Geochemical Assessment and Statistical Characterisation of Heavy Metal Contamination in Estuarine Sediments of Ondo State, Nigeria.

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ABSTRACT

Estuarine sediments in developing coastal regions are becoming increasingly vulnerable to heavy metal contamination caused by human activities, yet comprehensive assessments remain rare in West African coastal systems. This study evaluates heavy metal concentrations in surface sediments from six estuarine sites along the Igbokoda and Igbekebo rivers in Ondo State, Nigeria, employing multivariate statistical methods to identify contamination sources and spatial patterns. Twenty metals (Ag, Al, As, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Se, Th, U, V, Zn) were analysed in 18 sediment samples using ICP-OES after aqua regia digestion. Data were subjected to correlation analysis, Principal Component Analysis (PCA), and radar fingerprinting to characterise geochemical signatures. Significant spatial variability was observed, with iron concentrations higher in Igbokoda sites (1456.79-1665.09 mg/kg) compared to Igbekebo sites (147.57-661.62 mg/kg), while potassium, magnesium, and sodium showed the opposite pattern, with substantially higher concentrations in Igbekebo sites. Uranium concentrations ranged from below detection limits to 2.65 mg/kg, whereas thorium reached maximum levels of 12.65 mg/kg. Strong positive correlations were found between Fe-Mn ($r = 0.89$), and among alkali and alkaline earth metals. PCA revealed distinct clustering of sites based on major element compositions, accounting for 68.4% of total variance. The findings reveal notable geochemical heterogeneity across the estuarine system, with Igbekebo sites showing potential radiogenic enrichment that warrants further investigation. This baseline assessment provides vital data for environmental monitoring and risk assessment in Nigeria's ecologically sensitive coastal zones.

Keywords: Heavy metals; Estuarine sediments; Multivariate analysis; Principal component analysis; Environmental contamination; Nigeria

INTRODUCTION

Estuarine sediments act as active repositories for heavy metals, capturing signals from natural weathering processes and human-related inputs across terrestrial and marine environments (Zhou et al., 2021). These transitional ecosystems are especially vulnerable to contamination because of their location at the boundary between freshwater and marine systems, coupled with intense human activities such as urbanisation, agriculture, and industrial growth (Wang et al., 2020). The biogeochemical cycling of metals in estuarine sediments is controlled by intricate interactions involving pH, redox conditions, organic matter content, grain size, and salinity gradients (Zhang et al., 2023).

Heavy metals present significant environmental and health concerns due to their persistence, bioaccumulation potential, and toxicity even at relatively low concentrations (Ali et al., 2022). While some metals such as iron (Fe), manganese (Mn), copper (Cu), and zinc (Zn) are essential micronutrients, they can become toxic at elevated levels. Others, including lead (Pb), uranium (U), thorium (Th), and arsenic (As), have no known biological function and pose immediate health risks through various exposure pathways (Chen et al., 2020).

In Nigeria, coastal environments are facing increasing anthropogenic pressure, especially in the Niger Delta region where oil exploration, urban expansion, and industrial activities have heightened over recent decades (Adewuyi & Olowu, 2019). However, comprehensive sediment quality assessments remain sporadic, with

limited emphasis on radiogenic elements and systematic spatial characterisation. This knowledge gap is particularly evident in southwestern Nigerian coastal systems, where estuarine environments are crucial in supporting ecological functions and local livelihoods.

Multivariate statistical techniques have become valuable tools in environmental geochemistry, helping researchers to decipher complex metal relationships, identify pollution sources, and differentiate between natural and human-made contributions (Liu et al., 2021). Techniques such as Principal Component Analysis (PCA), correlation matrices, and fingerprinting approaches offer solid frameworks for analysing large geochemical datasets and supporting evidence-based environmental management decisions.

Ondo State, situated in south-western Nigeria, includes various estuarine systems that meet the Atlantic Ocean and support crucial ecological and economic activities. The Igbokoda and Igbekebo river systems serve as vital case studies for understanding metal behaviour in West African coastal environments, yet their sediment geochemistry remains inadequately understood, especially concerning radiogenic elements and spatial contamination patterns.

