



## Comparison of rare earth element geochemistry and Nd isotopes in two adjacent tropical estuaries: Van Uc and Cam-Nam Trieu, Northern Vietnam

Quoc Viet Pham<sup>1</sup>, Vu Duy Vinh<sup>1,\*</sup>, Sylvain Oulon<sup>2</sup>, Catherine Jeandel<sup>2</sup>

<sup>1</sup>*Institute of Science and Technology for Energy and Environment, VAST, Vietnam*

<sup>2</sup>*Laboratoire d'études en Géophysique et Océanographie Spatiales (LEGOS), CNES, CNRS, IRD, UT3, Université de Toulouse, France*

Received: 21 January 2025; Accepted: 4 March 2025

### ABSTRACT

Concentrations of rare earth elements (REE) were measured in surface waters collected from the Van Uc and Cam estuaries, from the inner river to the estuarine transition zone. Additionally, the neodymium isotope composition (Nd-IC) of two river water samples was analyzed to compare the two adjacent rivers under different geochemical conditions and anthropogenic influences. Water samples were preconcentrated using Nobias<sup>®</sup> resin prior to REE analysis by Sector Field-ICP-MS, while Nd-IC measurements were performed on a Thermal Ionization Mass Spectrometer (TIMS) after several treatments. The total REE concentrations ( $\Sigma$ REE) in the Van Uc estuary ranged from 10.5 to 23.6 nmol/kg, significantly higher than those in the Cam-Nam Trieu estuary, which ranged from 2.14 to 6.34 nmol/kg. Both Van Uc and Cam riverine and estuarine water are enriched in the middle REE (MREE) relative to light REE (LREE), with depletion observed in heavy REE (HREE) when normalized to shale compositions. No negative cerium anomalies ( $\text{Ce}^*/\text{Ce}$ ) were observed in any sample, reflecting the predominance of riverine influence in the estuarine mixing zone. Gadolinium anomalies ( $\text{Gd}^*/\text{Gd}$ ) were uniformly positive but low ( $\leq 1.3$ ), implying minimal inputs from gadolinium-based MRI contrast agents or sufficient dilution to suppress detectable anthropogenic Gd signals. Nd-IC of the Van Uc water was  $\epsilon_{\text{Nd}} = -10.5$  while of Cam-Nam Trieu water was less radiogenic, with  $\epsilon_{\text{Nd}} = -11.3$ .

**Keywords:** Dissolved rare earth element, Neodymium isotopic composition, Gd anomaly, Van Uc estuary, Cam-Nam Trieu estuary.

\*Corresponding author at: Institute of Science and Technology for Energy and Environment, No. 18 Hoang Quoc Viet Street, Nghia Do Ward, Hanoi City, Vietnam. E-mail addresses: [vinhimer@gmail.com](mailto:vinhimer@gmail.com)

## Introduction

The Van Uc River, the third-largest river in the Red River Delta, plays a crucial role in sustaining local livelihoods and supporting the economic development of Hai Phong City, a key urban and industrial center in northern Vietnam [1]. Its estuary is characterized by pronounced seasonal hydrological variations, shaped by the combined impacts of tourism and rapid urbanization [2]. Despite their close proximity and similar tidal dynamics, the Cam River and Nam Trieu Estuary—hereafter referred to as the Cam-Nam Trieu Estuary—differ in their functional significance. The Cam-Nam Trieu Estuary, which hosts Hai Phong's extensive port system, serves as a critical gateway for northern Vietnam's integration into global trade networks. However, increasing siltation within the port has required large-scale interventions, leading to substantial impact on the morphology and hydrology of the estuary [3]. Consequently, these two estuaries exhibit similarities in their hydrological systems but are subject to differing anthropogenic impacts, which play a dominant role in shaping their environmental conditions and geochemical processes.

Rare earth elements (REEs) are essential in various modern technologies and industrial applications due to their distinctive physical and chemical properties [4]. This group includes 14 lanthanide elements, which share similar geochemical characteristics [5]. In natural conditions, REEs mostly exist in a trivalent state, with the exceptions of Ce (IV) and Eu (II), which exhibit unique chemical behaviors. REEs can be divided into three categories: light REEs (LREEs: La, Ce, Pr, Nd), middle REEs (MREEs: Sm, Eu, Gd, Tb), and heavy REEs (HREEs: Dy, Ho, Er, Tm, Yb, Lu). In aquatic environments, LREEs generally associate with particulate matter, while HREEs are more likely to form complexes with dissolved carbonates and organic ligands, enhancing their solubility [6]. The distribution of REEs in aquatic systems is influenced by a variety of factors, such as pH, redox conditions, salinity, and the presence of both organic and inorganic ligands [7–9]. These distribution patterns are typically assessed by normalizing REE concentrations to a reference standard, which

helps illustrate their relative abundances, or "the REE patterns" [10]. Understanding the geochemical behavior of REEs in aquatic environments, especially in estuarine systems, is crucial for knowing their transport, partitioning, and potential ecological consequences.

