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GEOCHEMISTRY AND ECOLOGICAL RISK ASSESSMENT OF SEDIMENTS IN THE ESTUARY MANGROVE FORESTS OF GBARAMATU KINGDOM OF NIGER DELTA, NIGERIA

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ABSTRACT

Mangrove sediments serve as natural sinks for metals from both natural and human-impacted watersheds. This study investigated the geochemical composition and environmental status of sediments in the Gbaramatu Kingdom, Niger Delta, through a comparative analysis of the Oporoza, Okerenkoko, Kurutie, and Kunuma stations. The research employed multivariate geostatistical techniques, including correlation matrices and hierarchical cluster analysis, to distinguish between natural lithogenic signatures and anthropogenic impacts. Geochemical results revealed that Oporoza sediments were primarily silica-rich (SiO_2: 31.85–49.84 mg/kg), whereas the Okerenkoko, Kurutie, and Kunuma (OKK) stations were dominated by iron oxides (Fe_2O_3: 48.41–538.85 mg/kg) and higher sodium levels. Heavy metal concentrations across all sites remained well within WHO permissible limits, suggesting negligible toxic metal enrichment at the time of the study. However, organic geochemical analysis highlighted significant environmental stressors: mean Total Petroleum Hydrocarbon (TPH) and Total Hydrocarbon Content (THC) at the OKK stations (276.12 mg/kg and 331.29 mg/kg respectively) substantially exceeded DPR target value of 50 mg/kg, while Oporoza remained largely within regulatory thresholds. Multivariate analysis identified a dominant lithogenic factor governing major oxides, but revealed distinct hydrocarbon fingerprints. At Oporoza, TPH was specifically associated with vanadium ($r = 0.927$), an indicator of petroleum derived input. Conversely, at the OKK stations, TPH showed near perfect correlations with aluminum and iron oxides ($r > 0.94$), indicating a more uniform integration of hydrocarbons into the fine-grained mineral matrix. Dendrogram analysis confirmed these patterns, showing isolated hydrocarbon clusters at Oporoza compared to more integrated clusters at the OKK stations. These findings demonstrated the efficacy of multivariate geostatistics in identifying localized pollution dynamics and provide a vital baseline for the sustainable management of the Niger Delta mangrove ecosystems.

Keywords: Mangrove forest, Heavy metals, Niger Delta, Ecosystem.

INTRODUCTION

Nigeria hosts the world's third-largest mangrove ecosystem, covering approximately 975,000 km² of coastal swamps from Badagry to Bakassi (World Bank, 1995). This ecosystem reaches its peak complexity in the Niger Delta, where an intricate network of creeks and rivers

facilitates significant nutrient and organic matter input. While this rich base supports massive biomass, the resulting anaerobic, sulphide-rich sediments are prone to retaining water-borne heavy metals (Tam *et al.,* 2000). Tidal fluctuations further complicate this by allowing metal mobilization and bioavailability through sulphide oxidation. In the Gbaramatu region, these ecosystems are inextricably linked to anthropogenic pressures. Due to their high fine-particle and organic content, mangrove sediments serve as natural sinks for metals from both natural and human-impacted watersheds (Marchand *et al*., 2011). The partitioning of metals across phases, such as carbonates, sulphides, and iron-manganese oxyhydroxides (Chakraborty *et al.,* 2016) is governed by sediment pH, redox potential, and particle size (Otero *et al*., 2009). These factors are influenced by forest zonation, local hydrology, and specific tree species (Marchand *et al*., 2003, 2004). Oil refining activities further exacerbate metal accumulation. During diagenesis, metals can be released into pore waters under suboxic or anoxic conditions (Marchand *et al*., 2012; Chakraborty *et al.,* 2016), eventually reprecipitating (Noël *et al.,* 2014) or exporting to surface waters (Holloway *et al.,* 2016). This contamination spreads to living organisms, including fish, crabs, and mangrove tissues (Parvaresh *et al.*, 2011; Chakraborty *et al*., 2014). With global mangrove loss at 1% annually (Duke *et al*., 2007), sediment oxidation risks severe acidification (Dent, 1986). Understanding these behaviours is vital for maintaining ecosystem services (Brander *et al*., 2012; Lee *et al.,* 2014). Although Solomon *et al*. (2022) successfully categorized the origins of organic matter in the Cross River Estuary, there remains a notable scarcity of specific geochemical data for the Gbaramatu Kingdom. Current information for this region is insufficient to form a comprehensive environmental profile. Consequently, this research is designed to evaluate sediment geochemistry, pinpoint primary sources of contamination, and conduct a thorough assessment of associated ecological risks.