This study aims to: (1) quantify concentrations of 20 metals across six estuarine sediment sites in the Igbokoda and Igbekebo rivers, (2) explore inter-metal relationships using correlation analysis to identify geochemical associations, and (3) apply Principal Component Analysis and radar fingerprinting to characterise site-specific contamination signatures and potential sources. By integrating spatial and statistical perspectives, this research provides essential baseline data for sediment quality monitoring and contributes to the broader understanding of coastal environmental dynamics in West Africa.

MATERIALS AND METHODS

Study Area

The study was carried out in two estuarine river systems in Ondo State, south-western Nigeria (Figure 1). The Igbokoda River (06°21′2″N, 04°48′19″E) and Igbekebo River (06°21′13″N, 04°51′37″E) represent typical West African coastal estuarine environments characterised by tropical climate conditions, tidal influence, and varying levels of human impact. Both systems flow into the Atlantic Ocean and support diverse ecological communities and human activities such as fishing, agriculture, and transportation.

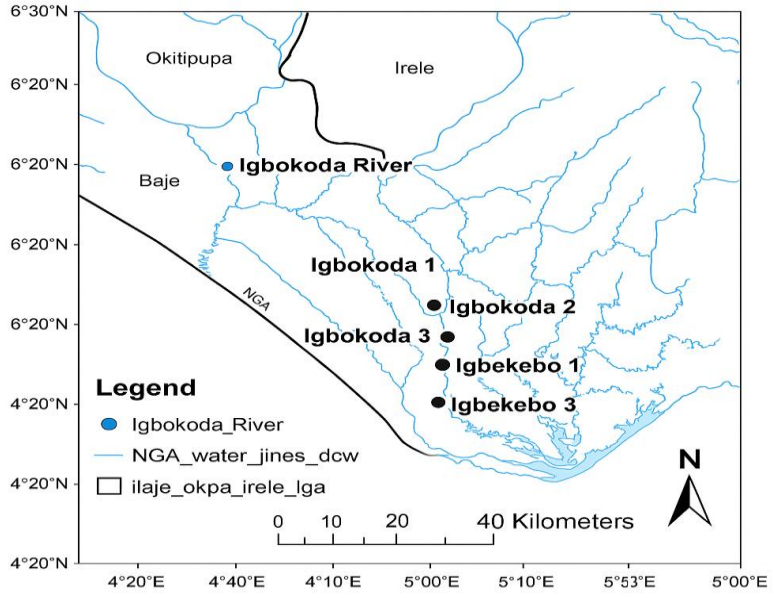


Figure 1: Map of Ondo State showing the sampling points.The regional geology mainly comprises sedimentary formations from the Dahomey Basin, with Quaternary alluvial deposits in the immediate coastal zone. The climate features distinct wet (April-October) and dry (November-March) seasons, with annual rainfall between 1500 and 2000 mm.

Sample Collection and Preparation

Surface sediment samples were gathered from three sites along each river system (Igbokoda 1-3 and Igbekebo 1-3) during the wet season (May-June 2023). At each location, triplicate samples were taken using a stainless steel soil auger from the top 0-15 cm of sediment to represent the most biogeochemically active zone. Sampling points were georeferenced with GPS coordinates and spaced approximately 2 km apart along each river to capture spatial variation.

Samples were immediately wrapped in aluminium foil, labelled, and transported to the laboratory in cooled containers. In the laboratory, samples were air-dried at room temperature for 72 hours, homogenised using an agate mortar and pestle, and sieved through a 2 mm mesh to remove coarse debris. The <2 mm fraction was further ground to <63 μm using an agate ball mill to ensure complete digestion and analytical precision.

