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Enrichment Patterns and Geochemical Behavior of Rare Earth Elements in the Sediments of the Linggi River, Malaysia

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Abstract Sediment samples from seven sites along the Linggi River (Malaysia) were collected in the dry season to study their spatial distribution, enrichment patterns, and geochemical behavior of REEs and Fe. Surface sediments were analyzed by neutron activation analysis, adhering to strict quality control procedures that included standard reference materials IAEA-Soil-7, SL-1, and MIX PTS-16/17. The results obtained show that total REE concentrations range from 166.6 to 206.1 ppm, with a dominance of LREEs over HREEs (LREE/HREE = 7.4–10.5). The concentrations of La (47.7–60.4 mg/kg), Ce (93–116 mg/kg), and Sm (8.2–10.4 mg/kg) are constantly greater than their UCC values, whereas Dy (7.6–14 mg/kg), Tb (1.4–1.8 mg/kg), and Yb (5.3–8.7 mg/kg) are enriched up to fourfold. Spatial patterns include the following: upstream Dy and Yb enrichment, midstream variability related to industrial inputs, and downstream increases of La and Ce due to estuarine trapping. Ce/Ce* ratios of between 0.95 and 1.11 indicate stable oxic depositional conditions, while a negative Eu anomaly (Eu/Sm = 0.09–0.14) reflects felsic lithological sources. Enrichment factors (EF): Moderate to strong enrichment of Dy, Tb, and Yb is suggested by EF values up to 6.8, whereas the values of Igeo (-0.99 to 1.42) suggest the sediment to be non-polluted to slightly polluted, having hotspots at S1 and S5. Taken together, the results imply that the present REE concentration patterns in the sediment of the Linggi River are mainly controlled by felsic weathering materials, overlain by industrial influences.

Keywords Environmental Pollution, Mangrove, Rare Earth, Neutron Activation

1. Introduction

Rare earth elements (REEs) have moved from a geochemical curiosity to critical raw materials underpinning modern technologies, including permanent magnets, batteries, catalysts, and many components of electronics and clean-energy systems [1,2]. As demand for REEs has grown worldwide, so has interest in their environmental cycling and the consequences of their release into surface environments [3]. Although REEs are often treated together with conventional “trace metals,” their coherent but subtly fractionated geochemical behavior and increasing anthropogenic mobilisation require focused study, especially in sediments where they accumulate and record both natural background and human influence [1,4].

Sediments function as both sinks and secondary sources of REEs in aquatic systems. Particulate adsorption, mineral authigenesis, and association with organic matter and iron–manganese oxyhydroxides cause REEs to be removed from the water column and sequestered in sediments, where they may persist, be remobilised under changing redox or pH conditions, or become bioavailable to benthic organisms [2,5]. Consequently, sedimentary REE concentrations and their fractionation patterns are widely used as tracers of provenance, depositional conditions, and anthropogenic input [6]. Recent sediment studies show that anthropogenic activities notably mining and mineral processing, coal combustion (and subsequent fly ash), electronic waste, industrial discharges, and fertilizer/agronomic use, have measurably increased REE loads in many coastal, lacustrine and riverine sediments worldwide [2].

Major anthropogenic sources deserve special emphasis because they shape both spatial patterns of contamination and the forms in which REEs enter sediments [7]. Mining and ore processing release REE-bearing particulates and acid mine drainage; coal combustion concentrates REEs in fly ash that may be disposed of on land or discharged and later transported to water bodies; and rapidly growing e-waste streams and industrial effluents can introduce discrete REE-rich particles and soluble complexes [8]. In some regions, legacy industrial waste and poorly managed tailings are the dominant local source; in others, the diffuse input from agricultural amendments and atmospheric deposition of combustion by-products can be important. The recognition that by-products such as coal fly ash can both concentrate REEs (and thus be a potential resource) and act as a contaminant source complicates management choices [2,8].

Geochemical behaviour and diagnostic signatures of REEs in sediments differ from those of classic heavy metals and are central to interpreting contamination. REEs display coherent patterns when normalised to shale or continental crust values, but anomalies most notably positive or negative cerium (Ce) and europium (Eu) anomalies and light (LREE) versus heavy (HREE) fractionation reveal redox conditions, authigenic enrichment processes, and inputs from anthropogenic sources with non-crustal signatures [9]. For example, Ce anomalies are widely used as redox indicators because Ce(III) is oxidised to less soluble Ce(IV) under oxic conditions and scavenged by Mn/Fe oxides, producing characteristic depletions or enrichments in sediments. Interpreting REE patterns therefore requires integrated mineralogical, redox, and particle-reactivity perspectives [10].

From an environmental-risk perspective, REEs are increasingly regarded as “emerging contaminants.” Historically considered of low ecotoxicological concern because of low natural concentrations and presumed low bioavailability, a growing body of laboratory and field ecotoxicology now documents adverse effects on aquatic organisms (including oxidative stress, disruption of calcium-metabolism pathways, enzyme inhibition and reproductive impacts), with evidence that some HREEs or specific REE species may be more toxic than others [11]. The toxicological database remains less complete than for conventional heavy metals, and differences in speciation, mixture interactions, and organismal uptake pathways complicate ecological risk assessments. Nevertheless, both laboratory toxicity studies and field correlation analyses indicate that elevated sedimentary REE concentrations can translate into ecological hazard, particularly for benthic and sediment-exposed species [2,11].