MATERIALS AND METHODS

Study Area

The study area is located in Gbaramatu Kingdom, Warri South-West LGA, Delta State, Nigeria. The region is characterized by extensive mangrove vegetation and an intricate network of creeks. The study identified twelve distinct stations within Okerenkoko ($5^0$37’58’N, $5^0$23’43’E), Kurutie ($5^0$35’00’N, $5^0$20’34’E), Kunukunuma ($5^0$35’05’N, $5^0$19’49’E), and Oporoza ($5^0$35’58’N, $5^0$16’13’E) (Figure 1).

Sample Collection and Preparation

Sediment samples were collected from twelve locations across Okerenkoko (OK1-OK3), Kurutie (KT1-KT3), Kunukunuma (KU1-KU3), and Oporoza (OPZ1-OPZ3) with a sample grab and then placed inside a plastic ziplock. Samples for organic analyses were placed in a metal container and marked differently to identify each sample. Samples were air-dried, homogenized, and preserved for further analysis.

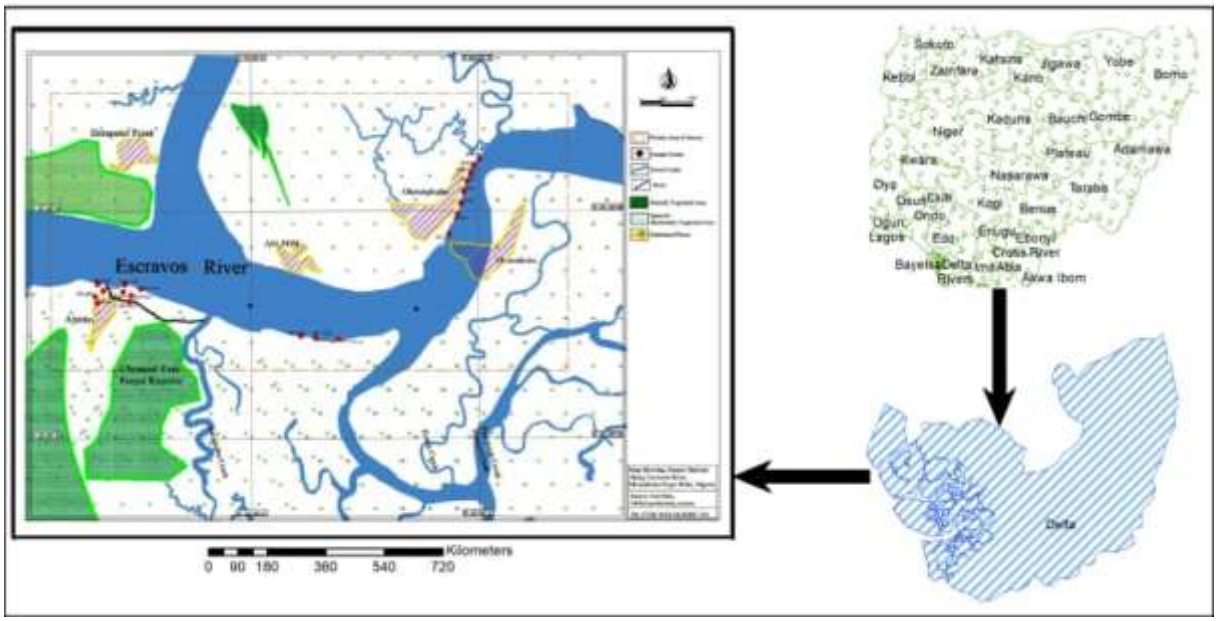


Figure 1: Map of the communities showing sampling locations

Determination of Heavy Metals

Approximately 20g of sediment was air-dried and crushed to fine powder for homogeneity. Samples were acid digested using nitric acid on hot plates. The digest was filtered and made up to 50 ml and subsequently analyzed for heavy metal content using the atomic absorption spectrophotometer (AAS) (Unicam 700 series) to quantify concentrations of vanadium, barium, copper, nickel, zinc, chromium, and selenium (Wilson *et al*., 2025). Appropriate quality control measure was routinely followed to ensure accuracy of results.