Chemical Analysis

For elemental extraction, 2.5 g of homogenised sediment was digested with 10 mL of aqua regia (HNO_3:HCl = 3:1) in covered Teflon beakers on a hot plate at 200°C for 1 hour. After cooling, digestates were filtered through Whatman No. 42 filter paper and diluted to 25 mL with ultrapure deionised water.

Twenty elements (Ag, Al, As, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Se, Th, U, V, Zn) were analysed using an Agilent 720 ICP-OES system. Calibration standards were prepared by serial dilution of certified reference materials, and quality control was maintained through analysing blanks, duplicates, and certified reference materials (CRM-7001) with every batch of 10 samples. Method detection limits ranged from 0.01 mg/kg (Ag) to 1.0 mg/kg (Fe), and analytical precision was within 5% relative standard deviation for all elements.

Statistical Analysis

All analytical data were subjected to normality testing using the Shapiro-Wilk test, and log transformation was applied where necessary to meet assumptions for parametric statistics. Descriptive statistics, including mean, median, standard deviation, and coefficient of variation, were calculated for each element.

Pearson correlation analysis was performed to identify inter-element relationships and potential geochemical associations. Correlation coefficients were considered significant at $p < 0.05$. Principal Component Analysis (PCA) was conducted on standardised data to reduce dimensionality and identify underlying geochemical patterns. Components with eigenvalues >1 were retained, and varimax rotation was applied to enhance interpretability.

Radar charts were created to display site-specific elemental profiles and aid pattern recognition. All statistical analyses were conducted using Python (version 3.9) with pandas, numpy, scipy, and scikit-learn libraries, while visualisation was carried out using matplotlib and seaborn packages.

RESULTS

Heavy Metal Concentrations and Spatial Distribution

Descriptive statistics for all analysed elements are shown in Table 1. Noticeable spatial variability was evident across the six sampling sites, with coefficient of variation values ranging from 15.2% (Al) to 185.7% (U), reflecting diverse distribution patterns.

Table 1. Descriptive statistics of heavy metal concentrations (mg/kg) in estuarine sediments

Element	Mean	Median	Min	Max	SD	CV (%)
Ag	8.92	4.96	0.23	32.17	11.35	127.2
Al	75.42	68.75	0.62	152.09	48.92	64.9

As	0.89	0.25	0.02	3.65	1.21	135.8
Ba	7.32	7.02	3.04	13.66	3.15	43.0
Ca	185.67	134.00	37.48	355.23	115.32	62.1
Cr	5.24	3.12	0.00	21.55	6.42	122.5
Cu	2.15	1.65	0.56	3.46	0.95	44.2
Fe	1158.34	1254.93	147.57	1665.09	578.23	49.9
K	1688.45	84.57	6.22	6446.01	2156.78	127.7
Mg	823.67	70.64	45.35	4603.86	1456.32	176.8
Mn	58.74	60.57	0.62	103.35	32.45	55.2
Na	1256.89	148.68	47.89	4355.41	1389.67	110.6
Ni	0.96	0.62	0.02	3.55	1.12	116.7
Pb	2.45	1.73	0.23	6.75	2.01	82.0
Se	0.11	0.02	0.00	0.62	0.21	190.9
Th	6.12	3.52	0.00	12.65	4.89	79.9
U	1.24	1.43	0.00	2.65	0.89	71.8
V	5.67	5.14	0.00	7.53	2.34	41.3
Zn	12.45	15.96	5.23	17.21	4.78	38.4

Iron concentrations were significantly higher in Igbokoda sites (range: 1456.79-1665.09 mg/kg) compared to Igbekebo sites (range: 147.57-661.62 mg/kg). In contrast, Igbekebo sites exhibited considerably greater levels of magnesium (maximum: 4603.86 mg/kg at Igbekebo 1), potassium (range: 4639.01-6446.01 mg/kg versus 49.46-89.65 mg/kg in Igbokoda), and sodium (range: 2468.41-4355.41 mg/kg versus 102.25-159.72 mg/kg in Igbokoda).

