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ORIGINAL PAPER

Concentration of rare earth elements in Escravos River bottom sediments and associated ecological risk on aquatic organisms

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Abstract

Rare earth elements concentration in environmental media is currently attracting global attention due to its toxic nature when accumulated above threshold levels. This research aims to provide updated information on the concentration levels, sources, and distribution patterns of rare earth elements in the Escravos River Channel, located in the Niger Delta region of Nigeria. Bottom sediment samples were collected from nine stations along a 28.5 km stretch of the Escravos River Channel. The samples were air-dried, prepared, and analyzed using an Inductively Coupled Plasma Mass Spectrometer. The results show that Lanthanum had the highest concentration, ranging from 46.28 to 113.14 mg/kg. In contrast, Terbium and Holmium had concentrations at or below the threshold value of 1 mg/kg. Average concentrations were ≤ 5 mg/kg for Gadolinium, ≤ 3 mg/kg for Dysprosium, and ≥ 1 mg/kg for Europium. Geospatial maps revealed that REE concentrations in the Escravos River bottom sediments were predominantly distributed according to source, with anthropogenic inputs being the primary contributor. Cluster analysis and correlation matrix analysis of the rare earth elements indicated a strong positive correlation ($r = 0.999$, $p < 0.05$) among the elements. Overall, the quality of Escravos River bottom sediments is poor, raising urgent environmental concerns due to the bioaccumulative nature of toxic metals like rare earth elements and their potential harm to biota through the food chain.

Keywords Blue economy · Economic minerals · Gbaramatu · High-tech mineral · Marine science · Toxicology

Introduction

Over the past five to ten decades, an era marked by industrialization and population growth, there has been a significant increase in the release of persistent and emerging contaminants into the global environment (Adimalla et al. 2020; Ekperusi et al. 2024; Omorogieva et al. 2024a). Despite expanding research efforts (Sutorius et al. 2022; Sakellariadou et al. 2021) on chemical contaminants in marine ecosystems, there remains a substantial knowledge gap, particularly regarding rare earth elements (REEs). While the presence of heavy metals in sediments, water, soil, and seafood is well documented (Omorogieva and Tonjoh 2020; Membere and Abdulwasiu 2020; Omorogieva et al. 2024a, b), and studies on per- and polyfluoroalkyl substances (Ekperusi et al. 2024), polycyclic aromatic hydrocarbons (Okpoebi et al. 2024; Bariweni et al. 2024), and petroleum hydrocarbons (Ewutanure et al. 2022; Ewutanure and Binyotubo 2021) exist, data on REEs as emerging marine contaminants remain scarce (Herrmann et al. 2016; Fisher and Kara 2016).

Globally, interest in REEs concentrations is growing due to their widespread applications in electronics industry, biomedicine, geological tracing, and as additives in phosphate fertilizers applied in agricultural activities (Goitom 2011; Gwenzi et al. 2021; Gao et al. 2023; UNDOA/ISA 2004). Although REEs occur naturally in minerals, carbonates, and paralkaline rocks (Neira 2022), anthropogenic activities can significantly elevate their concentrations (Ekperusi et al. 2023; Omorogieva et al. 2023; Arienzo et al. 2022). While REEs have economic value, concentrations above threshold levels in coastal and marine ecosystems may be injurious to benthic organisms, seafood, and humans via bioaccumulation and biomagnification (Sojka et al. 2021; Best 2015;

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Deng et al. 2017; Neira et al. 2022; Balaram 2019; Censi et al. 2004; Jiang et al. 2022).

The Escravos River (ER) plays a vital role in the economy of the Niger Delta and contributes significantly to Nigeria's maritime industry (Ugwuja 2022; Adebayo 2022). It provides employment for fishers and sustains local livelihoods through fishing and marine resources (Ekperusi and Asiwa 2022; Oguguah et al. 2017; Effah et al. 2021). However, there is limited data on REEs concentrations, sources, and distribution in Escravos River bottom (ERB) sediments. This knowledge gap motivated the current study.

The study aimed at generating a robust scientific data and evidence-based insights into REEs concentrations, sources, and distribution in ERB sediments to support sustainable development efforts. The specific objectives are: 1) to collect bottom sediment samples from strategic locations along the ER system; 2) to determine REEs concentrations using appropriate analytical techniques; 3). to apply multivariate statistical methods for data interpretation, and 4) to develop geospatial maps illustrating REEs distribution along the river system. The findings will provide a valuable baseline for future research and contribute to the United Nations Sustainable Development Goals (UN-SDGs), particularly Goal 11 (Sustainable Cities and Communities) and Goal 14 (Life below Water).

The study was conducted across nine sampling stations along the Escravos River Channel (ERC) between May and June 2024.

Materials and methods

Site location and description

The study area, the ERC, is an estuarine waterway and major navigation route within the Niger Delta sedimentary province of Nigeria. It lies between coordinates 05°38′20.7″N, 005°24′22.3″E and 05°36′22.4″N, 005°11′46.7″E (Fig. 1). According to Augustyn et al. (1998), the ERC is a tributary of the River Niger and spans approximately 56 km from Warri (the nearest urban center) to the Gulf of Guinea, transitory through mangrove swamps and coastal sand ridges