Determination of Total Organic Carbon (TOC)

The TOC was measured using UV-Visible Spectrophotometry. For analysis, 1.0g of sample was used for expected carbon content of 1−3%, and 2.0g for content <1%. The organic geochemistry analysis was conducted on samples from Okerenkoko (OK stations) and Oporoza (OPZ stations) only, since these sites had artisanal refineries around them.

Ecological Risk Assessment Calculations
Contamination Factor (Cf)

The contamination factor is used to determine the degree of enrichment of a specific heavy metal in the sediment relative to its concentration in a pristine or background environment. It is calculated using the following formula:

Contamination factor (CF) = $C_{sample}/C_{bakground}$

Where: C_{sample} = measured concentration of heavy metal in the sediment sample

$C_{background}$ = background concentration of the same metal in pristine/unpolluted area

In the absence of site-specific pre-industrial data, researchers often use average shale values or regional background levels, such as the 30–100 mg/kg range cited for iron in the Niger Delta. The interpretation are given thus: Cf<1 indicates low contamination; 1≤Cf<3 indicates moderate contamination; 3≤Cf<6 indicates considerable contamination; and Cf≥6 indicates very high contamination.

Geo-accumulation Index (Igeo)

The Igeo is a standard geochemical method used to assess metal pollution in sediments by comparing current concentrations with pre-industrial levels (Buhari *et al*,. 2020). The formula is expressed as:

$$Igeo=\log_2(1.5\times BnCn)$$

Where: Cn is the measured concentration of the metal 'n' in the sediment.

Bn is the geochemical background concentration of the metal 'n'. 1.5 is a constant

This factor is included to account for natural fluctuations in the background levels of metals due to lithological variations (geogenic effects) in the sediment. The Igeo values are typically categorized into seven classes, ranging from Class 0 (Igeo≤0, unpolluted) to Class 6 (Igeo>5, extremely polluted).

Statistical Analysis

Descriptive statistics, Pearson correlation matrices, and hierarchical cluster analysis were used to interpret the data.

RESULTS

The geochemical compositions of sediments across the study sites (Okerenkoko, Kurutie, Kunuma, and Oporoza) are detailed in Table 1. A distinct variation in major oxide concentrations was observed between the stations. At the Okerenkoko (OK), Kurutie (KT), and Kunuma (KU) stations, Fe_2O_3 was the dominant oxide, with concentrations ranging from 48.41 mg/kg in OK2 to 538.85 mg/kg in OK1. In contrast, the Oporoza (OPZ) sediments were characterized by significantly higher SiO_2 levels (31.85–49.84 mg/kg) and lower Fe_2O_3 concentrations (9.66–11.66 mg/kg). Na_2O concentrations were notably higher in the OK, KT, and KU stations (88.17–126.73 mg/kg) compared to the OPZ station (0.13–0.18 mg/kg).

Table 1: Major oxide compositions (mg/kg) in sediments of the Estuary Mangrove Forests of Gbaramatu Kingdom, Niger Delta, Nigeria

Indices	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O
OK1	8.3	3.14	538.85	4.65	52.89	0.001	88.17	0.96
OK2	2.33	0.28	48.41	2.92	0.53	1.02	91.41	0.25
OK3	5.71	1.3	292.29	3.33	62.7	0.001	94.107	0.86
KT1	7.23	2.89	483.38	11.43	70.47	0.001	88.58	0.6
KT2	7.42	1.98	519.2	10.48	72.86	4.94	117.59	2.29
KT3	4.94	0.26	510.76	10.31	61.52	0.001	126.04	2.28
KU1	3.74	1.53	116.02	4.18	8.52	0.001	116.75	2.26
KU2	7.23	2.12	373.34	13.36	83.39	0.001	126.73	1.19
KU3	10.03	5.33	473.52	9.61	79.86	1.95	102.57	1.48
OPZ1	42.28	13.18	9.66	0.08	0.22	1.84	0.13	0.06
OPZ2	31.85	19.45	11.66	0.09	0.27	1.67	0.18	0.06
OPZ3	49.84	14.85	9.83	0.09	0.25	-	0.16	0.06

Key: SiO_2= silica, Al_2O_3 = aluminum oxide, Fe_2O_3= iron oxide, MnO= manganese oxide, MgO = magnesium oxide, CaO = calcium oxide, Na_2O= sodium oxide, K_2O= potassium oxide

The results of heavy metal concentrations alongside WHO (1996) regulatory standards are presented in Table 2. Across all sampled stations, concentrations of Cu, Ni, Zn, Cr, and Se remained well below the maximum permissible limits set by the WHO. The OPZ stations exhibited higher detectable levels of Vanadium (0.06–0.09 mg/kg), Barium (0.02–0.04 mg/kg), and Chromium (2.91–3.6 mg/kg) compared to the OK, KT, and KU (OKK) stations, where these elements were frequently below detection limits (<0.001 or <0.006 mg/kg).