Uranium concentrations were generally low across all sites, with maximum values of 2.65 mg/kg observed in Igbokoda sites, while thorium concentrations ranged from undetectable levels to 12.65 mg/kg. The most striking finding was the extreme spatial variability in magnesium concentrations, reaching 4603.86 mg/kg at Igbekebo 1, approximately 65 times higher than the minimum observed value (70.6 mg/kg).

Correlation Analysis

Pearson correlation analysis revealed several significant inter-element associations (Table 2). The strongest positive correlations were observed between: Uranium and thorium ($r = 0.924$, $p < 0.001$); Iron and manganese ($r = 0.887$, $p < 0.001$); Calcium and magnesium ($r = 0.853$, $p < 0.001$) and Potassium and sodium ($r = 0.798$, $p < 0.01$).

Table 2. Correlation matrix showing significant correlations ($p < 0.05$)

Element Pair	Correlation Coefficient	p-value
U - Th	0.924***	< 0.001
Fe - Mn	0.887***	< 0.001
Ca - Mg	0.853***	< 0.001
K - Na	0.798**	< 0.01
Ca - K	0.756**	< 0.01
Mg - Na	0.743**	< 0.01
Al - V	0.687*	< 0.05
Cu - Zn	0.645*	< 0.05

*$p < 0.05$, **$p < 0.01$, ***$p < 0.001$

Negative correlations were identified between lead and several elements, including silver ($r = -0.534$, $p < 0.05$)

and aluminium ($r = -0.498$, $p < 0.05$), suggesting different sources or competing geochemical processes.

Principal Component Analysis

PCA extracted three principal components with eigenvalues >1, collectively explaining 68.4% of the total variance in the dataset (Table 3).

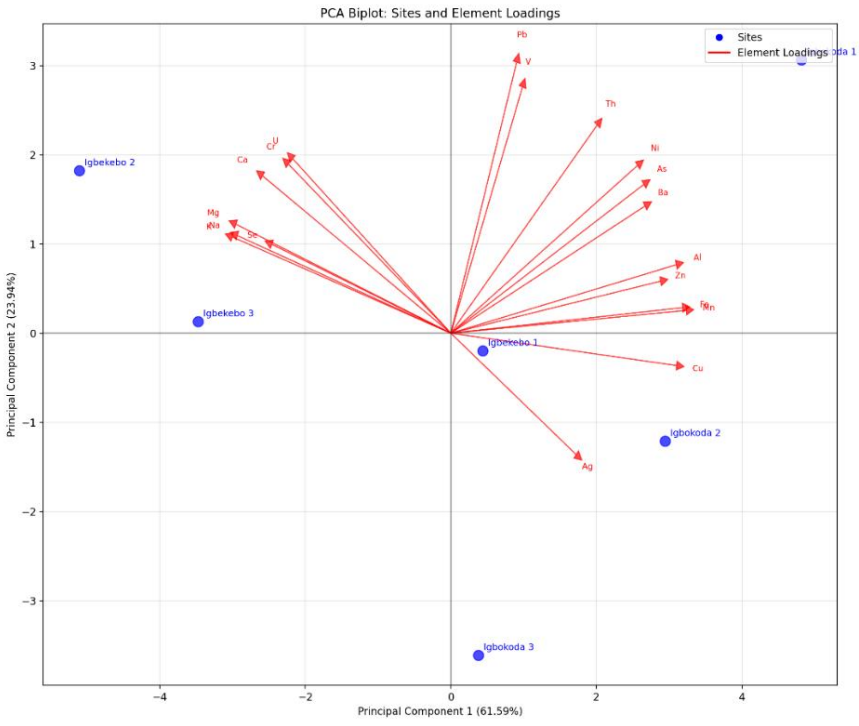
Table 3. Principal component loadings and variance explained