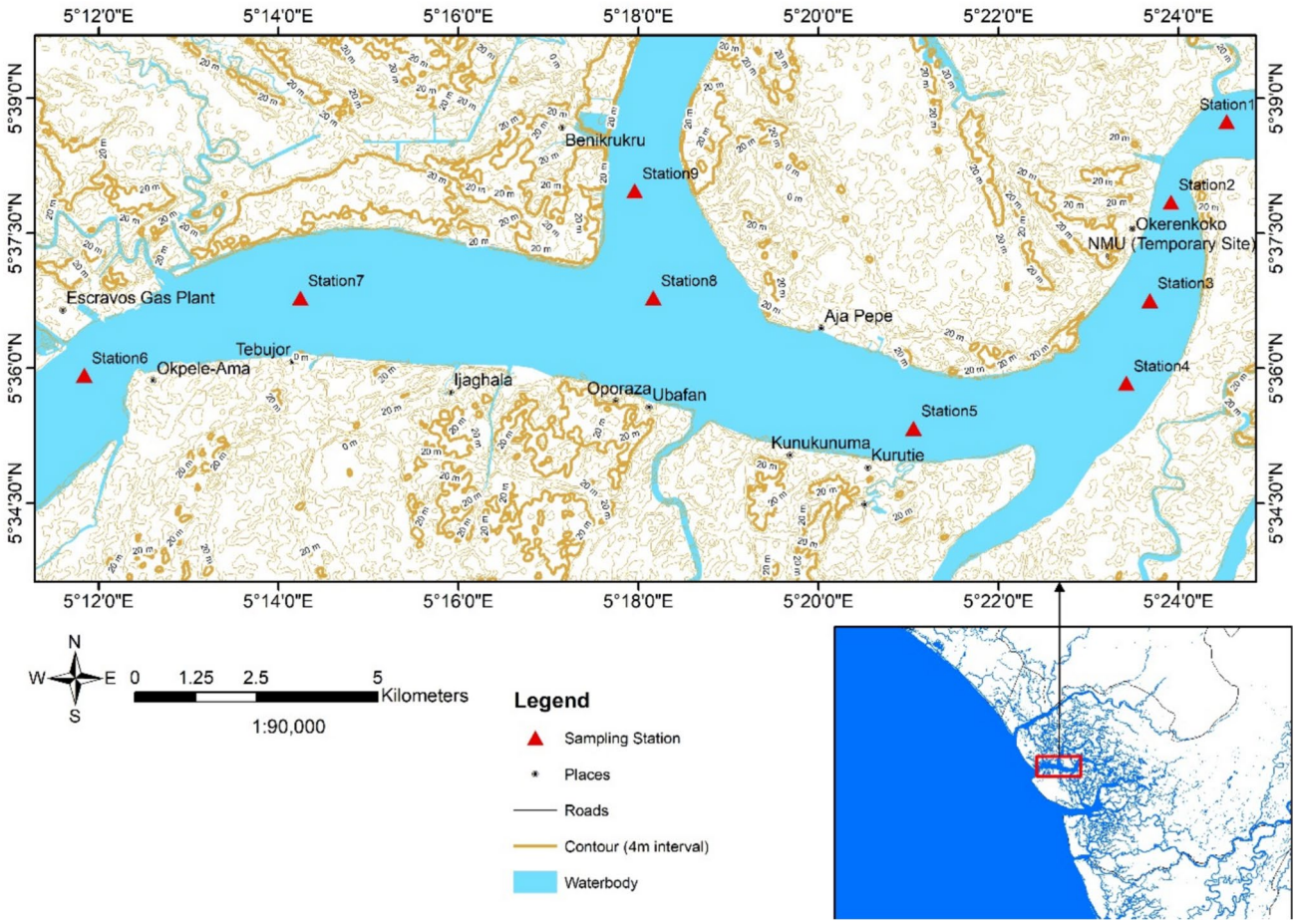


Fig. 1 Sample location map indicating the sampling points

(Tonjoh and Omorogieva 2020). This study covered a 28.5 km section from Jones Creek to Areton. Communities along the study stretch include Egwua I and II, Okerenkoko, Kurutie, Areton, Kunukunuma, Tebijor, Azama, Oporoza, and Benikrukru, among others. These communities are primarily engaged in fishing, subsistence farming, and lumbering (Omorogieva et al. 2024b) and function as maritime hubs for southern Nigeria. The area receives over 4000 mm (157.5 inches) of rainfall annually (Membere and Abdulwasiu 2020).

Geologically, the ER flows through the Mangrove Formation, underlain by the Warri Sombreiro (deltaic plain sands) and Overlain by the Beach Ridge Formations respectively (Akpoborie et al. 2015). These formations are recent deposits resulting from the weathering of the Benin Formation, the youngest in the Niger Delta Sedimentary Basin, dating from the Quaternary to Recent period (Omorogieva et al. 2023; Ugwuja 2022).

Sediment sampling

Sediment samples were collected from nine stations along the ERC between May and June 2024 using a grab sampler. A speedboat served as the platform for the sampling exercise. At each station, three composite samples were collected to represent the sediment profile. The samples were placed in pre-washed with clean water, permeable polythene bags (Dominic 2022) and transported to the Central Laboratory of the Faculty of Environmental Management, Nigeria Maritime University, where they were air-dried for analysis.

The depth of sampling; workstations and the coordinates of the sampling points using Global Positioning System (GPS) Garmin GSPMAP 64 s model are recorded in Table 1.

Sample preparation

Samples were air-dried under close monitoring in a dedicated section of the laboratory designed to prevent contamination. This setup helped avoid interference from airborne contaminants and minimized cross-contamination between individual samples. The dried samples were then pulverized and sieved using a 45 micron soil sieve. All equipment used was thoroughly cleaned with wipes between each measurement to maintain sample integrity. Each prepared sample, one hundred (100 g) was weighed and sealed in labeled polythene sachets. The samples were then mailed to Earth Lab at the University of Johannesburg, South Africa, for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for elemental analysis.

Total extraction, laboratory analysis and quality control/quality assurance

Fifty (50) mg of each sample was weighed into a 15 ml Savilex beaker containing 3 ml of ultra-high purity 2:1 HF:HNO_3. The beaker was capped and heated on a hotplate at 70 °C for 72 h. After digestion, the sample was dried down at 70 °C, and 3 ml of HNO_3 was added and evaporated. This process was repeated by adding another 3 ml of HNO_3, capping the beaker, and placing it on the hotplate at 70 °C for an additional 24 h. A final 3 ml of HNO_3 was added and allowed to evaporate.

After the final evaporation, 300 µl of HNO_3 was added, and the sample was diluted to 50 ml with (Dilution Factor 1:1000) 5% HNO_3, including 100 ppb Re and Rh, and 50 ppb In and Bi as internal standards. These standards were monitored throughout the analysis. Fluoride formation was minimized by limiting the contact time between the sample and HF, while still ensuring complete digestion. Samples were visually inspected for fluoride precipitates, which typically form after dilution.

Calibration standards were prepared at five different concentrations (10 ppb, 30 ppb, 50 ppb, 75 ppb, and 100 ppb) using a certified reference solution containing 40 target elements. All analyses were performed at Earth Lab, University of the Witwatersrand, on a Thermo Scientific iCAP RQ ICP-MS instrument. Measurements were performed in triplicate, and results were averaged. Any replicate showing a deviation greater than 2% was flagged.

Table 1 Sampling points, depth and coordinate

Work station	Sample location	Depth (m)	Northing	Easting
Station 1	Jones' Creek tributry	3.58 m	05°38′20.7″	005° 24′22.3″
Station 2	Okerenkoko (Debama Quarters) water front	2.55 m	05° 37′59.8″	005° 23′44.3″
Station 3	Okerenkoko University jetty water front	3.22 m	05° 37′08.1″	005° 23′24.8″
Station 4	Seitobobor polo	5.83 m	05° 35′38.0″	005° 23′43.1″
Station 5	Kurutie	2.82 m	05° 34′58.2″	005° 20′56.2″
Station 6	Areton	8.21 m	05° 36′16.2″	005° 11′35.7″
Station 7	Escravos water front	6.25 m	05° 36′22.4″	005° 11′46.7″
Station 8	Benin river tributary	9.77 m	05° 37′39.9″	005° 17′34.9″
Station 9	Benikrukru entrance	5.50 m	05° 38′01.1″	005° 17′35.8″

As part of quality control/assurance, Certified Reference Materials (CRMs) including BCR-1, BHVO-2, and BIR-1 were digested and analyzed alongside the samples. The CRMs returned results within 10% deviation of their known concentrations for all elements. Additionally, a Total Procedural Blank (TPB), that is, a beaker with no sample, taken through the full digestion process was analyzed alongside the samples to assess background contamination. All reported data were corrected by subtracting the TPB values.