Table 2: Heavy metal concentrations in the sediments of the Estuary Mangrove Forests of Gbaramatu Kingdom, Niger Delta, Nigeria

Indices	V	Ba	Cu	Ni	Zn	Cr	Se
OK1	<0.001	<0.001	1.56	1.64	-	<0.006	0.013
OK2	<0.001	<0.001	1.47	1.54	1.21	<0.006	0.11
OK3	<0.001	<0.001	1.76	1.32	1.27	<0.006	0.09
KT1	<0.001	<0.001	0.88	<0.001	1.20	<0.006	0.055
KT2	<0.001	<0.001	0.98	<0.001	1.40	<0.006	0.01
KT3	<0.001	<0.001	0.94	<0.001	1.07	<0.006	0.032
KU1	<0.0001	<0.001	1.2	<0.001	1.10	<0.006	0.043
KU2	<0.001	<0.001	1.34	<0.001	10.41	<0.006	0.065
KU3	<0.001	<0.001	0.94	<0.001	0.22	<0.006	0.032
OPZ1	0.06	0.02	6.85	6.78	1.10	3.60	0.32
OPZ2	0.09	0.04	6.49	8.11	25.30	3.18	0.75
OPZ3	0.06	0.04	6.76	9.2	30.76	2.91	0.66
WHO, 1996	NA	NA	100	50	300	100	10

Key: V= vanadium, Ba= barium, Cu= copper, Ni= nickel, Zn= zinc, Cr= chromium, Selenium

The organic geochemical parameters, including total organic carbon (TOC), total hydrocarbon content (THC), and total petroleum hydrocarbons (TPH), are summarized in Table 3. The mean THC and TPH concentrations at the Okerenkoko stations (331.29 mg/kg and 276.12 mg/kg respectively) significantly exceeded the DPR (2018) target value of 50 mg/kg. Conversely, mean concentrations at the Oporoza stations for THC (57.4 mg/kg) and TPH (28.47 mg/kg) were notably lower, with TPH values falling below the DPR target threshold.

Table 3: Organic geochemistry parameters in sediments of the Estuary Mangrove Forests of Gbaramatu Kingdom, Niger Delta, Nigeria

Parameters	TOC mg/kg	THC mg/kg	TPH mg/kg
MS. OK1	6.05	353.48	324.79
MS .OK2	5.66	328.38	243.85
MS. OK3	5.09	312.01	259.72
MS. OPZ 1	7.61	46.51	28.18
MS. OPZ 2	8.97	38.4	30.42
MS. OPZ 3	8.19	30.42	26.81
Mean concentration (OK)	5.6	331.29	276.12
Mean concentration (OPZ)	8.25	57.4	28.47
Target Value DPR, 2018	-	50	50
USEPA, 2023	20	-	-

Key: TOC= total organic carbon, THC= total hydrocarbon content, TPH= total petroleum hydrocarbons

The statistical relationships between major oxides, trace elements, and hydrocarbons are detailed in correlation matrices (Figure 2). The matrix revealed strong positive correlations among SiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, Na_2O, Zn, Ba, and Se. Specifically, SiO_2 showed a coefficient of 1.000 with both Zn and Se, and 0.980 with MnO. Al_2O_3 and Fe_2O_3 exhibited a correlation of 0.983, while MnO and Ba were perfectly correlated at 1.000. Conversely, CaO showed negative correlations with Ni (−0.984) and MnO (−0.798). Copper displayed strong negative correlations with Al_2O_3 (−1.000) and Fe_2O_3 (−0.986). Results from OKK stations showed that in the Okerenkoko, Kurutie, and Kunuma matrix, SiO_2 correlated with Al_2O_3 at 0.829 and Fe_2O_3 at 0.851. TPH exhibits near-perfect correlations with Al_2O_3 (0.985), Fe_2O_3 (0.945), and MnO (0.933). Vanadium, barium, and chromium remarkably showed zero correlation (0.000) with all other variables in this dataset.