Assessing the magnitude and origin of REE enrichment in sediments, therefore combines geochemical fingerprinting with quantitative contamination indices and risk metrics [12]. Studies commonly apply normalisation to reference shale or crustal composites, calculate enrichment factors (EF) and geoaccumulation indices (Igeo), and model bioavailability using speciation and sequential extraction techniques [2,13]. Such methods enable the differentiation of the lithogenic component and its surrounding anthropogenic enrichment and the prioritization of areas with succeeding levels of human influence. However, the methods themselves (baseline choice, extractant, and normalisation scheme) can impact the results and hence require transparent and replicable protocols in the study of REE sediments [9].

Considering the ever-increasing globalization and growing dependence on REEs in advanced technologies, renewable energy systems, and electronic industries globally, the environmental behavior of REEs has become of international concern. Riverine and estuarine sediments are considered critical archives of both natural and anthropogenic REE inputs, recording processes that are not restricted to local boundaries but are instead driven by global production, resource extraction, and consumption patterns. Therefore, the general goals of this study were to (i) quantify the concentration and spatial distribution of REEs in surface sediments along the Linggi River as a representative tropical river system, (ii) assess REE enrichment and levels of contamination based on internationally accepted indices such as EF and Igeo, and

(iii) interpret geochemical behavior and fractionation of REEs in the context of anthropogenic activities at the global scale and natural controls on lithogenic distribution. Using the Linggi River as a case study, this study endeavors to provide fundamental data and relevant comparative insight into the global assessment of REE pollution in riverine and coastal environments.

2. Methodology

The Linggi River is one of the prominent river basins in Negeri Sembilan, Peninsula Malaysia. It drains a significant area that supports various ecological functions and human activities. Starting from its headwaters through agricultural and residential regions to the industrial area before emptying into the Strait of Malacca, the Linggi River is a significant source of fresh water for various human uses. Due to enhanced urbanization and industrialization of its basin area, the Linggi River receives increasing pressure from human activities. Hence, it becomes a fitting system for assessing the variation of sediment quality and metal movement.

The seven sampling stations (S1-S7) as shown in Figure 1 were chosen to cover varying land use activities and possible human inputs for sampling along the Linggi River. Sampling Station S1 is situated near Kuala Linggi Port activities. Station S2 is located alongside aquaculture cage farms. Station S3 is dominated mainly by poultry farm activities. S4 is a site of mixed land use activities, which include farm lands and residential areas. S5 is situated downstream of palm oil plantations and a village. Stations S6 are dominated by residential areas and small industries. The last station S7 is situated near a charcoal factory. It is evident that S1 to S7 cover varying sediment characteristics that respond to varying human activities as listed in Table 1.

Field procedures followed standard sediment sampling protocols to preserve geochemical integrity and ensure reproducibility. Surface sediments (0–5 cm) were collected as the primary matrix for geochemical analyses because this horizon integrates recent inputs and is most relevant for benthic exposure. A stainless-steel Van Veen grab (0.1 m^2) or a hand-operated Ponar grab (where boat access was limited), was used to recover undisturbed surface sediments. Upon retrieval, the top 0–5 cm of the grab was sampled using acid-cleaned stainless steel spoons and placed into pre-cleaned high-density polyethylene (HDPE) jars. Care was taken to avoid the reworked edge material and surface floating debris. At each site, three replicate grabs were taken within a 5–10 m radius. Replicates were split: two replicates were retained as separate cores for variance assessment and one composite (equal aliquots from the three grabs) was prepared for bulk geochemical analyses. For grain-size sensitive analyses (e.g., metal normalisation), a separate aliquot was taken and stored unfrozen for later sieving. All tools in contact with sediments were washed with deionised water and rinsed with methanol between sites. Blank field controls (bottle blanks and field replicates) were collected at one upstream site to check for contamination during transport and handling. Samples were labelled with site ID (S1–S7), date, time and replicate number. Samples were placed on ice in coolers immediately after collection and transported the same day to the laboratory. In the laboratory, samples designated for geochemical and REE analysis were frozen at −20 °C, then freeze-dried and homogenised using an agate mortar and pestle. Prior to chemical analysis, samples were sieved to <63 µm to focus on the fine fraction that typically binds trace elements; the coarse fraction was archived [2,13].