Maps generation and statistical data analysis

Spatial distribution and sampling location maps were generated using Surfer 20.0 and ArcGIS. Initially, field data were converted to CSV format and imported into Surfer, where grid files were created to generate contour maps. These contour maps were then exported in a compatible format for further visualization in ArcGIS. In ArcGIS, the maps were refined using appropriate symbology, classification schemes, and threshold levels based on environmental or regulatory guidelines (Omorogieva and Ogieriakhi 2021). The final classified maps included a legend indicating the classification descriptions and showed the distribution of REEs in relation to environmental factors. The classification was grouped into four levels: low, moderate, high, and very high.

Statistical analysis was conducted using SPSS version 21 and PAST (Paleontological Statistics Software Package for Education and Data Analysis) version 3.02a. Analysis of variance (ANOVA), correlation, and cluster analyses were performed. Cluster analysis for REEs was based on the similarity index, using the unweight pair group method with arithmetic mean (UPGMA) and Euclidean distance as the similarity measure (Hammer et al. 2001).

Results and discussion

Table 2 represents the results of one way ANOVA for the REEs being investigated within the scope of study. The REEs were classified into three categories of light rare earth elements (LREEs), the middle rare earth elements (MREEs) and the high rare earth elements (HREEs). Classification of REEs are mainly based on the atomic number (Zepf 2013). Literally, REEs with lower atomic number are usually classified as LREE, whereas those with higher atomic numbers are seen as HREE, conversely, those between are often refer to as MREE (Brownlow 1996; Rollinson 1993). In this study, the LREEs include lanthanum (La), praseodymium (Pr), neodymium (Nd), and samarium (Sm). In the study, the concentration of La ranged from 46.28 mg/kg in work station 1 to 113.14 mg/kg in station 2. When the values obtained for La were compared to the average shale value (ASV) and Environmental Canada

Table 2 REEs concentration in ERB sediment and ASV as reference guideline, adopted from Diayi et al. (2023)

Element (mg/kg)	Stations									References	
	1	2	3	4	5	6	7	8	9		
La	100.4603 ± 0.003^{e}	113.1410 ± 0.006^{i}	103.1790 ± 0.006^{f}	46.2787 ± 0.332^{a}	59.1500 ± 0.000^{b}	73.6073 ± 0.013^{c}	74.1183 ± 0.009^{d}	108.9217 ± 0.072^{h}	104.3267 ± 0.003^{g}	43.00	
Pr	11.0960 ± 0.020^{e}	12.5273 ± 0.003^{i}	11.7293 ± 0.003^{f}	5.0573 ± 0.003^{a}	6.4693 ± 0.003^{b}	8.1353 ± 0.268^{c}	8.1883 ± 0.003^{d}	12.1113 ± 0.003^{h}	11.9323 ± 0.007^{g}	9.00	
Nd	41.0107 ± 0.003^{e}	45.4573 ± 0.013^{i}	42.9280 ± 0.010^{f}	19.4877 ± 0.003^{a}	23.4847 ± 0.003^{b}	30.1513 ± 0.007^{d}	29.9627 ± 0.003^{c}	45.0553 ± 0.003^{h}	44.1210 ± 0.006^{g}	33.00	
Sm	7.3227 ± 0.007^{e}	8.1127 ± 0.003^{i}	7.6707 ± 0.003^{f}	3.4847 ± 0.023^{a}	3.9677 ± 0.003^{b}	5.3290 ± 0.006^{c}	5.4727 ± 0.003^{d}	8.0070 ± 0.000^{h}	7.9027 ± 0.003^{g}	6.20	
Eu	1.5207 ± 0.007^{f}	1.0353 ± 0.003^{d}	1.5667 ± 0.017^{g}	0.4973 ± 0.013^{a}	0.7150 ± 0.000^{b}	0.7470 ± 0.000^{c}	1.1963 ± 0.003^{e}	1.6493 ± 0.003^{i}	1.6083 ± 0.009^{h}	1.20	
Gd	6.1887 ± 0.007^{e}	6.6680 ± 0.010^{h}	6.4593 ± 0.003^{f}	2.9187 ± 0.007^{a}	3.2990 ± 0.006^{b}	4.3787 ± 0.007^{c}	4.698 ± 0.012^{d}	6.7153 ± 0.003^{i}	6.5603 ± 0.003^{g}	5.10	
Tb	0.9793 ± 0.003^{i}	0.8047 ± 0.003^{e}	0.8280 ± 0.010^{f}	0.3403 ± 0.003^{a}	0.4203 ± 0.003^{b}	0.5410 ± 0.000^{c}	0.6180 ± 0.010^{d}	0.8637 ± 0.003^{h}	0.8540 ± 0.000^{g}	N/A	
Dy	4.4423 ± 0.003^{f}	3.9393 ± 0.003^{e}	4.4967 ± 0.017^{g}	1.6810 ± 0.100^{a}	2.3623 ± 0.007^{b}	2.8237 ± 0.003^{c}	3.4150 ± 0.070^{d}	4.8173 ± 0.013^{i}	4.6593 ± 0.003^{h}	N/A	
Ho	0.8260 ± 0.023^{f}	0.6570 ± 0.017^{d}	0.8193 ± 0.003^{e}	0.2880 ± 0.010^{a}	0.4267 ± 0.033^{b}	1.5013 ± 0.003^{i}	0.6250 ± 0.000^{c}	0.8843 ± 0.003^{h}	0.8537 ± 0.003^{g}	N/A	
Er	2.2313 ± 007^{e}	1.6280 ± 010^{d}	2.2223 ± 007^{e}	0.7287 ± 007^{a}	1.1947 ± 0.003^{b}	1.3317 ± 0.003^{c}	1.615 ± 0.120^{d}	2.4080 ± 0.010^{f}	2.3277 ± 0.017^{ef}	N/A	
Tm	0.3070 ± 000^{g}	0.2073 ± 0.013^{d}	0.3023 ± 0.007^{f}	0.0947 ± 0.003^{a}	0.1737 ± 0.003^{b}	0.1823 ± 0.003^{c}	0.2373 ± 0.013^{e}	0.3293 ± 0.003^{i}	0.3193 ± 0.003^{h}	N/A	
Yb	2.1463 ± 067^{g}	1.4073 ± 0.013^{d}	2.1107 ± 0.003^{f}	0.6773 ± 0.013^{a}	1.2680 ± 0.010^{b}	1.2907 ± 0.003^{c}	1.6690 ± 0.015^{e}	2.2737 ± 0.003^{i}	2.2037 ± 0.003^{h}	N/A	
Lu	0.2887 ± 007^{f}	0.1907 ± 0.003^{d}	0.2887 ± 0.007^{f}	0.0890 ± 0.006^{a}	0.1730 ± 0.000^{b}	0.1813 ± 0.007^{c}	0.2280 ± 0.010^{e}	0.3037 ± 0.003^{h}	0.2940 ± 0.000^{g}	N/A	