	SiO2	Al2O3	FeO3	MnO	MgO	CaO	Na2O	K2O	V	Ba
SiO2	1.000									
Al2O3	0.829									
FeO3	0.851	0.517								
MnO	0.538	0.266	0.619							
MgO	0.905	0.590	0.944	0.480						
CaO	0.163	-0.015	0.201	0.183	0.143					
Na2O	-0.036	-0.314	0.110	0.542	-0.070	0.199				
K2O	0.037	-0.169	0.253	0.271	0.080	0.360	0.787			
V	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
Ba	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Cu	-0.110	-0.032	-0.395	-0.669	-0.137	-0.310	-0.426	-0.505	0.000	0.0
Ni	-0.145	-0.046	-0.265	-0.761	-0.077	-0.188	-0.727	-0.647	0.000	0.0
Zn	-0.015	-0.123	0.220	-0.348	0.283	0.184	-0.662	-0.358	0.000	0.0
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0
Se	0.090	0.068	-0.095	0.131	0.109	-0.503	0.026	-0.180	0.000	0.0
TOC	0.324	0.540	0.398	0.367	0.120	0.117	-0.985	0.013	0.000	0.0
THC	0.539	0.724	0.604	0.578	0.352	-0.122	-0.998	0.250	0.000	0.0
TPH	0.916	0.985	0.945	0.933	0.812	-0.652	-0.792	0.745	0.000	0.0

Figure 2: Correlation Matrix of Okerenkoko, Kurutie, and Kunuma

The relationships among variables at the different study sites are further illustrated by the following hierarchical cluster diagrams. At Oporoza, the dendrogram in Figure 3 identified a primary cluster consisting of SiO_2, Se, Zn, Ba, MnO, MgO and Na_2O and a secondary cluster groups consisting of Fe_2O_3, Al_2O_3, and V. Nickel and chromium grouped together before associating with CaO whereas, THC and TPH formed an independent cluster that only merged with the other variables at large linkage distances. Furthermore, at Okerenkoko, Kurutie, and Kunuma stations the dendrogram in Figure 4 showed TPH integrating with major oxides at significantly shorter linkage distances than those observed in the Oporoza samples.