Estuaries, functioning as transitional zones between land and sea environments, experience complex interactions between freshwater and seawater, which play a significant role in the cycling of trace elements, including REEs. Despite increased research efforts in recent years, the behavior and fate of REEs in specific regions and ecosystems, such as Southeast Asia and mangrove areas, remain insufficiently understood and under-documented. This research aims to contribute to filling this gap by investigating the geochemical characteristics of REEs in the Van Uc and Cam-Nam Trieu estuaries. The specific objectives of the study are to (1) analyze the concentrations and distribution patterns of REEs in water (2) evaluate the impact of anthropogenic inputs on REE behavior, and (3) compare the findings between the two estuaries to identify key similarities and differences. The results of this study will contribute to a deeper understanding of REE geochemistry in tropical estuarine systems and provide valuable insights into the environmental processes that control trace element cycling in coastal area.

## Materials and methods

### *The study site*

The Van Uc and Cam rivers, situated in the northeastern part of Hai Phong City, Vietnam's third-largest urban area, play a crucial role in the region's hydrological dynamics. The Van Uc estuary, which is fed by the Van Uc River, has an estimated annual discharge of approximately  $17.7 \times 10^9 \text{ m}^3$  [11]. In contrast, the Nam Trieu estuary, influenced by both the Cam and Bach Dang rivers, receives a total annual discharge of about  $20.0 \times 10^9 \text{ m}^3$  [12]. Both estuaries are subject to a tropical monsoon climate, characterized by distinct wet and dry seasons. The region receives an average annual rainfall of 1,161 mm, based on data from Hon Dau

collected between 1978 and 2007, with 83% of this rainfall occurring during the summer monsoon period (May to October).

As part of the Red River system, both the Cam and Bach Dang rivers follow its hydrological cycle. Historical data from 1960 to 2010 show that the discharge at Son Tay for the Red River ranged from  $80.5$  to  $161 \times 10^9 \text{ m}^3$  annually, with an average discharge of  $110 \times 10^9 \text{ m}^3$ . The discharge exhibits significant seasonal variation, with 71–79% occurring during the rainy season and only 9.4–18% during the dry season [2].

The tidal regime also strongly influences these estuaries, primarily through diurnal tides. Tide gauge measurements from the Hon Dau station indicate tidal amplitudes ranging from 2.6 m to 3.6 m during spring tides and 0.5 m to 1.0 m during neap tides. Sediment analysis in the estuaries shows a dominance of clay and fine silt [3].

### Sample collection and analysis

Samples were collected during low tide from eight locations, including four sites within the Cam-Nam Trieu estuary (three river stations and one estuary station) and four sites within the Van Uc estuary (two river stations and two estuary stations), in September 2022 (Table 1, Fig. 1). The sampling was performed during the second half of the rainy season, a period characterized by elevated discharge fluxes, resulting in the penetration of fresh water into the sea during the ebb tide. Approximately 200 mL of water from each station (both river and estuary) was sampled at the depth of 5–10 cm using pre-cleaned LDPE bottles, following GEOTRACES cookbook recommendations (<https://geotraces-old.sedoo.fr/images/Cookbook.pdf>), these bottles were later used in REE concentration analysis.

Table 1. Field parameters characterizing the Van Uc River, Cam river and estuary surface water samples, with individual sampling location

Sample point	Latitude	Longitude	Station depth (m)	Temp (°C)	Salinity	Turbidity(NTU)
CNT-1	20°52'33.30"N	106°42'46.90"E	9.3	29.1	0.1	55.3
CNT-2	20°51'49.63"N	106°43'51.51"E	9.5	29.3	0.2	78.3
CNT-3	20°51'41.41"N	106°44'60.03"E	9.7	29.3	0.9	52.8
CNT-4	20°51'27.33"N	106°44'38.44"E	8.9	30.5	3.0	91.8
VU-1	20°41'49.56"N	106°40'46.14"E	16.1	28.6	0.0	69.8
VU-2	20°41'32.59"N	106°41'34.02"E	10.3	28.7	0.0	74.2
VU-3	20°39'39.48"N	106°42'58.92"E	8.0	28.8	8.7	77.3
VU-4	20°37'02.40"N	106°45'50.16"E	16.2	28.7	2.33	67.9

Water samples from river stations (salinity less than 1) were collected in 3 L volumes and stored in pre-cleaned HDPE containers for Nd-ICP-MS analysis. During sampling, salinity was measured with a ProPlus Multiparameter Meter (YSI Inc., USA) and hydrological parameters (e.g. velocity) were recorded by using an Acoustic Doppler Current Profiler (ADCP).