Mean value ± standard error of mean with different superscript alphabets along the same row are significantly different from each other ($P < 0.05$). N/A = Not Available

Sediment Quality Guideline Standard (ECSQGS) of recommended 43 mg/kg, it was observed that La in ERB sediment was highly contaminated. Pr and Nd concentration in the river bed were similar to the result obtained for La. The lowest values of 5.06 mg/kg and 19.49 mg/kg were both recorded in station 4, and the highest values of 12.53 mg/kg and 45.46 mg/kg in work station 2 respectively. The results for Pr and Nd in this study showed that 44.44% and 33.33% of ERB sediments were above the recommended value of ASV and ECSQGS. Samarium concentration within the scope of study were relatively low; the lowest being 3.49 mg/kg in station 4 and the highest value of 8.11 mg/kg in station 2 respectively. However, it was observed that the sediment was 33.33% impacted when compare to the threshold value of ASV.

The geospatial maps (Fig. 2) for the LREEs revealed higher concentrations at Work Stations 1, 8, and 9 along the Escravos River Channel (ERC) and its tributaries. These stations correlate with zones of intense human activity and the influx of contaminants transported by the river channel. Work Station 1 comprises Jones Creek and other adjoining creeks, whereas Stations 8 and 9 represent a three-arm trajectory of the ERC and the Benin River. This area is characterized by high turbulence and strong wave action.

However, the cluster analysis in Fig. 3 indicates that the LREEs likely originate from mixed sources within the ecosystem. Comparing the cluster analysis results with the correlation matrix for LREEs across the study area (Table 3) reveals a strong positive correlation ($r = 0.999$, $p < 0.05$).

The results obtained for MREEs, Europium (Eu), Gadolinium (Gd), Holmium (Ho), Terbium (Tb), and Dysprosium (Dy), and the HREEs—Erbium (Er), Thulium (Tm), Ytterbium (Yb), and Lutetium (Lu) showed relatively low concentrations. Notably, Tb and Ho had threshold values of ≤ 1 mg/kg across all MREEs, while average concentrations of ≤ 5 mg/kg, ≤ 3 mg/kg, and ≥ 1 mg/kg were recorded for Gd, Dy, and Eu, respectively. ERB sediments were observed to be impacted, with 66.66% of Eu and 55.55% of Gd samples exceeding the Average Shale Value (ASV) used as a background reference.

For the HREEs, Tm and Lu exhibited similarly low concentrations (< 1 mg/kg), consistent with the levels observed in the MREEs, while Er and Yb had concentrations of ≤ 1 mg/kg. The geospatial maps for LREEs, MREEs, and HREEs (Figs. 2, 4, and 5) illustrated the distribution patterns of REEs across the study area, indicating higher concentrations in zones influenced by human activities.