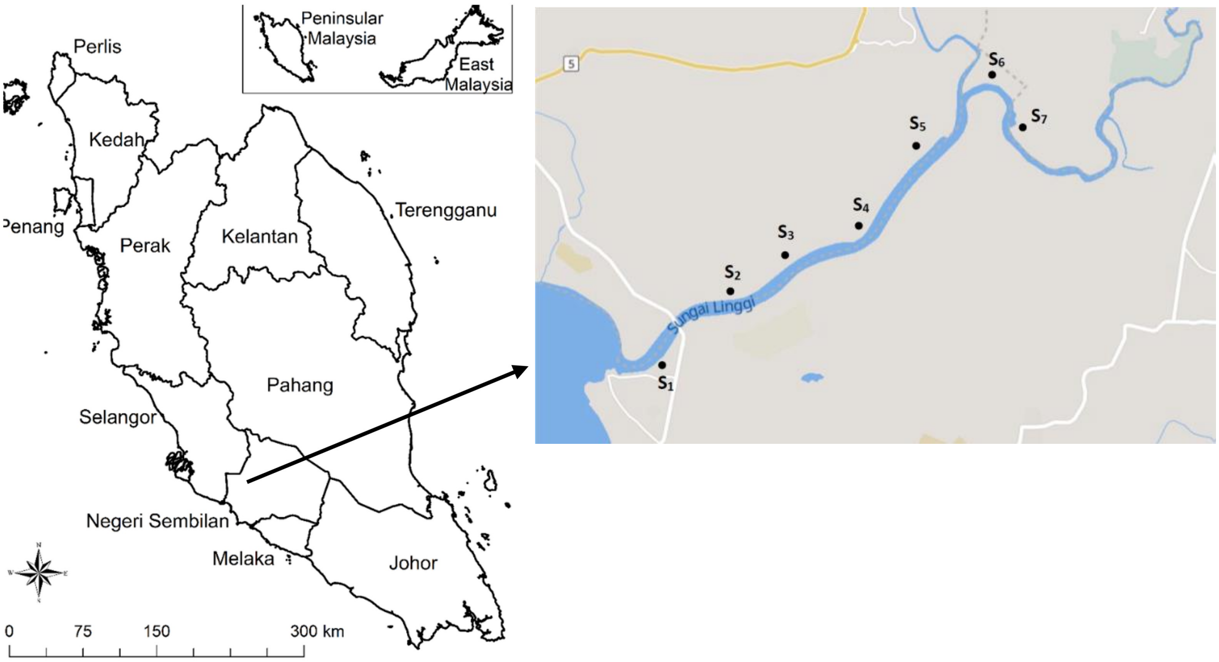

Figure 1. Map of Sampling Locations

Table 1. Sampling Station GPS Coordinates and Near by Activity

Station	GPS Coordinate	Near by Activity
S1	2°23′26″N, 101°58′26″E	Kuala Linggi Port
S2	2°24′18″N, 101°59′08″E	Aquaculture Cages
S3	2°25′12″N, 101°59′53″E	Poultry Farms
S4	2°26′06″N, 102°00′38″E	Agriculture Farm, Residential Area
S5	2°27′00″N, 102°01′23″E	Palm Oil Plantation and Village
S6	2°27′54″N, 102°02′10″E	Residential Area and Small Industry Area
S7	2°28′48″N, 102°02′56″E	Charcoal Factory

In this study, three replicate experiments in all samples of the analysis samples were weighted approximately 150 mg for short irradiation and 200 mg for long irradiation. The certified IAEA-Soil-7 was used as a multielement comparator. As calibration and Quality control procedures, blank samples, standard reference material IAEA-Soil-7, SL-1, MIX PTS-16 and 17 were then irradiated with thermal neutron flux of $3\text{-}4\times10^{12}$ n $cm^{-2}s^{-1}$ at the MINT TRIGA Mark II research reactor operated at 750 kW where a pneumatic transport facility was used. For short irradiation, the samples were radiated for 1 minute, and counting times for short irradiation were 5 minutes and 20 minutes after a cooling time of 20 minutes and 24 hours, respectively. For long irradiation, the samples were irradiated for 6 hours and counted for 1 hour after a cooling time of 3-4 days and 21-28 days [2,13].

3. Results

The concentrations of selected rare earth elements (REEs) and iron (Fe) in surface sediments collected along the Linggi River are summarized in Table 2. All analyzed elements exhibit distinct spatial variability across the seven sampling sites (S1–S7), reflecting heterogeneity in sediment composition along the river continuum.

Among LREEs, La concentrations vary from 47.67 to 60.40 mg/kg, with the minimum at S5 and the maximum at S7. Ce, the most abundant REE analyzed in this study, ranges from 93.00 to 116.33 mg/kg, with relatively high concentrations compared with other stations at upstream S1–S2 and downstream S7. These ranges of values are similar to and somewhat higher than those measured in tropical riverine and estuarine sediments in Southeast Asia, including Malaysian mangrove and estuarine environments [14,15]. Sm varies between 8.17 and 10.40 mg/kg, showing a gradual downstream increase, which is in good agreement with those reported for river sediments showing predominantly continental crustal contribution [16].

The HREEs exhibit measurable spatial variation. Dy concentrations range between 7.60 and 14.03 mg/kg, with higher values characterizing the upstream sites, S1–S3, and lowervalues for downstream areas. Tb ranges from 1.44 to 1.75 mg/kg, while Yb (5.35–8.68 mg/kg) shows relatively raised values at S1, S6, and S7. Total Dy, Tb, and Yb in general outweigh the average UCC values [14–16] and are comparable to those reported for sediments of river catchments influenced by urbanized or industrialized regions [17]. On the contrary, the concentrations of Eu are low, ranging from 0.76 to 1.10 mg/kg, and remain close to the reported crustal background values [14].

Iron (Fe) concentrations show considerable variation between 18,096 and 30,870 mg/kg. Concentrations of Fe are highest at stations S2 and S3 and near the UCC reference value of approximately 30,890 mg/kg [14]. However, much lower values have been found at station S5. Overall, concentrations of Fe are in the same range as those reported for Malaysian river and mangrove sediments [15].

Across all sampling sites, the total REE pool is dominated by LREEs, with La and Ce contributing the largest proportion. This dominance of LREEs over HREEs is consistent with patterns widely reported for riverine and estuarine sediments worldwide [2,15].

3.1. Enrichment Factor (EF)

The Enrichment Factor (EF) helps to identify whether the elements are from natural sources or due to anthropogenic activities. Iron (Fe) is used as the reference element. EF values greater than 2 suggest moderate to significant enrichment, indicating human-induced pollution. EF of heavy metals was determined based on the equation below [17]:

$$\mathrm{EF}_{\mathrm{metal}} = \frac{\left(\dfrac{\mathrm{M}_{\mathrm{exp}}}{\mathrm{Fe}_{\mathrm{exp}}}\right)_{\mathrm{sample}}}{\left(\dfrac{\mathrm{M}_{\mathrm{ref}}}{\mathrm{Fe}_{\mathrm{ref}}}\right)_{\mathrm{shale}}}$$

The terms $\mathrm{M}_{\mathrm{exp}}$ or $\mathrm{Fe}_{\mathrm{exp}}$ refer to the concentration of an element in the experimental sample, while $\mathrm{M}_{\mathrm{ref}}$ or $\mathrm{Fe}_{\mathrm{ref}}$ represent the concentration of a commonly abundant reference element in average shale, as reported by Turekian [18]. The enrichment factor (EF) is interpreted as follows:

- EF < 1 indicates no enrichment,
- EF between 1 and 3 suggests minor enrichment,
- EF between 3 and 5 indicates moderate enrichment,
- EF between 5 and 10 shows moderately severe enrichment,
- EF between 10 and 25 reflects severe enrichment,
- EF between 25 and 50 suggests very severe enrichment, and
- EF greater than 50 indicates extremely severe enrichment.

