The enrichment of 4- and 5-ring compounds at these sites is consistent with known emission profiles of gas flares.

Mixed Sources (Site H): The conflicting diagnostic ratios at Site H (HMW/LMW = 0.97, Phe/Ant = 17.52, Flu/(Flu+Pyr) = 0.73) suggest multiple contamination events from different sources or significant weathering transformations. The presence of Dibenzo[a,h]anthracene at 51.00 mg/kg at this site is particularly concerning, as this compound possesses a toxic equivalency factor (TEF) of 1.0 and poses significant carcinogenic risk.

Toxic equivalent quantity (TEQ) and ecological risk assessment

The TEQ values recorded at Sites A (121.31 mg/kg BaP-eq), F (127.66 mg/kg BaP-eq), and H (126.11 mg/kg BaP-eq) represent some of the highest ever reported for crude oil-impacted soils globally. These values exceed the Canadian Council of Ministers of the Environment (CCME) residential soil guideline of 0.6 mg/kg by approximately 200-fold. BaP alone accounted for 75–80% of the TEQ at these sites, underscoring its critical role as a driver of ecological and public health risk.

The Risk Quotient (RQ) analysis provides corroborating evidence of severe ecological impairment. RQ values for soil invertebrates ranged from 4.78 to 6.76 at the most contaminated sites, while plant RQ values ranged from 3.19 to 13.52. These values indicate PAH concentrations 3 to 13 times higher than levels known to cause adverse effects in soil biota[8].

The ecological consequences of such contamination are multifaceted: (1) alteration of soil microbial community structure, potentially inhibiting nitrogen fixation, nitrification, and organic matter decomposition; (2) suppression of seed germination, root elongation, and overall plant growth; (3) population declines in soil fauna, including earthworms and collembola; and (4) biomagnification through food webs, potentially affecting higher trophic levels[9-15].

Regulatory non-compliance and policy implications

Comparison of PAH concentrations with international regulatory standards reveals systematic and severe non-compliance. BaP, BaA, BkF, and DahA concentrations at contaminated sites exceed Canadian (CCME), United States (USEPA), and Dutch guidelines by factors ranging from 10 to over 600,000[16-25].

The absence of Nigerian-specific soil quality guidelines represents a critical regulatory gap. The international guidelines applied in this study are based on temperate climates and native species unrepresentative of the tropical conditions prevalent in the Niger Delta[25-30]. PAH behavior-including persistence, bioavailability, and toxicity-is strongly influenced by climatic factors such as temperature, precipitation, and solar radiation. Tropical soils, with their high organic matter content and rapid microbial turnover, may exhibit different PAH dynamics than temperate soils upon which international guidelines are based. Consequently, the development of Nigerian-specific screening values should be an urgent priority for regulatory agencies[30-37].

Study Limitations and Future Research Directions

- While this study provides a comprehensive assessment of PAH contamination in the Eleme Oil Field, several limitations merit acknowledgment:
- **Temporal variability:** The single-campaign sampling design precludes assessment of temporal trends or the effectiveness of future remediation interventions.

- **Bioavailability:** Total PAH concentrations may overestimate the fraction bioavailable to soil organisms and plants, as bioavailability is influenced by soil organic matter content, clay mineralogy, and contaminant aging.
- **Human health risk:** This study assessed ecological risk but did not include a quantitative human health risk assessment, which would require data on exposure pathways, population demographics, and local consumption patterns.
- **Alkylated PAHs:** The exclusion of alkylated PAHs-which may be more abundant in crude oil and exhibit different toxicity profiles-represents a potential underestimation of environmental risk.
- **Groundwater transport:** PAHs can leach from soils into groundwater, potentially affecting aquatic ecosystems and drinking water supplies, which were not investigated in this study.

Future research should address these limitations through:

a. long-term monitoring programs to assess temporal trends
b. bioavailability studies using passive samplers or biomimetic extractions
c. Comprehensive human health risk assessments; (4) inclusion of alkylated PAHs and other petroleum hydrocarbons
d. Integrated assessments of soil, groundwater, and surface water contamination.

Broader implications for the niger delta

The findings of this study have significant implications for the Niger Delta region as a whole. The contamination documented in Eleme is not an isolated case; similar conditions likely exist in other oil-producing areas, including Ogoni, Warri, and Bayelsa states. The persistence of PAH contamination reflects a systemic failure of environmental governance, characterized by weak regulatory enforcement and inadequate corporate responsibility.