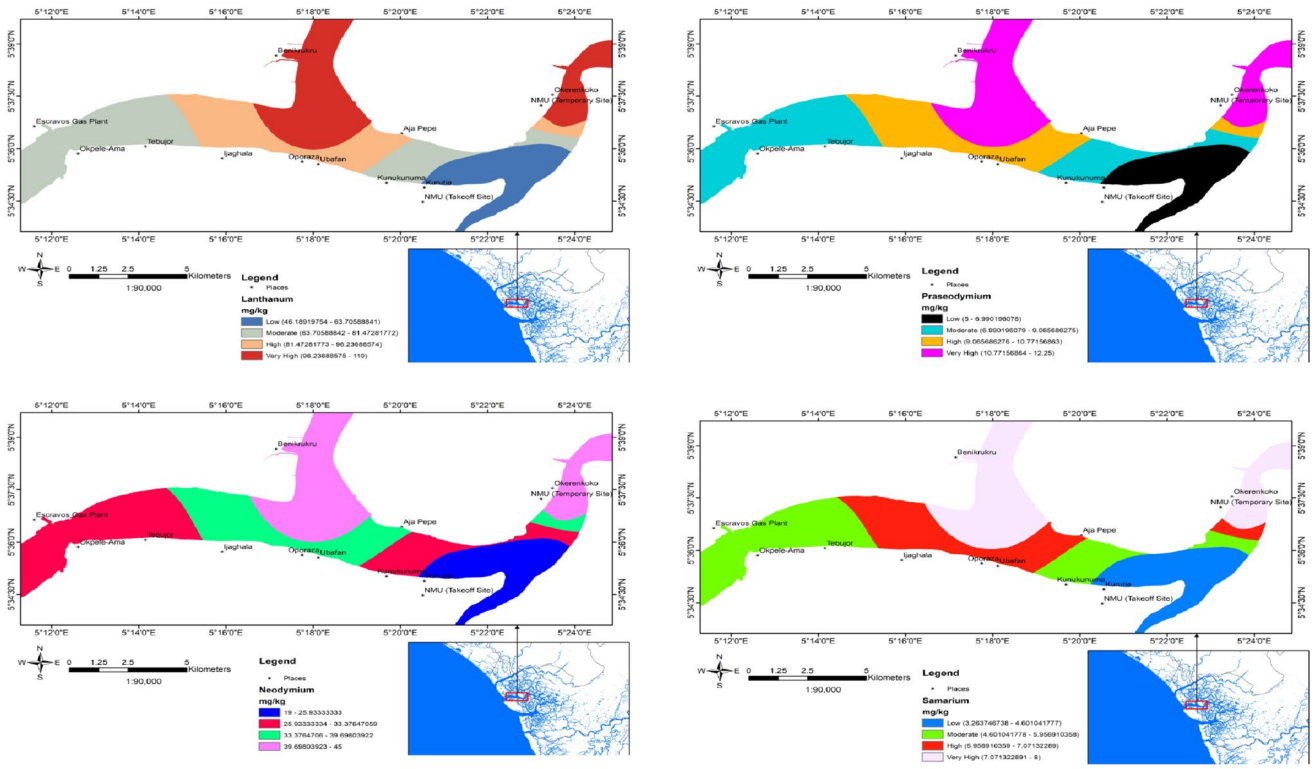


Fig. 2 Geospatial maps of LREEs in the nine work stations

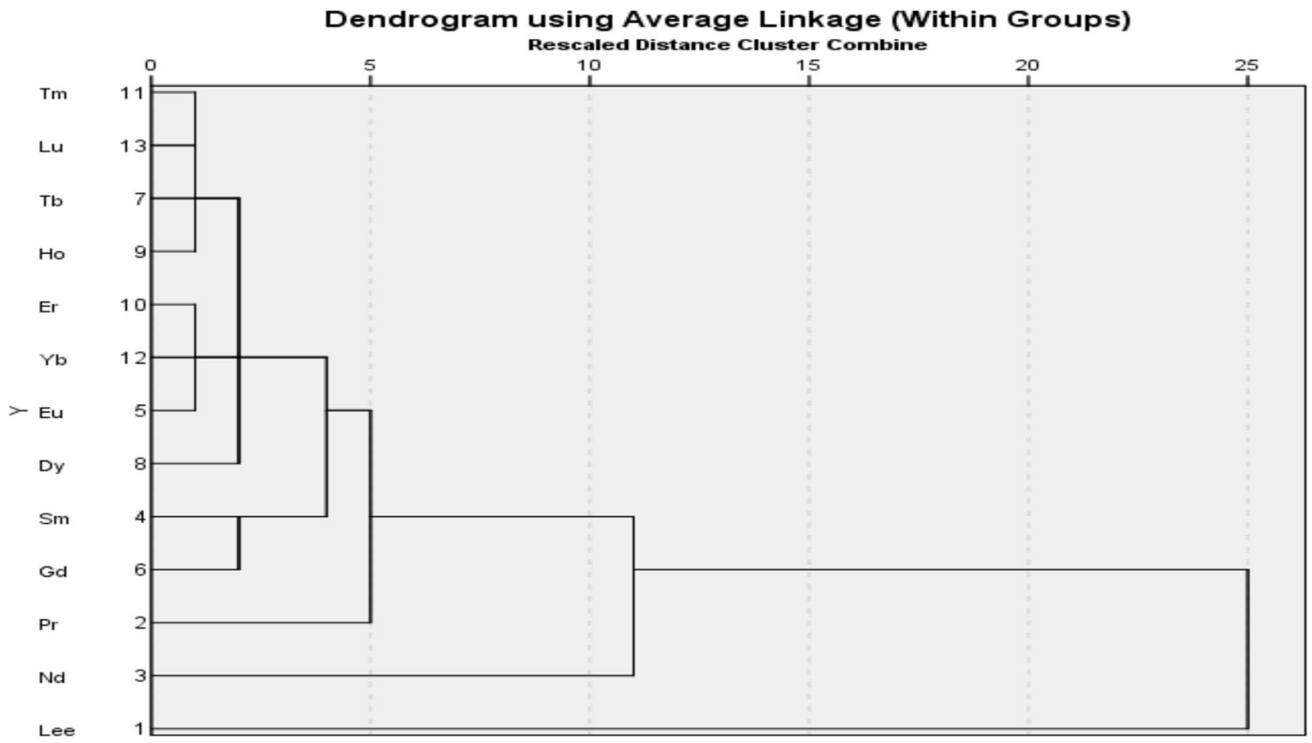


Fig. 3 Dendogram for cluster analysis of variables

Table 3 Correlation coefficient of sediment matrix for REEs

REEs	La	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La	1												
Pr	.999**	1											
Nd	.997**	.999**	1										
Sm	.995**	.997**	.999**	1									
Eu	.832**	.843**	.851**	.857**	1								
Gd	.993**	.995**	.997**	.999**	.876**	1							
Tb	.940**	.939**	.942**	.945**	.911**	.954**	1						
Dy	.944**	.950**	.954**	.956**	.966**	.966**	.964**	1					
Ho	0.358	0.360	0.366	0.363	0.258	0.352	0.338	0.354	1				
Er	.874**	.883**	.890**	.890**	.987**	.904**	.934**	.982**	0.360	1			
Tm	.826**	.836**	.842**	.842**	.987**	.860**	.904**	.962**	0.352	.994**	1		
Yb	.805**	.815**	.821**	.820**	.982**	.839**	.891**	.951**	0.351	.989**	.999**	1	
Lu	.803**	.813**	.818**	.817**	.976**	.836**	.887**	.948**	0.378	.986**	.997**	.999**	1

Bold values * = significant whereas bold values ** = highly significant

*, ** indicated a high level of confidence and better results

Discussion

The results obtained revealed that REEs in ERB sediments are more concentrated in areas with evident anthropogenic activities, particularly at the confluence points where creeks and feeder rivers discharge into the ER (Fig. 6a and b). Gao et al. (2023) made a similar observation, noting that REEs distribution and sources in the Yongding River within the Tianjin and Beijing urban systems were driven by anthropogenic processes, specifically the discharge of human waste into the river system. Up to 20.51 ng/L of Gd (a MREE) was measured, which eventually settled to the bottom and accumulated over time. Similarly, Sojka et al. (2021) reported that the occurrence and distribution