The enrichment factor values computed using Fe as a normalizing factor are shown in Table 3. Range of EF values of the studied REEs is between 1.22 and 6.82, indicating minor to moderately severe enrichment, as per typical standards of classification.

Dysprosium has EF values ranging between 3.05 and 5.18, which is a moderate to moderately severe enrichment in most locations. Similar EF ranges were documented in the sediment samples collected from Asian river basins affected by either industrial or urban activities [13,17]. Ytterbium has the highest EF enrichment among all the other REEs examined and has the widest range with a value of 2.81 to 6.82 EF units, and is highly enriched in sample S5 to concentrations above those in pristine river basins [17].

The EF values for samarium (Sm), terbium (Tb), lanthanum (La), and cerium (Ce) ranged from 2 to 4, indicating slight to moderate enrichment factors. These results are comparable with the levels found in moderately affected estuarine and mangrove sediments [2,13,15]. In contrast, europium (Eu) displays consistently low EF values (1.22–1.47), closely approximating unity and similar to background-dominated conditions reported for uncontaminated sediments [14,16].

3.2. Geoaccumulation Index (Igeo)

The Geoaccumulation Index (Igeo) was proposed by Muller G. [19] and is widely applied to assess the extent to which the level of a given heavy metal is elevated above its natural abundance. The index allows the assessment of the severity of contamination on the basis of the extent to which the measured concentration exceeds the natural level. A Igeo > 0 indicates contamination, and a Igeo > 4 represents very heavy to extremely heavy contamination. Seven different classes are established on the basis of the severity of the level of metal contamination proposed according to Müller’s scheme. The Igeo formula is given by:

$$I_{geo} = log_2\left[\frac{c_n}{1.5 \times B_n}\right]$$

Table 2. Average concentrations (mg/kg, mean ± SD, n=3) of selected rare earth elements (REEs) and Fe in surface sediments of the Linggi River

Element	S1	S2	S3	S4	S5	S6	S7
Dy	14.0 ±0.4	12.8 ±0.3	12.7 ±0.5	11.0 ±0.9	7.63 ±0.32	7.70 ±0.36	7.60 ±0.26
Sm	8.68 ±0.67	8.25 ±0.39	8.17 ±0.06	8.32 ±0.26	8.32 ±0.20	9.03 ±0.11	10.4 ±0.2
Yb	8.54 ±0.64	6.60 ±0.33	5.35 ±1.76	7.58 ±0.17	7.76 ±0.13	8.06 ±0.10	8.68 ±0.15
La	56.4 ±1.6	53.5 ±2.3	51.6 ±0.6	50.7 ±1.0	47.7 ±1.2	51.5 ±0.3	60.4 ±1.3
Ce	115 ±4	114 ±3	104 ±3	103 ±5	93.0 ±2.7	100 ±2	116 ±2
Tb	1.75 ±0.04	1.63 ±0.02	1.59 ±0.04	1.51 ±0.08	1.44 ±0.03	1.61 ±0.09	1.67 ±0.01
Eu	0.960 ±0.030	1.07 ±0.02	1.10 ±0.06	0.910 ±0.160	0.760 ±0.010	0.920 ±0.010	1.05 ±0.04
Fe	27,100 ±1600	30,900 ±1700	30,300 ±1050	24,400 ±3230	18,100 ±48	23,800 ±320	25,000 ±170

Table 3. Enrichment factor of REEs in the surface mangrove sediment of Linngi River, Malaysia

Element	S1	S2	S3	S4	S5	S6	S7
Dy	5.18	4.15	4.20	4.53	4.22	3.24	3.05
Sm	2.39	1.99	2.01	2.54	3.43	2.83	3.10
Yb	5.02	3.40	2.81	4.95	6.82	5.39	5.53
La	2.43	2.02	1.99	2.43	3.07	2.53	2.82
Ce	2.32	2.03	1.88	2.31	2.81	2.31	2.55
Tb	3.53	2.88	2.87	3.38	4.36	3.71	3.66
Eu	1.24	1.22	1.27	1.31	1.46	1.35	1.47
Dy	5.18	4.15	4.20	4.53	4.22	3.24	3.05

In the Igeo calculation, Cn signifies the concentration of the element in the sample, whereas Bn represents the background or baseline concentration. A constant factor of 1.5 is added in order to allow for possible natural variation in the background values due to lithological differences in the sediments. The classes of Igeo values range from unpolluted to extremely polluted conditions, in a total of seven classes, as follows:

- Igeo < 0: Class 0 – unpolluted
- 0 ≤ Igeo < 1: Class 1 – unpolluted to moderately polluted
- 1 ≤ Igeo < 2: Class 2 – moderately polluted
- 2 ≤ Igeo < 3: Class 3 – moderately to heavily polluted
- 3 ≤ Igeo < 4: Class 4 – heavily polluted
- 4 ≤ Igeo < 5: Class 5 – heavily to extremely polluted
- Igeo ≥ 5: Class 6 – extremely polluted

The geoaccumulation index (Igeo) values for individual REEs are shown in Table 4. Igeo values of all elements at all sites range between –0.99 and 1.42, indicating that the sediments are unpolluted to moderately polluted according to the classification described by Müller [19]. Dy has Igeo values >1 at some sites, which fall into the "moderately polluted" category at these stations. Yb has similar trends, with Igeo values ranging between 0.70 and 1.40 for several sites, which includes multiple site values in the moderately polluted class. These ranges agree with ranges reported in the literature from river sediments influenced by both natural and anthropogenic inputs [20,21]. In contrast, samarium (Sm), lanthanum (La), cerium (Ce), and terbium (Tb) generally show Igeo values between 0 and 1, corresponding to unpolluted to moderately polluted conditions and comparable to those reported for slightly impacted tropical river and estuarine sediments [22]. Europium (Eu) consistently exhibits negative Igeo values (–0.99 to –0.44) across all sampling sites, similar to values reported for sediments dominated by lithogenic sources with minimal anthropogenic influence [2,13,23].