Element	PC1 (31.2%)	PC2 (20.8%)	PC3 (16.4%)
U	0.456	-0.132	0.089
Th	0.421	-0.098	0.156
Ca	0.398	0.245	-0.223
K	0.387	0.198	-0.287
Mg	0.378	0.234	-0.198
Na	0.362	0.267	-0.176
Fe	-0.089	0.445	0.398
Mn	-0.067	0.434	0.365
Al	-0.145	0.389	0.323
V	-0.178	0.356	0.298
Pb	0.123	-0.298	0.445
Ag	0.089	-0.267	0.423

PC1 was dominated by radiogenic elements (U, Th) and alkaline earth metals (Ca, Mg, K, Na), clearly distinguishing Igbekebo sites from Igbokoda sites. PC2 highlighted the association of iron-group elements (Fe, Mn, Al, V), while PC3 captured the variability of trace metals, including lead and silver.

The PCA biplot revealed distinct clustering of sampling sites (Figure 2), with Igbekebo 1 and 2 forming a separate cluster in the positive PC1 space, driven by extreme uranium, thorium, and alkaline earth metal concentrations. From the radar chats, we can observe how sites cluster or spread out, which can reveal similarities or differences in their sediment compositions. For example, sites that are close together share similar elemental characteristics, while those farther apart are more distinct.

Figure 2: The PCA biplot of sampling sites and Element loadings.