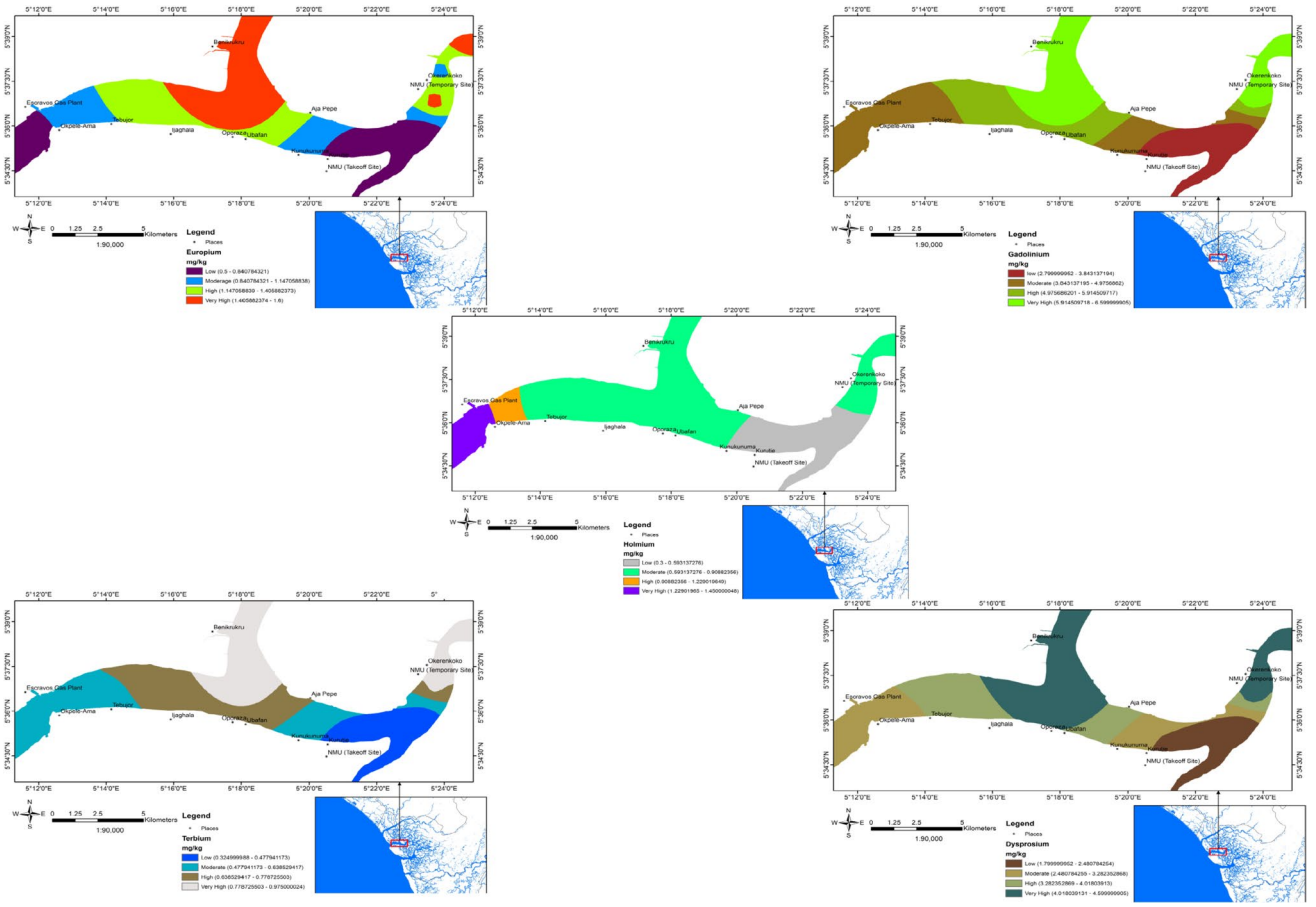


Fig. 4 Geospatial map for MREEs concentration in ERB bottom sediments

of REEs in the bottom sediments of lakes in Bory Tucholskie, Poland, were influenced by both anthropogenic factors and local geology. Studies have shown that ecological factors such as abundant vegetation, organic matter, microbial activity, and climate change also play significant roles in the mobility, occurrence, and distribution of REEs in fluvial ecosystems (Zaharescu et al. 2017).

In India, the geogenic input of La in the Gomati River over a 900 km stretch ranged from 29—34 ppm upstream and progressively increased to 329 ppm downstream as the river passed through zones of intense anthropogenic activity (Yadav et al. 2022). It was also reported that La concentrations in the Hindon River's bottom sediments were extremely high due to the introduction of electronic waste into the system. In comparison with the present study, La (a LREE) concentrations at the nine sampled stations were relatively high, ranging from 46.28 to 113.14 mg/kg, the value is higher than both values reported in previous studies and concentrations of other REEs measured in ERC. Stations with evident anthropogenic influence (Stations 1, 2, 3, 7, 8, and 9) recorded higher concentrations compared to stations with little or no anthropogenic activity (Stations 4, 5, and 6) in Figs. 4, 5, and 6. This can be attributed to the high levels of electronic waste and other human-related activities, including the discharge of untreated wastewater into the river by oil and gas companies and local residents who use the river as a dumpsite (Tonjoh and Omorogieva 2020).

Cluster analysis (Fig. 3) revealed that La in ERB sediments likely originates from a singular source, further supporting the influence of anthropogenic input. Several studies, including those by Aide et al. (2019), Arienzo et al. (2022), Ikhayel et al. (2018), Tan et al. (2015), Deng et al. (2017), Cao et al. (2017), and Gutierrez-Gutierrez et al. (2015), have confirmed that the occurrence, sources, and distribution of REEs in coastal, riverine, and fluvial environments are predominantly driven by human activities, with minimal input from natural processes and catchment lithology. Furthermore, electronic waste has been identified as a major contributor of Eu; up to 72% in estuarine ecosystems (Resende and Morais 2010). The use of the ER as a dumping ground for untreated industrial effluents and byproducts from numerous flow stations remains the primary driver of REEs concentrations in ERB sediments. These harmful activities contribute significantly to the accumulation of REEs in ERC.