The total concentration of rare earth elements (ΣREE), light rare earth elements (ΣLREE), heavy rare earth elements (ΣHREE), and their indicator ratios of ΣLREE/ΣHREE, lanthanum to ytterbium (La/Yb), europium to samarium (Eu/Sm), lanthanum to samarium (La/Sm), cerium to lanthanum (Ce/La), and cerium anomaly (Ce/Ce*) of the ten surface sediment samples from the mangrove area are presented in Table 5.

The distribution of rare earth elements (REEs) in the Linggi River sediments shows a characteristic enrichment of light rare earth elements (LREEs) compared to heavy rare earth elements (HREEs), a pattern consistent with natural sedimentary systems influenced by continental inputs. The contributions of total REE concentrations in all seven sampling sites are generally determined by the LREE, which can be inferred from the LREE/HREE ratio ranging from 7.43 to 10.48. This high ratio generally indicates large differences in the concentrations of the two sets of REEs, and this is an indication that the sediments were mainly obtained from the weathering process of felsic rock sources, which generally contain higher concentrations of LREE than those of HREE. This pattern is normal in river and estuarine environments across the world, where the dominance is generally influenced by mineralogical and hydrodynamic processes [14,22,23].

These facts are further corroborated by the high La/Yb ratios, which range from 6.15 to 9.65, indicating strong fractionation between LREEs and HREEs. These values are considerably higher than the chondritic ratio and reflect the comparative depletion of HREEs in sediments. Such depletions may be linked to the higher solubility and mobility of HREEs in aqueous systems, particularly under slightly acidic to neutral pH, which favors their preferential transport as dissolved phases rather than particulate retention. The La/Sm ratios vary from 5.71 to 6.50, which indicates that the enrichment of LREEs is not exactly uniform among all the light elements but rather displays a moderate fractionation with respect to middle rare earth elements. From this, it could be presumed that the differences in weathering intensity and source rock mineralogies provide the main cause for differential mobility. Cerium (Ce) and europium (Eu) anomalies provide additional insights into the redox and mineralogical conditions of the Linggi River sediments.

Table 4. Geoaccumulation index (Igeo) of REEs in the surface mangrove sediment of Linngi River, Malaysia

Element	S1	S2	S3	S4	S5	S6	S7
Dy	1.42	1.29	1.28	1.07	0.540	0.550	0.530
Sm	0.300	0.230	0.210	0.240	0.240	0.360	0.560
Yb	1.37	1.00	0.700	1.20	1.23	1.29	1.40
La	0.330	0.250	0.200	0.170	0.080	0.200	0.420
Ce	0.260	0.250	0.120	0.100	-0.050	0.060	0.280
Tb	0.870	0.760	0.730	0.650	0.590	0.750	0.800
Eu	-0.640	-0.480	-0.440	-0.720	-0.990	-0.710	-0.520

Table 5. Concentration of light and heavy REEs and ratios of REEs in the surface sediment

Element	S1	S2	S3	S4	S5	S6	S7
Ce (mg/kg)	115	114	104	103	93	100	116
Dy (mg/kg)	14.0	12.8	12.7	11.0	7.63	7.70	7.60
Eu (mg/kg)	0.960	1.07	1.10	0.910	0.757	0.917	1.05
La (mg/kg)	56.4	53.5	51.6	50.7	47.7	51.5	60.4
Tb (mg/kg)	1.75	1.63	1.59	1.51	1.44	1.61	1.67
Sm (mg/kg)	8.68	8.25	8.17	8.32	8.32	9.03	10.4
Yb (mg/kg)	8.54	6.60	5.35	7.58	7.76	8.06	8.68
Total (mg/kg)	205	198	189	183	167	179	206
LREE (La+Ce+Sm+Eu)	181	177	165	163	150	162	188
HREE (Tb+Dy+Yb)	24.3	21.0	19.7	20.1	16.8	17.4	18.0
LREE/HREE	7.43	8.43	8.40	8.10	8.90	9.31	10.5
La/Yb	6.60	8.12	9.65	6.69	6.15	6.39	6.96
La/Sm	6.50	6.49	6.32	6.10	5.73	5.71	5.81
Ce/La	2.03	2.14	2.02	2.03	1.95	1.95	1.93
Eu/Sm	0.111	0.130	0.135	0.109	0.091	0.101	0.101
Yb/Sm	0.984	0.800	0.655	0.911	0.932	0.892	0.835
Ce/Ce*	1.06	1.11	1.04	1.03	0.958	0.954	0.952

The total REE was used to determine the distribution patterns of the light (LREE) and heavy (HREE) rare earth elements and the correlations between the Ce anomalies. The natural odd–even effects of REE concentrations were obtained by using the elemental concentration value of the shale standard as mentioned in [23]. The anomaly of Ce was calculated based on the following equation:

$$Ce/Ce^{*} = 2[Ce/Ce_{\mathrm{shall}}][La/La_{\mathrm{shale}} + Sm/Sm_{\mathrm{shall}}]^{-1}$$

The calculated Ce/Ce* ratios range from 0.95 to 1.11, and hence, the values are close to unity. This indicates the absence of significant Ce anomalies, which are believed to be produced under redox-driven processes. In oxic conditions, Ce can be oxidized to Ce(IV) and precipitate out from the solution by being adsorbed onto Fe–Mn oxides, forming a negative anomaly, while in reducing conditions it is mobilized, thereby creating a positive anomaly. Hence, Ce/Ce* values close to unity here indicate that the sediments were deposited under fairly stable oxic conditions with little post-depositional remobilization of Ce.