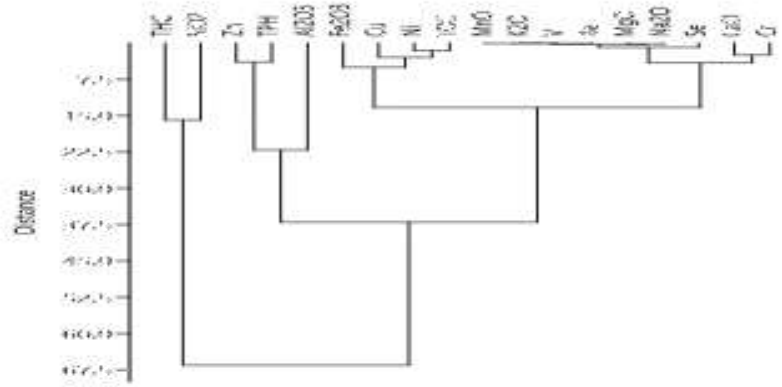


Figure 3: Dendogram of Oporoza

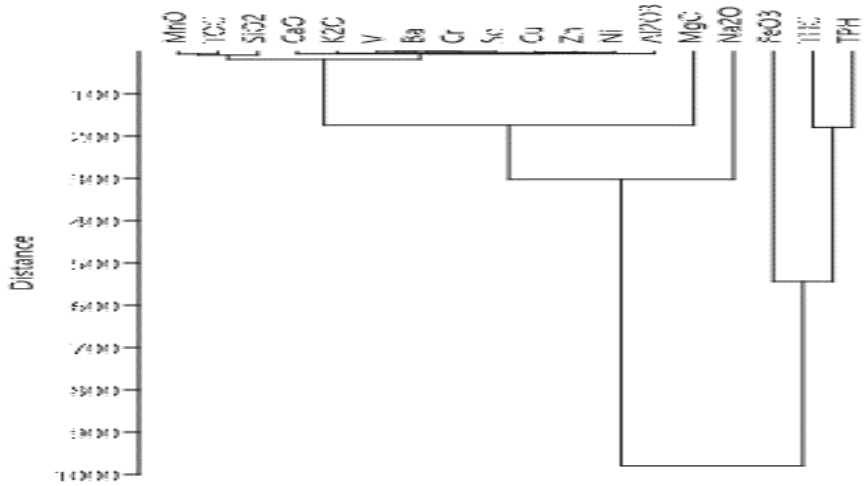


Figure 4: Dendrograam of Okerenkoko, Kurutie and kunuma

DISCUSION

The geochemical composition of sediments across the Gbaramatu Kingdom is largely controlled by lithogenic processes, indicating that the weathering of parent rocks and subsequent sediment transport are the dominant factors governing the distribution of major oxides and several trace elements. The strong correlations among SiO_2, Al_2O_3, Fe_2O_3, MnO, and MgO suggest that these oxides are derived from common mineralogical sources and have experienced comparable weathering, transport, and depositional histories. This pattern is typical of estuarine and deltaic environments, where aluminosilicate

minerals form the dominant component of the sediment matrix and largely determine the distribution of major elements through natural geological processes. Similar observations have been widely reported for tropical deltaic systems, where sediment chemistry primarily reflects the combined influence of continental rock weathering, riverine transport, and sediment deposition. Despite the overall dominance of lithogenic controls, the spatial variability observed in the major oxide composition indicates that the geological framework is not entirely homogeneous across the study area. In particular, the elevated concentrations of iron oxides at the Kurutie and Kunukunuma stations point to more intense weathering of iron-rich parent materials and favourable oxidizing conditions during sediment deposition. Such spatial variations are common in estuarine environments, where local differences in sediment provenance, hydrodynamic conditions, and redox processes influence the accumulation of iron-bearing minerals. Beyond their geological significance, iron oxides play a critical ecological role because they represent highly reactive mineral phases capable of adsorbing phosphorus and a wide range of trace metals. This adsorption process reduces phosphorus bioavailability and influences nutrient cycling, contaminant mobility, and overall sediment geochemistry (Sabur, 2019). Comparable iron enrichment has been documented in mangrove and estuarine sediments of other tropical coastal environments, where ferric oxides act as efficient scavengers of nutrients and potentially toxic elements, thereby regulating sediment fertility and controlling redox-sensitive biogeochemical processes.

Conversely, the Okerenkoko station exhibits a mineralogical framework dominated by silica and alumina, reflecting a greater contribution of terrigenous detritus derived from upstream weathering processes. Such silica-rich sediments are commonly associated with quartz-dominated deposits originating from prolonged mechanical weathering and riverine transport. Similar observations have been reported for other sections of the Niger Delta, where sediment composition is strongly influenced by continental weathering products transported through distributary channels (Okiotor and Ighodaro, 2020). Comparable lithogenic dominance has also been documented in estuaries of the Ganges-Brahmaputra Delta and the Mississippi Delta, where quartz and aluminosilicate minerals constitute the principal sediment-forming materials due to intense fluvial input (Konta, 2009). Another notable feature of the sediments is the widespread occurrence of sodium oxide across all sampling locations. This pattern reflects the influence of saline pore waters resulting from regular tidal inundation and marine intrusion (Heiss *et al*., 2022). Elevated salinity is a defining characteristic of mangrove ecosystems and plays a major role in shaping both sediment geochemistry and ecosystem functioning. Excessive salinity imposes osmotic stress on mangrove vegetation, limits nutrient uptake, disrupts physiological processes, and reduces the reproductive capacity of species such as *Rhizophora* (Duarte, 2016). Comparable sodium enrichment has been documented in mangrove ecosystems across Southeast Asia and West Africa, where increasing marine influence alters sediment chemistry while

also affecting vegetation structure and productivity (Alsamadany *et al.*, 2020). Although the sediments throughout the study area share a common lithogenic origin, multivariate geostatistical analysis revealed subtle, but important mineralogical differences among the sampling stations. Oporoza showed a stronger association between silica and selected trace elements, particularly zinc and selenium, suggesting that these elements are partly incorporated within the primary silicate minerals. In contrast, the Okerenkoko, Kurutie, and Kunukunuma (OKK) stations exhibited a more complex mineralogical assemblage in which silica is closely associated with aluminium and iron oxides rather than with trace metals. Similar spatial variations have been reported from other petroleum-producing deltaic environments, where differences in sediment provenance, depositional energy, and anthropogenic disturbances produce distinct mineralogical signatures despite an overall common geological setting.

