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Distributions of Rare Earch Element (REE) in Mangrove Surface Sediment by Nuclear Technique

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Abstract

The Juru rivers are highly industrial, urbanised, and agricultural. The aim of the study was to examine the geochemical bases and enrichment of rare earth elements (REEEs) in Juru mangrove sediments. This study is carried out to investigate the concentrations of rare earth elements (REEEs) Samarium (Sm), Europium (Eu), Yttrium (Yb), Lutetium (Lu), and Terbium (Tb) present in surface mangrove sediments of the Juru River, West Coast of Peninsular Malaysia. The concentrations of rare earth elements in the sediments were determined by using the instrumental neutron activation analysis (INAA) method. For calibration and quality control procedures, standard reference material SL-1 and blank samples were irradiated together with sediment samples. The degree of anthropogenic impact on sediments was computed using enrichment factor. The concentration and enrichment factor of all the REE elements ranged between 0.42 mg/kg (Lu), 7.55 mg/kg (Sm), 0.77 mg/kg (Lu), and 2.96 mg/kg (Tb), respectively. The geochemical behaviour of REEs in surface sediments and normalized patterns (chondrite and shale) has been studied. These findings indicate that the level of pollution has not reached an extreme or severe level, but ongoing studies should be carried out on the inputs of anthropogenic activities at the Juru River.

Keywords

Rare earth elements, Enrichment, Neutron activation

Introduction

Due to human-induced causes, toxic metal concentrations in many ecosystems have lately been discovered to be at unpredictable levels (Ahmed et al., 2006; Davydova et al., 2005; Nour et al., 2019). Toxic elements enter mangrove habitats in trace amounts from various sources and anthropogenic activities, which include sewage and industrial effluents. Toxic metals, which can be found in the dissolved content of sediments, are classified as rare earths, trace metals, and heavy metals. Advection and convection, turbulence, diffusion, and other physical activities alter trace constituents, which are also influenced by biological processes such as

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ingestion, excretion, and biodegradation (Naser et al., 2013; Brügmann et al.,1999; Sun et al., 2017).

The atomic number of the rare earth elements (REEs) (also known as lanthanides) ranged from 57 to 71. Light REEs (LREEs) and heavy REEs (HREEs) are the two types of REEs. La, Pr, Nd, Ce, Eu, Sm, and Pm are light REEs (LREEs: 57–62), while Gd, Dy, Ho, Tb, Er, Yb, Tm, and Lu are heavy REEs (HREEs: 63–71) (Hu Z et al., 2006, Balaram 2019). Because of their ability to act as an electron donor and acceptor, they are used in a variety of fields, including electrical, optical, magnetic, glass fibres, and catalytic applications (Eliseeva et al., 2011). Aside from their use, the downsides of REEs from an ecotoxicological standpoint, as well as their risk to the environment, are little known. Because REEs are anthropogenic rather than naturally occurring, they reach the environment in significantly more soluble (water solubility) and reactive ionic forms, making them more accessible. REEs have an ecotoxicological effect that is virtually identical to that of critical metals, although with a lower impact at low concentrations. At the same time, at a larger amount, it becomes more poisonous (Kulaksız et al., 2013). REEs are more harmful because they disturb biological processes in living creatures by disrupting calcium ions due to their similar size or by having a strong affinity for phosphate groups in biological macromolecules. REEs have thus so far played no significant role in the lives of humans, plants, or animals.

There have been several studies on the geochemistry of river sediments in Peninsular Malaysia, but none on the element REEs in surface sediments, particularly in mangrove areas, which are one of the most productive ecosystems and one of the most essential determinants for economic growth. As a result, the current investigation was carried out to determine the distribution and concentration of REEs components in surface sediment from mangrove areas, Juru, Penang by using Instrumental Nuclear Activation Analysis (INAA).

Methodology

Sediment samples were taken from the mangrove area along the Juru River, Penang, Malaysia, as shown in Figure 1. The sampling took place in January 2012 to detect hazardous substances at trace levels. The mangrove of Juru River is roughly a 12 km drive south of Butterworth. Juru River flows from Bukit Minyak to the West till it reaches the South China Sea, with a calculated length of 7.95 km from upstream.

Ten sediment samples were collected and mixed for homogeneity to represent the distribution based on the various sampling locations. The surface sediment samples were collected at a depth of approximately 5.0 cm and within the range of 3.0 – 5.0 m adjacent to each other by scraping off the surface layer using a clean knife (Yap et al., 2002). The surface sediment samples collected were then placed in re-sealable zipper polyethylene plastic bags with labels and kept in an ice box at 4°C. To eliminate the moisture, the surface sediments were dried in an oven at 80°C for at least 72 hours to a consistent dry weight. The powdered materials were sieved through a 63 μm stainless steel aperture after being powdered in an agate mortar with an agate pestle. The samples were stored in plastic pillboxes after being forcefully shaken (Rezaee et al., 2011).

The powdered samples collected from each location were replicated four times, approximately 150 mg and 200 mg, and stored separately in heat-sealed polyethylene vials for short and long radiations, respectively. Concentrations of elements were determined using the INAA comparative method. The standard reference material SRM SL–1 (Lake Sediment) was used as a multi-element comparator. For quality assurance purposes, blank samples and standard reference materials were irradiated together in a pneumatic transport facility at the research reactor operated at 750 kW (MINT TRIGA) with a thermal neutron flux of 4.0 x 1012 cm-2 s-1. The samples were radiated for 60 seconds and then counted for 300 and 1200 seconds, respectively, after cooling times of 1200 and 8640 seconds, during short radiation. For long radiation, the samples were irradiated for 21600 seconds and counted for 3600 seconds after a cooling time of 3–4 and 21–28 days. Counting of radiated samples was performed using a calibrated high-resolution HPGe detector. The distance between the detector and the sample was maintained approximately at 12 cm (short radiation) and 2 cm (long radiation) (Ashraf et al., 2016).