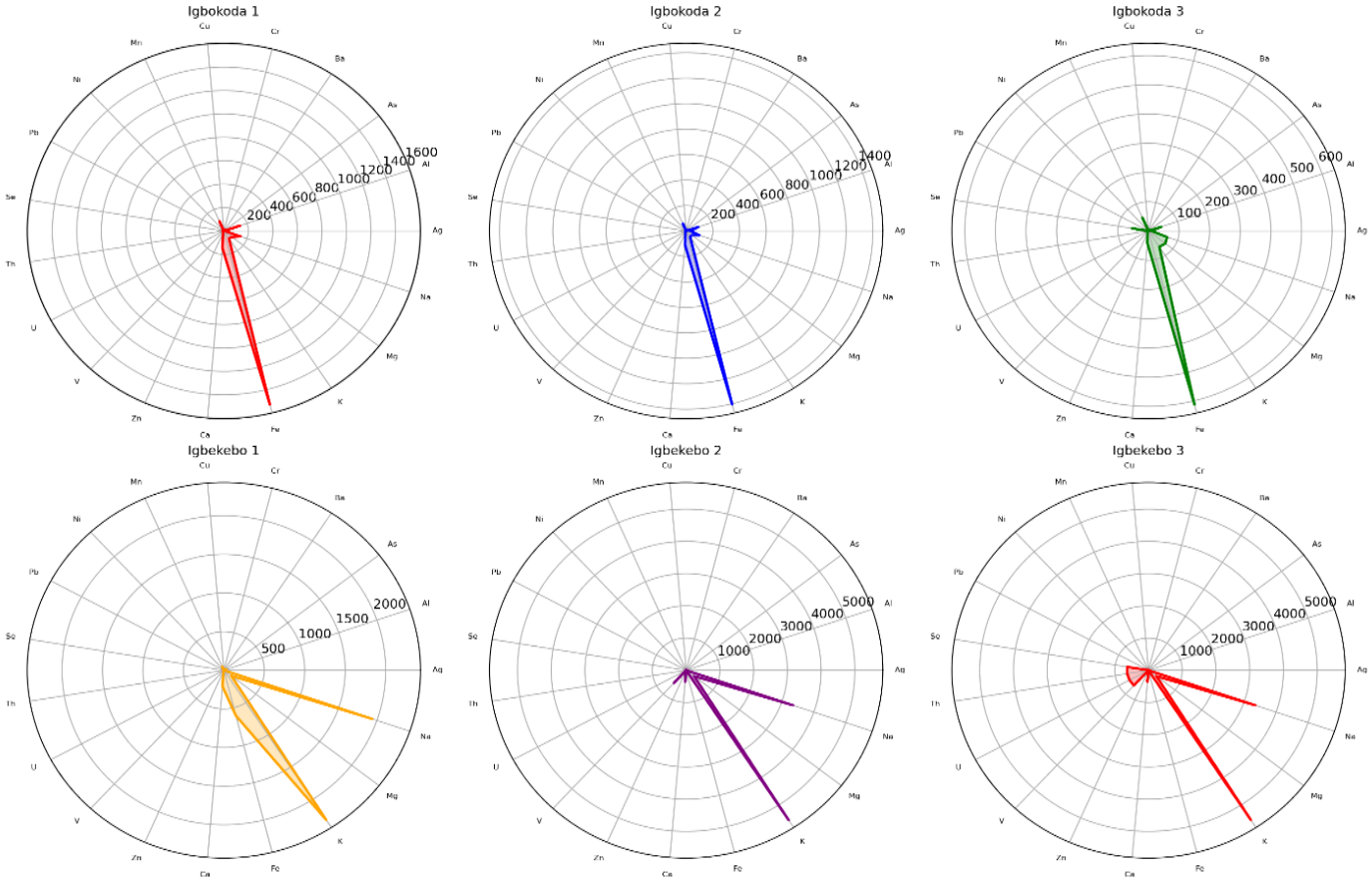


Site-Specific Geochemical Fingerprinting

Radar charts constructed for each sampling site revealed distinct elemental fingerprints (Figure 3). Igbokoda sites were characterised by elevated iron, aluminium, and manganese signatures, consistent with typical aluminosilicate sediment compositions. In contrast, Igbekebo sites displayed prominent spikes for uranium, thorium, calcium, and magnesium, suggesting distinct geochemical processes or source materials.

The radar fingerprinting approach effectively discriminated between the two river systems, with Igbekebo profiles showing sharp, angular patterns dominated by a few highly enriched elements, while Igbokoda profiles exhibited more balanced, rounded patterns across multiple elements.

Figure 3: The radar fingerprinting of Elements in each Site.



DISCUSSION

Spatial Geochemical Variability

The pronounced spatial variability observed in heavy metal concentrations reflects the complex interplay of geological, hydrological, and anthropogenic factors influencing estuarine sediment geochemistry. The distinct clustering of Igbekebo and Igbokoda sites in multivariate space suggests fundamentally different geochemical environments or source materials contributing to sediment composition. The color intensity indicates the level of concentration, with brighter colors showing higher values. This visualization helps identify patterns, such as which sites have elevated levels of certain elements (Figure 4).

The uranium concentrations observed (maximum 2.65 mg/kg) are generally within or slightly below typical crustal abundance ranges (2.8 mg/kg), while thorium concentrations (maximum 12.65 mg/kg) are elevated compared to average crustal values (9.6 mg/kg). The spatial distribution patterns suggest localized geochemical processes influencing radiogenic element accumulation (Kumar et al., 2020).

Geochemical Associations and Source Identification

The strong positive correlation between uranium and thorium (r = 0.924) is consistent with their common occurrence in heavy mineral assemblages and radiogenic source rocks. This association,