The distribution of trace metals further indicates that natural lithogenic processes alone cannot account for the observed geochemical patterns. Oporoza exhibited localized enrichment of zinc, nickel, and copper, suggesting that anthropogenic inputs are superimposed on the natural geological background. Considering its proximity to the Escravos industrial corridor, these enrichments are most likely linked to petroleum exploration and production, shipping operations, industrial discharges, and increased maritime activities. Similar localized heavy metal enrichment has been reported in other parts of the central Niger Delta, where industrial activities have created contamination hotspots within otherwise geologically comparable environments (Egirani and Alaowei, 2024). Although the concentrations of several trace metals remain within internationally accepted guideline limits, their presence in sediments remains environmentally important because sediments act as long-term sinks for contaminants. Changes in physicochemical conditions, including fluctuations in redox potential, pH, or physical disturbance of the sediment, can remobilize these metals into the overlying water column through desorption and oxidation-reduction reactions. Consequently, sediments represent not only repositories of contamination but also potential secondary sources of pollution that may pose chronic ecological risks to aquatic organisms and mangrove ecosystems. Selenium is widely distributed throughout the study area and deserves particular attention because it exhibits a dual role in the environment. While it is an essential micronutrient at low concentrations, excessive selenium becomes toxic to plants and aquatic organisms. Elevated selenium concentrations can damage chlorophyll, induce leaf chlorosis, impair photosynthesis, and reduce the overall growth and vitality of mangrove species (Silva *et al.*, 2018). Similar selenium enrichment has been reported in estuarine environments affected by petroleum-related wastes, coal combustion residues, and industrial effluents, where selenium accumulates efficiently in sediments and may subsequently biomagnify through aquatic food webs. The observed distribution therefore highlights the importance of continuous environmental

monitoring to minimise potential long-term ecological impacts on the mangrove ecosystem.

Whereas most major oxides display consistent lithogenic behaviour, some elements exhibit distinct geochemical characteristics that point to alternative sources or mineral hosts. Calcium oxide behaved independently of the dominant silicate assemblage, indicating that carbonate minerals represent a separate geochemical phase within the sediments. These carbonate materials are most likely derived from shell fragments, biogenic debris, and localized marine sedimentation rather than from continental weathering processes. Similar separation between silicate and carbonate mineral assemblages has been widely reported in estuarine sediments worldwide (Torres *et al*., 2020). Copper also displayed behaviour that differed from the principal lithogenic framework, suggesting contributions from localized mineralisation or anthropogenic activities. In petroleum-producing environments, copper is commonly associated with corrosion products, industrial wastes, antifouling paints, and oil-related operations rather than with natural weathering alone. Comparable patterns have been documented in coastal sediments of the Niger Delta and other hydrocarbon-producing regions, where localized industrial activities are recognised as important sources of copper enrichment (Jeyasingh *et al.,* 2026). The statistical independence of vanadium, barium, and chromium within the OKK stations further suggested that these elements are controlled by geochemical processes different from those influencing the dominant lithogenic components. At Oporoza, however, these elements cluster with other geochemical variables, indicating stronger associations with specific mineral phases and industrial inputs. Likewise, the separation of nickel and chromium into distinct geochemical populations supports the presence of multiple sediment sources and heavy mineral assemblages that differ from the dominant aluminosilicate matrix. Such geochemical differentiation is widely recognized as evidence of mixed natural and anthropogenic controls on sediment composition (Pawar and Pawar, 2016).

Hydrocarbon-related variables displayed contrasting relationships with sediment minerals across the study area, reflecting differences in the extent and nature of petroleum contamination. At Oporoza, petroleum hydrocarbons are closely associated with vanadium, a trace element widely recognized as a reliable geochemical indicator of crude oil contamination. Vanadium is naturally concentrated in petroleum because it occurs within porphyrin compounds and is therefore frequently used to distinguish petroleum-derived contaminants from natural geochemical backgrounds. Similar associations between vanadium and petroleum hydrocarbons have been reported throughout the Niger Delta and other oil-producing regions, confirming its value as a tracer of hydrocarbon pollution (Awan *et al*., 2021). The hierarchical cluster analysis reinforced this interpretation by showing that hydrocarbon variables form a distinct geochemical group at Oporoza. This clustering suggests that petroleum contamination represents an external anthropogenic input superimposed upon the