However, the Eu/Sm ratio values (0.09-0.14) demonstrate the existence of negative Eu anomalies in all the stations. Negative Eu anomalies are known to be related to the plagioklas fractionation mechanism because Eu has a higher affinity to feldspars in magma differentiation. Weathering of feldspars also favors the easy release of other rare earth elements relative to Eu; hence, Eu is absent in sediment deposits [14]. The retention of the negative Eu anomalies in the Linggi sediment deposits indicates a felsic input from the geology in Peninsular Malaysia due to the granites and metamorphic geological formations in Peninsular Malaysia.

Yb/Sm ratios (0.64–0.83) additionally show the selective enrichment of LREEs over HREEs, with the latter being relatively depleted. This type of characteristic is expected for sediments that are strongly influenced by the weathering of continental crust rather than mafic or ultramafic sources. These have flatter REE patterns. Based on the aforementioned patterns of the REE distribution in the Linggi River sediments, the sediments are strongly source-controlled by felsic lithologies with further fractionations due to hydrodynamic sorting, adsorption on fine particles, and selective mineral weathering.

In general, the REE geochemistry of sediments around the Linggi River suggests that their source material is mainly from the weathering of felsic rocks and are characterized by enrichment in LREEs, a weak Ce anomaly, and a negative Eu anomaly. The lack of Ce anomalies of either depletion or enrichment indicates little concern for oxic conditions during transport and deposition, while negative Eu for some samples may indicate a contribution from a source rich in plagioclase. The deduction made here is supported geologically and comparable observations from tropical river systems worldwide that show chemical weathering under warm and wet conditions affects REE distribution.

4. Discussion

The patterns observed for the distribution of the rare earth elements (REEs) in the sediments of the Linggi River are comparable to those observed in riverine and estuarine environments where continental crust supplies the major sources. This large positive bias towards the light rare earth elements (LREEs) over the heavy rare earth elements (HREEs) indicated by the high ΣLREE/ΣHREE and La/Yb ratios is very close to that observed in sediments from the tropical river systems of Southeast Asia and other wet climates [2,13]. This bias towards the LREEs has been related to the influence of the weathering of felsic rocks with significant contributions from the LREE-bearing phases of these rocks, which include feldspars, monazite, and allanite in the river basin systems [14,16]. The observed patterns of fractionation have been observed in the sediments of the mangrove-associated sediment profiles of Malaysia, the southern Chinese estuaries, and the tropical river courses of the Indian subcontinent, where the ΣLREE/ΣHREE values exceed 6 and show very significant continental influence [15,22,23]. The sediments of the Linggi River range within the reported values, indicating that the major control on the REE composition is the regional geology.

The Eu anomalies found in the Linggi River sediment appear to be a normal characteristic for felsic sediment, as reported by numerous studies carried out on riverine and estuarine sedimentation systems within Peninsular Malaysia, as well as the general region of Southeast Asia [24]. Negative Eu anomalies correlate to the separation of the plagioclase feldspar, which is caused by the residual concentration of Eu oxide within the feldspar minerals during the weathering process, as it is selectively enriched rather than being dispersed into the pore solution [25]. This Eu depletion characteristic is also found in the Selangor River, the Klang River estuary, as well as the tropical riverine systems associated with granitic drainage basins around the world [2,25]. On the other hand, the Ce/Ce* ratios of close to 1 reflect the non-selective redox separation associated with sediment transport and deposition under sediment transport conditions. A similar characteristic is also reported among numerous riverine sediment studies, namely the tropical Malaysian rivers, the southern Chinese rivers, as well as the tropical estuarine sediment systems around the world, as related to this study [26,27].

While lithogenic sources dominate the overall REE budget, enrichment factor (EF) and geoaccumulation index (Igeo) results indicate localized anthropogenic enrichment, particularly for dysprosium (Dy) and ytterbium (Yb). Moderate to moderately severe enrichment of these HREEs has been reported in sediments influenced by industrial, urban, and electronic-waste-related activities in other Asian river systems [17,21,26]. For example, elevated EF values for Dy and Yb comparable to those observed in the Linggi River have been documented in the Pearl River estuary (China) and in urbanized river basins in India, where inputs from high-technology manufacturing, wastewater discharge, and atmospheric deposition were identified as contributing factors [24,26]. In Malaysian contexts, similar HREE enrichment patterns have been observed in sediments near industrial corridors and densely populated catchments [21,23].

The relatively low EF and consistently negative Igeo values for europium (Eu) contrast sharply with the behavior of Dy and Yb, reinforcing its predominantly lithogenic origin. This conservative behavior of Eu has also been noted in other river sediment studies and is often used as a reference for distinguishing natural from anthropogenic REE contributions [14,16].