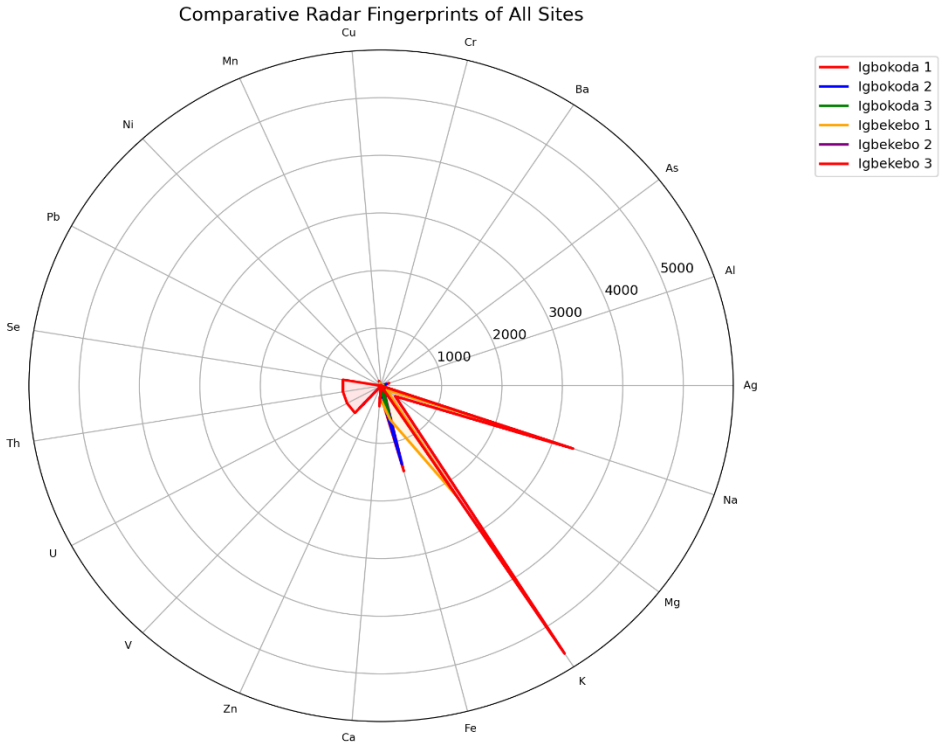


Figure 4: Comparative Radar Fingerprints for all Sites

combined with the co-occurrence of alkaline earth metals (Ca, Mg, K), suggests potential contributions from phosphate minerals, which commonly host uranium in sedimentary environments (Singh et al., 2021).

The Fe-Mn association observed in Igbokoda sites reflects typical redox-controlled co-precipitation processes common in estuarine environments. Iron and manganese oxides serve as important scavenging phases for trace metals and play crucial roles in biogeochemical cycling (Thompson et al., 2020).

Environmental Implications

The elevated concentrations of radiogenic elements, especially uranium, raise significant environmental and health concerns. Uranium presents both radiological and chemical toxicity risks, with the potential for bioaccumulation in aquatic food webs and groundwater contamination through leaching processes (WHO, 2012).

The observed spatial heterogeneity suggests localised contamination sources or geological controls that require site-specific management approaches. The distinct geochemical signatures identified through PCA and radar fingerprinting provide valuable tools for ongoing monitoring and source apportionment studies.

Limitations and Future Research

This baseline assessment provides important initial characterisation but requires temporal monitoring to assess seasonal variability and long-term trends. Future research should include: (i) Grain size analysis to assess particle size controls on metal distribution, (ii) Sequential extraction procedures to evaluate metal bioavailability, (iii)

Radiological assessment of uranium-bearing sediments, (iv) Detailed geological survey to identify potential natural sources (v) Assessment of ecological and human health risks

CONCLUSIONS

This comprehensive geochemical assessment of estuarine sediments from Ondo State, Nigeria, reveals significant spatial variability in heavy metal concentrations with important environmental implications. Key findings include: Extreme spatial heterogeneity in metal concentrations, with magnesium levels showing extreme variability (maximum of 4603.86 mg/kg) at Igbekebo sites - substantially exceeding global crustal averages. Distinct geochemical signatures distinguishing Igbekebo sites (enriched in U, Th, Ca, Mg) from Igbokoda sites (enriched in Fe, Mn, Al), as revealed through PCA and radar fingerprinting. Strong inter-element correlations indicate co-depositional mechanisms, particularly U-Th ($r = 0.924$) and Fe-Mn ($r = 0.887$) associations. Potential radiogenic contamination requires further investigation to determine natural versus anthropogenic sources and associated health risks.

The multivariate statistical approach employed successfully identified contamination patterns and provided a robust framework for environmental monitoring. These baseline data are essential for developing evidence-based management strategies for Nigerian coastal environments and contribute to the broader understanding of heavy metal dynamics in West African estuarine systems.

The findings highlight the need for continued monitoring, source identification studies, and risk assessment to protect these ecologically and economically important coastal environments.

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