The Nigerian government has enacted environmental legislation, including the National Environmental Standards and Regulations Enforcement Agency (NESREA) Act, yet enforcement has been inconsistent. The findings of this study underscore the urgent need for: (1) strengthened regulatory enforcement and imposition of significant penalties for non-compliance; (2) development of Nigerian-specific environmental quality guidelines; (3) increased investment in remediation technologies; (4) elimination of gas flaring through adoption of gas recovery technologies; and (5) greater transparency and accountability in the petroleum industry.

Representation of PAHS from chromatograms of (GC-FID)

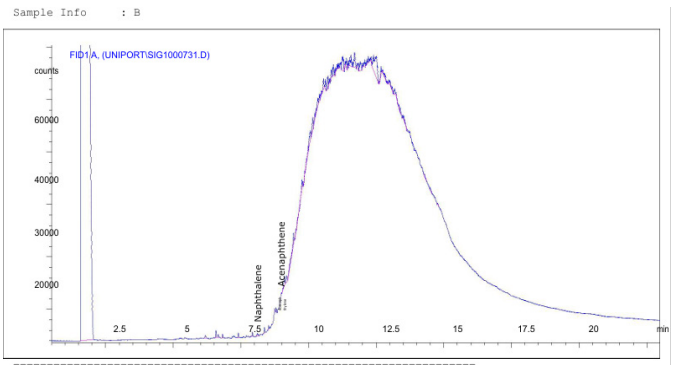

Figure 2: Representation of Chromatogram of PAH (in sample D)).

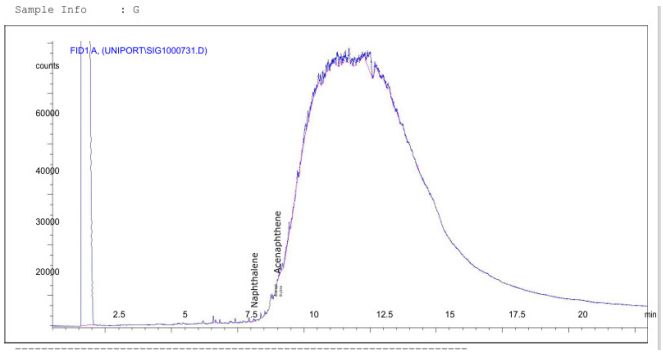

Figure 3: Representation of Chromatogram of PAH in sample (G).

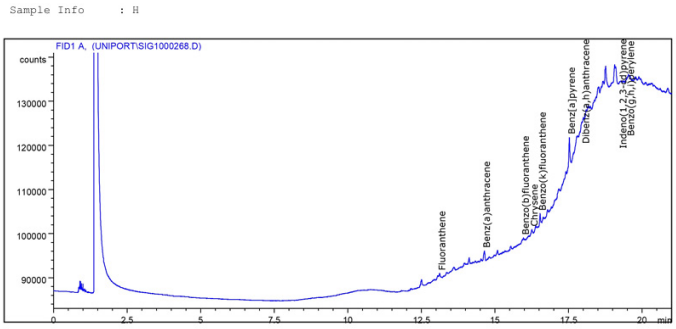

Figure 4: Representation of Chromatogram of PAH in sample (H)

Conclusions

The study reveals severe polycyclic aromatic hydrocarbon (PAH) contamination across the assessed soils, with total concentrations reaching up to 676.20 mg/kg-placing these sites among the most heavily impacted by crude oil globally. Diagnostic ratios confirm a dual-source origin, driven by both petrogenic inputs (crude oil spills) and pyrogenic activities (gas flaring). The environmental and biological risks are profound: Toxicity Equivalent (TEQ) values exceed international safety standards by up to 200-fold, while risk quotients demonstrate PAH levels 3 to 13 times higher than thresholds known to harm soil biota. Driven by extreme concentrations of potent carcinogens such as Benzo(a)pyrene and Benzo(k)fluoranthene, regulatory non-compliance was widespread across almost all sampling sites. These findings underscore an alarming ecological and public health risk, highlighting an urgent need for immediate regulatory intervention and target remediation strategies.

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