Spatial Variability and Estuarine Trapping Processes Spatial variations in REE enrichment within the Linggi River system are consistent with patterns reported in estuarine environments, where hydrodynamic sorting and sediment trapping strongly influence metal and REE distributions. Downstream and estuarine zones commonly act as sinks for fine-grained, REE-rich particles, leading to higher concentrations and enrichment indices relative to upstream locations [22,25]. Similar downstream enrichment trends have been reported for REEs in mangrove sediments from Malaysia, Thailand, and southern China, where reduced flow velocities promote the accumulation of clay-associated and organic-bound REEs [21,23,25]. The elevated enrichment of selected REEs at particular sites along the Linggi River aligns with these observations, suggesting that depositional processes amplify localized enrichment signals.

When contrasted with global values, REEgeo values in sediments of the Linggi River are remarkably similar to tropical riverine patterns characterized by high degrees of chemical weathering associated with tropical climatic regimes [14,22]. High degrees of chemical weathering under these climatic regimes favor REE mobilization in parent rocks but also favor their retention in sediments. Both high lithogenic values and moderate anthropogenic values reflect the high sensitivity of REE values, especially HREE values, in tracing human impacts in fluvial and estuarine systems. In conclusion, REE variations in sediments of the Linggi River follow global trends, in which geological constraints are predominant in controlling REE values, while human influences are reflected in REE enrichments. This observation corroborates earlier findings while underlining the importance of REE concentration, EF, and Igeo in sediment quality assessment in tropical rivers.

5. Conclusions

The current investigation offers a thorough evaluation of the geochemistry of rare earth elements in surface sediment along the Linggi River and discloses the coexistence of both lithological and local anthropological influences in their distributions. The preponderance of LREE to HREE and corresponding high ΣLREE/ΣHREE and La/Yb ratios in the surface sediment along the Linggi River indicates that the sediment geochemistry is dominated by felsic source rock typical of this riverous topological area in terms of geological characteristics and processes. The presence of negative Eu anomalies in all samples supports felsic source rock dominance in sediment geochemistry along the Linggi River; moreover, the near-binary Ce/Ce* ratio in sediment geochemistry in the surface sediment along the river indicates purely depositional conditions and lack of redox-induced transfer in the sediment geochemistry along the riverous topological area. Even in the face of geologically dominated geochemical distribution in sediment geochemistry along the riverous topological area, selected enrichment factor and geoaccumulation index support moderate enrichment in selected HREEs like dysprosium and ytterbium in sediment geochemistry along the river. The variations in REE concentration and degree of REE enrichment also suggest the influences of hydrodynamic sorting, as well as estuarine trapping, with the downstream areas acting as sinks for fine REE particles. In general, the REEs of the Linggi River sediment deposits present a mixed response to the geochemical alteration, wherein natural weathering processes define the REE composition, and anthropogenic influences, being localized, demonstrate measurable disturbances to the REE deposits. The REEs, particularly the HREEs, being very sensitive, not only indicate the subtle influences of anthropogenic activities on the tropical rivers, as the present work demonstrates, but also, as a whole, the monitoring of REEs, together with the analysis of metallic components, would help to accurately determine the long-term concentration of REEs, as demand increases worldwide.

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REFERENCES

[1] Leal Filho W., Kotter R., Özuyar P. G., Abubakar I. R., Eustachio J. H. P. P., Matandirotya N. R., "Understanding Rare Earth Elements as Critical Raw Materials," *Sustainability*, vol. 15, no. 3, pp. 1919, 2023. DOI: 10.3390/su15031919.

[2] Kumar K., Saion E., Halimah M. K., et al., "Rare earth element (REE) in surface mangrove sediment by instrumental neutron activation analysis," *Journal of Radioanalytical and Nuclear Chemistry*, vol. 301, pp. 667–676, 2014. DOI: 10.1007/s10967-014-3221-z.

[3] Ma S., Han G., "Rare earth elements reveal the human health and environmental concerns in the largest tributary of the Mekong River, Northeastern Thailand," *Environmental Research*, vol. 252, pp. 118968, 2024. DOI:

10.1016/j.envres.2024.118968.

[4] Ejaz U., Khan S. M., Shah S. F. A., Khalid N., Jehangir S., Rizvi Z. F., Svenning J. C., "Advanced integrative analytics for data-driven risk assessment of ecological and human health risks from heavy metal contaminations in soil," *Journal of Hazardous Materials Advances*, vol. 17, pp. 100596, 2025. DOI: 10.1016/j.hazadv.2025.100596.

[5] Wang P., Deng Y., Zhang G., Liu D., Ma J., Liu C., Zheng X., Zhu Y., Cao J., Chen F., "Impact of iron biogeochemical cycling in deep-sea environments on rare earth element enrichment," *Chemical Geology*, vol. 692, pp. 122951, 2025. DOI: 10.1016/j.chemgeo.2025.122951.

[6] Fang X., Peng B., Guo X., Wu S., Xie S., Wu J., Yang X., Chen H., Dai Y., "Distribution, source and contamination of rare earth elements in sediments from lower reaches of the Xiangjiang River, China," *Environmental Pollution*, vol. 336, pp. 122384, 2023. DOI: 10.1016/j.envpol.2023.122384.

[7] Lafrenière M., Lapierre J., Ponton D. E., Guillemette F., Amyot M., "Rare earth elements (REEs) behavior in a large river across a geological and anthropogenic gradient," *Geochimica et Cosmochimica Acta*, vol. 353, pp. 129–141, 2023. DOI: 10.1016/j.gca.2023.05.019.

[8] Thomas B. S., Dimitriadis P., Kundu C., Vuppaladadiyam S. S. V., Raman R. S., Bhattacharya S., "Extraction and separation of rare earth elements from coal and coal fly ash: A review on fundamental understanding and on-going engineering advancements," *Journal of Environmental Chemical Engineering*, vol. 12, no. 3, pp. 112769, 2024. DOI: 10.1016/j.jece.2024.112769.