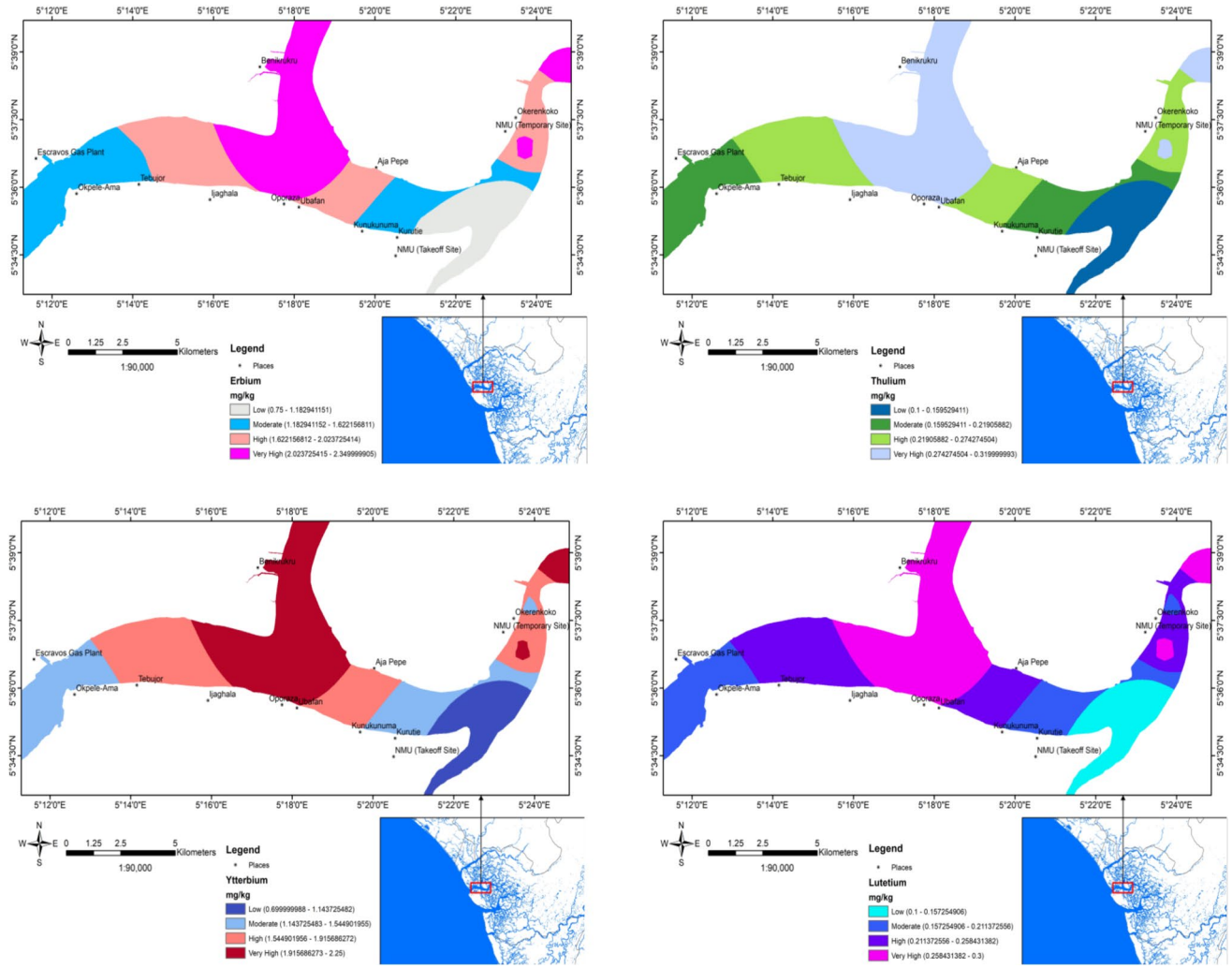


Fig. 5 Geospatial map for HREEs concentration in ERB bottom sediments

Additionally, Fig. 6a and b show the concentration and distribution patterns of REEs across the nine stations. From the charts, REEs concentrations around Stations 4, 5, and 6 were relatively low, as these areas lack intense anthropogenic activities and catchment streams. In contrast, Stations 1, 2, 3, 7, 8, and 9, which are subject to intense anthropogenic influence, recorded higher REEs values. When the results of this study were compare to background shale values and the Environmental Canada Sediment Quality Guideline Standard (Diayi et al. 2023), it is evident that ERB sediments are severely impacted (Table 3). This current state of contamination warrants urgent attention.

Rare earth elements and ecological implications

REEs have been recognized as emerging contaminants in coastal and marine ecosystems due to their bioaccumulative properties. The results obtained in this study indicate that sediment quality in the ERB is poor and may be responsible for recurring fish mortality in the ERC via the food chain. Low dose REEs exposure over extended periods may adversely affect human metabolic processes and aquatic resources, such as seafood (Gwenzi et al. 2021; Gao et al. 2023). Studies have shown that excessive consumption of REEs can lead to abnormal biochemical markers in the human body and increased cholesterol levels in the bloodstream (Song et al. 2017; Goitom 2011; Zhang et al. 2000). The decomposition of Gd chelates in vivo allows it to accumulate in human bones, tissues, and the brain (Prince et al. 2008; Thomsen et al. 2017; Song et al. 2017). Besides Gd, elevated levels of La and Sm have also been linked to negative ecological effects. Leguille (2017), and Parant et al. (2019) demonstrated that Gd bioaccumulation as low as 20 ng/L in freshwater bivalve tissues can alter biochemical processes and inhibit growth. Due to their ability to bioaccumulate and biomagnify, REEs pose a particular risk

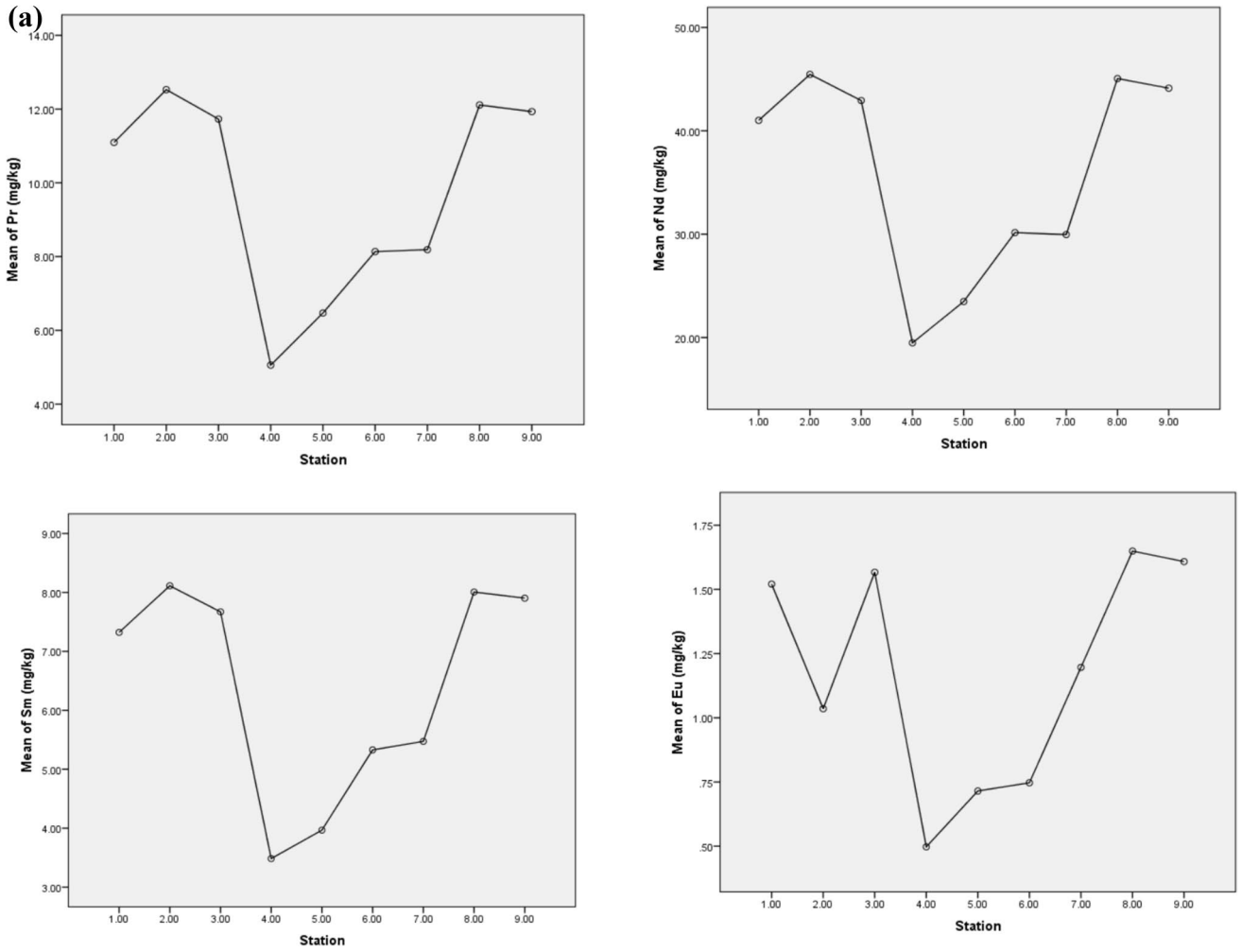


Fig. 6 **a** Distribution of REEs in ERB sediment. **b** Distribution pattern of REEs in ERC

to organisms at lower trophic levels in coastal and marine ecosystems. When marine organisms are exposed to REEs, especially MREEs to HREEs like Gd, significant damage can occur to their cells, tissues, organs, and biological systems, potentially resulting in long-term toxicity (MacMillan et al. 2017). For example, the embryonic development of zebrafish, sea urchins, and other benthic organisms has been shown to be impaired by REEs exposure. This is attributed to the disruption of enzyme activity and ion regulation; particularly calcium and magnesium, both essential for normal cellular function (Revel et al. 2024). To mitigate the impact of REEs contamination in the ERC, the government should strengthen environmental legislation to prohibit the dumping of unauthorized materials into water bodies, with strict penalties imposed on violators. This study is timely, providing updated information on the concentrations, distributions, and sources of REEs in the Escravos River to support necessary action by stakeholders in the region.