natural sedimentary system rather than a component of the background geochemistry. This finding agreed with previous investigations in the Niger Delta, where petroleum hydrocarbons commonly occurred as discrete contaminant phases associated with oil exploration, pipeline leakages, and shipping activities (Elekima *et al*., 2026). In contrast, the OKK stations exhibited a different hydrocarbon signature in which petroleum-related compounds are closely associated with alumina, iron, and manganese oxides. This relationship indicates that hydrocarbons have become adsorbed onto clay minerals and iron oxide surfaces, resulting in a more diffuse distribution throughout the sediment matrix rather than occurring as isolated contaminant accumulations. Similar adsorption mechanisms have been widely reported in estuarine environments, where fine-grained sediments provide extensive surface areas for hydrocarbon sorption and long-term preservation (Ugochukwu, 2011). This mechanism explains why petroleum residues often persist within mangrove sediments long after visible surface contamination has disappeared. These contrasting hydrocarbon signatures highlight the importance of distinguishing localized point-source contamination from widespread diffuse pollution when evaluating environmental quality. Such interpretations are consistent with environmental assessment frameworks proposed by the Department of Petroleum Resources (DPR, 2018) and the World Health Organization (WHO, 1996), both of which recommend integrating geochemical indicators with multivariate statistical techniques to distinguish natural background conditions from anthropogenic contamination.

The distribution of organic matter is also closely linked to sediment texture and mineralogical composition throughout the study area. Fine-grained sediments enriched in alumina, iron oxides, and clay minerals provide abundant adsorption sites that promote the accumulation and long-term preservation of both naturally derived organic matter and petroleum hydrocarbons. This relationship is well established in sediment geochemistry because clay minerals and iron oxides possess high specific surface areas and strong adsorption capacities that enhance the retention of organic compounds (Cai *et al*., 2013). At Oporoza, the close association between organic carbon and clay-rich minerals indicates that fine-grained sediments serve as important repositories for both terrestrial organic matter and petroleum-derived contaminants. Similar relationships have been documented in mangrove ecosystems in Brazil, India, China, and the Niger Delta, where organic carbon storage is strongly influenced by sediment grain size and mineral surface characteristics (Ugochukwu, 2011). The OKK stations, however, displayed a contrasting pattern in which sodium-rich minerals appear to limit the accumulation of organic matter and hydrocarbons. This relationship most likely reflects the influence of elevated salinity on sediment biogeochemistry. Increased salinity can modify pore-water chemistry, reduce the adsorption efficiency of organic compounds, and alter microbial degradation pathways, ultimately affecting carbon preservation within mangrove sediments (Luo *et al*., 2019). Comparable trends have been observed in hypersaline estuarine

environments, where elevated sodium concentrations significantly influence microbial activity and organic carbon cycling (Zhang *et al*., 2021). Overall, the combined application of correlation matrix analysis and hierarchical cluster analysis demonstrates that, although the sediments of the Gbaramatu Kingdom share a common lithogenic origin, their geochemical characteristics vary spatially due to differences in mineralogical composition, hydrocarbon inputs, industrial activities, sediment texture, and estuarine hydrodynamics. The interplay between natural weathering processes and anthropogenic influences has shaped the present geochemical characteristics of these sediments. These findings highlight the value of multivariate geostatistical techniques in distinguishing natural geochemical backgrounds from contamination signals, thereby providing a robust scientific basis for environmental monitoring, pollution assessment, and the sustainable management of the Niger Delta mangrove ecosystem.

CONCLUSION

This study demonstrated that the distribution of major oxides is largely controlled by lithogenic processes, with strong associations among SiO_2, Al_2O_3, Fe_2O_3, MnO, and MgO reflecting their common origin through parent-rock weathering, fluvial transport, and sediment deposition. However, spatial variations in elemental associations indicate that local sediment provenance, estuarine hydrodynamics, and depositional conditions also influence sediment composition. Although heavy metal concentrations generally remain below the permissible limits recommended by WHO, their distribution revealed localized anthropogenic impacts, particularly around Oporoza, where enrichments of zinc, nickel, copper, selenium, and vanadium are consistent with petroleum exploration, industrial activities, and maritime operations. The close association between vanadium and petroleum hydrocarbons at Oporoza indicates a distinct crude oil contamination signature, whereas the integration of hydrocarbons with fine-grained, alumina- and iron-rich sediments at the Okerenkoko, Kurutie, and Kunukunuma (OKK) stations suggests long-term retention of petroleum residues. The elevated total hydrocarbon content (THC) and total petroleum hydrocarbon (TPH) concentrations at the OKK stations, which exceeded DPR target values, further highlight the persistence of hydrocarbon contamination.

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