[9] Zhou W., Han G., Liu M., Song C., Li X., "Geochemical distribution characteristics of rare earth elements in different soil profiles in Mun River Basin, northeast Thailand," *Sustainability*, vol. 12, no. 2, pp. 457, 2020. DOI: 10.3390/su12020457.

[10] Xu H., Liu P., Zhao S., Wen Y., Tang Y., "Developing a rate law for Ce(III) oxidation by manganese oxides," *Environmental Science & Technology*, vol. 59, no. 25, pp. 12606–12617, 2025. DOI: 10.1021/acs.est.4c12688.

[11] Hatje V., Schijf J., Johannesson K. H., Andrade R., Caetano M., Brito P., Haley B. A., Lagarde M., Jeandel C., "The global biogeochemical cycle of the rare earth elements," *Global Biogeochemical Cycles*, vol. 38, no. 6, pp. e2024GB008125, 2024. DOI: 10.1029/2024gb008125.

[12] Liu Z., Gu X., Lian M., Wang J., Xin M., Wang B., Ouyang W., He M., Liu X., Lin C., "Occurrence, geochemical characteristics, enrichment, and ecological risks of rare earth elements in sediments of 'the Yellow River−Estuary−Bay' system," *Environmental Pollution*, vol. 319, pp. 121025, 2023. DOI: 10.1016/j.envpol.2023.121025.

[13] Ashraf A., Saion E., Gharibshahi E., Kamari H. M., Kong Y. C., Hamzah M. S., Elias M. S., "Rare earth elements in core marine sediments of coastal East Malaysia by instrumental neutron activation analysis," *Applied Radiation and Isotopes*, vol. 107, pp. 17–23, 2015. DOI: 10.1016/j.apradiso.2015.09.004.

[14] Taylor S. R., McLennan S. M., *The Continental Crust: Its Composition and Evolution*, Oxford: Blackwell Scientific, 1985, p. 312.

[15] K. Kumar and E. B. Saion, "Distributions of rare earth element (REE) in mangrove surface sediment by nuclear technique," *Inti Journal*, vol. 2022, no. 03, 2022.

[16] Wang S., Wang Z., Gao S., Zhang X., Zeng J., Wu Q., "Rare earth elements in lake sediments record historic environmental influences from anthropogenic activities," *Ecological Indicators*, vol. 159, pp. 111680, 2024. DOI: 10.1016/j.ecolind.2024.111680.

[17] Chen D. W., Zhang M., Shrestha S., "Compositional characteristics and nutritional quality of Chinese mitten crab (*Eriocheir sinensis*)," *Food Chemistry*, vol. 103, no. 4, pp. 1343–1349, 2007. DOI: 10.1016/j.foodchem.2006.10.047.

[18] Turekian K. K., Wedepohl K. H., "Distribution of the elements in some major units of the Earth's crust," *Bulletin of the Geological Society of America*, vol. 72, pp. 175–192, 1961.

[19] Muller G., "Index of geoaccumulation in sediments of the Rhine River," *Geojournal*, vol. 2, no. 3, pp. 108–118, 1969.

[20] Henderson P., *Rare Earth Element Geochemistry: Developments in Geochemistry*, vol. 2, Amsterdam: Elsevier, 1984, 510 p.

[21] Hedayatzadeh, F., Ildoromi, A., Hassanzadeh, N., Bahramifar, N., & Banaee, M., "Rare earth elements as emerging contaminants in the surface sediments of Maroon-Jarahi sub-basin (Persian Gulf coasts): assessment of pollution, distribution, and potential ecological-health risk," *Environmental Geochemistry and Health*, vol. 47, no. 11, 2025. DOI: 10.1007/s10653-025-02798-x.

[22] Rezaee, K., Saion, E.B., Wood, A.K., Abdi, M.R., "Rare earth elements distribution in marine sediments of Malaysia coasts," *J. Rare Earths*, vol. 27, no. 6, pp. 1066–1071, 2009. DOI: 10.1016/S1002-0721(08)60390-7.

[23] Rezaee, K., Saion, E.B., Wood, A.K., Abdi, M.R., "Rare earth elements determination and distribution patterns in surface marine sediments of the South China Sea by INAA, Malaysia," *J. Radioanal. Nucl. Chem*, vol. 283, pp. 823–829, 2010. DOI: 10.1007/s10967- 009-0421-z.

[24] Raza, M., Zakaria, M. P., Hashim, N. R., Yim, U. H., Kannan, N., & Ha, S. Y., "Composition and source identification of polycyclic aromatic hydrocarbons in mangrove sediments of Peninsular Malaysia: indication of anthropogenic input," *Environmental Earth Sciences*, vol. 70, no. 6, pp. 2425–2436, 2013. DOI: 10.1007/s12665-013-2279-1.

[25] Weill, D. F., & Drake, M. J., "Europium Anomaly in Plagioclase Feldspar: Experimental Results and Semiquantitative Model," *Science*, vol. 180, no. 4090, pp. 1059–1060, 1973. DOI: 10.1126/science.180.4090.1059.

[26] Khan, A. M., Yusoff, I., Bakar, N. K. A., Bakar, A. F. A., & Alias, Y., "Assessing anthropogenic levels, speciation, and potential mobility of rare earth elements (REEs) in ex-tin mining area," *Environmental Science and Pollution Research*, vol. 23, no. 24, pp. 25039–25055, 2016. DOI: 10.1007/s11356-016-7641-x.

[27] Xu, Z., Lim, D., Choi, J., Yang, S., & Jung, H., "Rare earth elements in bottom sediments of major rivers around the Yellow Sea: implications for sediment provenance," *Geo-Marine Letters*, vol. 29, no. 5, pp. 291–300, 2009. DOI: 10.1007/s00367-009-0142-x.