Implications and limitation of the study

Anomalies in REEs concentrations in the ERB sediments have significant implications and limitations. They may indicate environmental pollution resulting from human activities and could also signal the presence of mineral deposits or geological anomalies, a key information for seabed mineral exploration and exploitation. Additionally, REEs signatures are useful for identifying sediment sources and tracking sediment transport pathways, which support provenance studies. Elevated REE concentrations may pose ecological risks; however, the toxicity of individual REEs remains poorly understood and warrants further investigation.

This study faces several limitations. REE concentrations can naturally fluctuate due to underlying geological and geochemical processes, making it difficult to clearly differentiate between anthropogenic and natural sources. While the findings suggest that REEs anomalies are frequently associated with human activity, geological contributions cannot be ruled out. Further research is needed to clarify

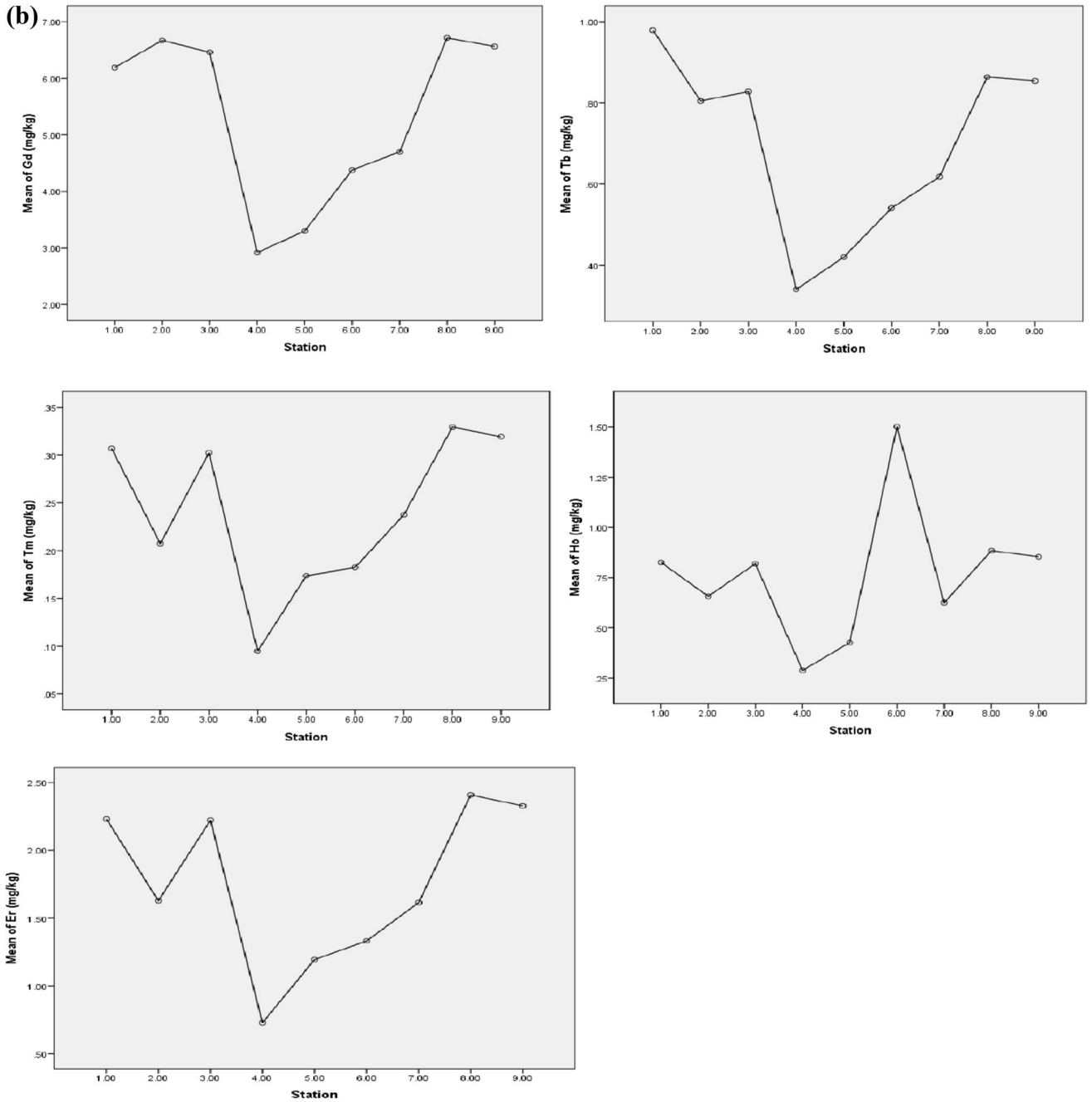


Fig. 6 (continued)

this variability. Moreover, the toxicity and bioavailability of REEs in aquatic environments are not yet fully defined, limiting the ability to establish clear environmental management guidelines. Accurate interpretation of REEs data also requires consideration of factors such as sediment type, grain size, and mineralogy; these parameters are not addressed in this study. Overall, the results highlight the complexity of assessing REEs contamination in ERB sediments and emphasize the need for comprehensive, multidisciplinary research.

Conclusion

Evidence from this study indicates that the primary sources of REEs in ERB bottom sediments are anthropogenic, with minimal contributions from geological or natural processes. The extremely high concentration of La was attributed to frequent dumping of refuse including e-waste and untreated industrial effluent, by operations of oil and gas companies along the riverbanks. The bioaccumulation and biomagnification of REEs in bottom sediments could be fed on by

benthic organisms at the lower trophic level, may lead to toxicity of living marine resources and human exposure through the food chain. Regular monitoring and public awareness campaigns are recommended to educate communities on sediment quality and the interrelationship between living organisms vis a vise the potential harmful effects when accumulates and magnify in aquatic ecosystems overtime. These efforts will help to establish effective environmental management strategies that promote sustainable development and protect life below water and on land.

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Data availability Data used in the study will be available on request.

Declarations

Conflict of interest There is no conflict of interest in this work.

Statement of human rights The research do not involve the use of human nor animal for testing.

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