For this work, the enrichment factor (EF) was used to assess the distribution of REE elements and contamination of mangrove sediments, Juru, Penang. The enrichment factor (EF) can be assessed using the equation below:

$$EF_{metal} = \frac{\left(\frac{M_{exp}}{Fe_{exp}}\right)_{sample}}{\left(\frac{M_{ref}}{Fe_{ref}}\right)_{shale}}$$

M_{ref} or Fe_{ref} refers to a common abundant element in the average shale, while M_{exp} or Fe_{exp} refers to element concentration in the experimental sample (Mucha et al., 2003). Table 1 indicates the classification and sediment contamination status.

Table 1. Classification of Enrichment Factor (EF)

EF	Sediment enrichment status	Reference
≤ 2	Low enrichment	Diop et al. (2015)
2–5	Moderate enrichment	
5–20	High enrichment	
20–40	Very high enrichment	
> 40	Extreme enrichment	

Results and Discussion

The quality and validity of the analytical method were checked with standard reference material (SRM) SL–1. The concentrations of standard and measured values and the average

concentrations of the target element in sediments are shown in Table 2. The recoveries resulting from the nuclear and atomic methods are within the range of acceptable, 70.6 –110%.

Table 2. The analysis of the standard reference material and comparison with certified values of SL–1

Elements	Standard Value	Measured Value	Recovery (%)
Eu	1.6	1.76	110
Lu	0.54	0.381	70.6
Tb	1.4	0.99	70.7
Sm	9.25	8.82	95.4
Yb	3.42	3.73	109

The concentration of REE elements is presented in Table 3. The INAA and alternative technique, AAS, were used to identify and quantify a total of five elements in sediments. Samarium (Sm) was discovered to be the most abundant element in sediment at trace levels, while lutetium (Lu) was the least abundant element in the sediment. Overall, the abundance of target elements was observed in the following order in sediments: Sm > Tb > Yb > Eu > Lu. The composition of naturally occurring sediments and their anthropogenic sources around the sampling site may determine the order of abundance of the components. The ∑LREE/∑HREE ratio is greater than one, indicating that LREE should be more abundant in the samples than HREE. Coastal mixing processes, hydrodynamic dynamics, and sediment transport could all contribute to this. Furthermore, there is a significant likelihood of LEEE uptake on clay, which is a rich matrix in coastal environments.

The average shale PAAS (Post Archean Australian average shale) of Eu, Lu, Tb, Sm, and Yb were found to be 1.08 mg/kg, 0.433 mg/kg, 0.774 mg/kg, 5.65 mg/kg, and 2.82 mg/kg, respectively (Pourmand et al., 2012). Most of the REEs concentrations found in this study showed more or less the same concentrations as PAAS average shale concentrations, except for Tb (4.22 mg/kg), which is much higher compared with PAAS values for Tb (0.774 milligram/kilogram). As a comparison, the concentrations of Yb, Tb, and Lu of the present study were found to be higher than those of REEs in other studies by Sepetiba Bay, SE Brazil (Wasserman et al., 2011).

Table 3. The concentrations of trace elements (mg/kg)

Element	Minimum	Maximum	Mean	Standard Deviation	Other Studies (Mean)	Average Shale Value
Eu	1.11	1.74	1.38	0.26	1.60**	1.08*
Lu	0.38	0.48	0.42	0.04	0.40**	0.433*
Tb	3.57	4.84	4.22	0.56	1.10**	0.774*
Sm	6.74	8.12	7.55	0.62	8.20**	5.65*
Yb	2.83	4.56	3.65	0.78	1.90**	2.82*

Note. Eu = europium; Lu = lutetium; Tb = terbium; Sm = samarium; Yb = ytterbium. *Average shale values from Pourmand et al. (2012). **Values from Wasserman et al. (2011).

The EF values for all sampling sites are shown in Table 4. The average shale value of Fe was used as a normalizing element. Overall, the enrichment factor for the abundance of target components was found to be in the following sequence in sediment: Tb > Yb > Eu > Sm > Lu. REEs elements of Eu, Sm, and Lu in mangrove sediments at Juru, Penang showed low to moderate EF, indicating that the sediments are still in an unpolluted condition or natural weathering processes. The EF values for Tb and Yb were found to be above 2.0, indicating that the sediments were moderately polluted. The poorly enriched elements (Eu, Sm, and Lu) could have come from natural sources, whilst the significantly or moderately enriched elements (Tb and Yb) could have been sourced from anthropogenic sources, including industrial effluents and air deposition (Chunye et al., 2012).

Table 4. Enrichment factor (EF).

Element	Enrichment Factor (EF)
Eu	0.84
Lu	0.77
Tb	2.96
Sm	0.80
Yb	1.05

Conclusions

Evaluation based on the calculation of a single element, enrichment shows that at the sampling location, minor enrichment by metals, Yb, Eu, Sm, and Lu has occurred. Sampling locations were in unpolluted conditions to moderately polluted conditions for Tb metal. Although the concentration levels of most of the REE elements in the surface sediments have not reached extreme or severe EF values, it is highly recommended that further biological investigation studies should be continuously done on the inputs of anthropogenic activities into mangrove area ecosystems.

Analysis of REEs from the surface sediments of the mangrove showed that LREE is enriched compared to HREE. The findings of this study indicated that the enrichment factor of REEs of Juru River in the present study ranged from low to moderate contamination. Although the concentration level of most of the REE elements in the surface sediments has not reached extreme or severe EF values, it is highly recommended that further investigation studies be continuously done on the inputs of anthropogenic activities into this mangrove ecosystem.

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