Samples were kept at 2°C and transported to the laboratory within 3 hours. Water was filtered using 0.45 µm polycarbonate membranes (Nuclepore®), with filtration equipment cleaned with 0.5 M HNO<sub>3</sub> and rinsed with deionized water (DIW). All the filtering systems were pre-cleaned

with 0.5 M clean HNO<sub>3</sub> prior to use. The filtered aliquot was acidified to pH ≤ 2.0 with 2 mL of Suprapur 30% HCl and stored for transport.

Filtered water samples were analysed with consideration of their salinity to prevent salt contamination of the mass spectrometer. For river water samples (Salinity < 1), analysis was conducted directly using ICP-MS. For samples with salinity greater than 1, preconcentration was performed using Nobias Chelate-PA1® resin in a preconcentration manifold [13]. Briefly, pre-weighted samples were spiked with an appropriate amount of solution containing <sup>150</sup>Nd, <sup>151</sup>Eu, <sup>157</sup>Gd, and <sup>172</sup>Yb. Aliquots were

adjusted to a pH of  $4.7 \pm 0.2$  using ultrapure  $\text{NH}_4\text{OH}$  or glacial acetic acid (Optima Grade, Fisher®). The samples were then loaded onto the preconditioned column of the manifold at a flow rate of 1 mL/min. The columns were rinsed with 10 mL of diluted buffer (0.05 M ammonium acetate, pH  $4.5 \pm 0.1$ ) at 3 mL/min. Elution was performed by passing 3 mL of 3 M  $\text{HNO}_3$  at a flow rate of 0.5 mL/min in reverse flow direction. The eluent was collected in a clean vial and subsequently analysed using iCAP™ TQ ICP-MS (Toulouse, France). The addition of  $^{156}\text{Gd}$  to the trispike protocol [14], commonly used for open ocean studies, aimed to enhance the precision of Gd analysis and potentially identify any anthropogenic Gd signals. Each sample was analysed in duplicate to ensure accuracy and reliability. The elements were analyzed in MS/MS mode with oxygen mode to remove polyatomic interferences. Data analysis was conducted by combining external calibration with isotopic dilution, following the methodology outlined by Pham et al. [14].

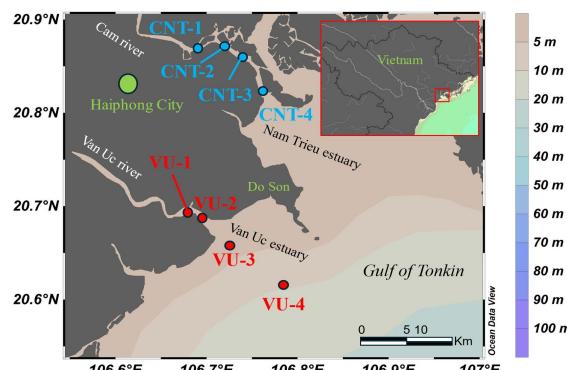


Figure 1. Sampling locations. Samples collected in the Cam-Nam Trieu estuary are identified by blue circles (CNT-1 to CNT-4); samples collected in the Van Uc estuary are identified by red circles (VU-1 to VU-4). The small inset shows the geographical location of these estuaries

The oxides formation for low masses metals were evaluated by measurements using single element solutions (La, Ce, Pr, Nd, Sm, Eu, Gd and Tb) at 1,000 ng/L concentration. The highest oxide level was observed for  $\text{CeO}_2$ , which remained below 0.5%. As oxide formation was below 1% for all investigated elements, the

influence of polyatomic interferences was considered negligible. Procedural blanks were prepared by applying the sample preparation and preconcentration protocols to DIW acidified to 2%  $\text{HNO}_3$  to closely match the sample matrix. Blank levels represent < 1% of the LREE signals and < 0.6% for MREE and HREE signals.

Method validation was performed by analyzing the replicate of randomly selected samples that were prepared, preconcentrated and analyzed to assess the reproducibility of the procedure. The riverine reference solutions (SLRS-6) were used to estimate column recovery. Since this certified reference material (CRM) is not certified for REEs. We compared our measured values to the commonly agreed-upon values reported following an international inter-calibration exercise of SLRS-6 [15]. Recoveries were within  $90 \pm 11\%$  for all REEs, reproducibility of this method is 1.5% (1 RSD). The limit of detection, calculated as three times the standard deviation of the procedural blank, is 0.09 nmol/kg.

Neodymium isotopic compositions of the Van Uc and Cam rivers water samples were determined using thermal ionization mass spectrometry (TIMS). The Nd isotopic composition is expressed as epsilon neodymium units, defined as follows:

$$\epsilon_{\text{Nd}(0)} = \left[ \frac{\left( \frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{measured}}}{\left( \frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{CHUR}}} \right] \times 10^4$$

where: measured refers to the values obtained from the measurements; CHUR stands for Chondritic Uniform Reservoir which represents the modeled average Earth value, currently  $0.512630 \pm 11$  ( $2\sigma$ , [16]).

Prior to being analysed, the freshwater samples were evaporated to near dryness and then dissolved and diluted with 1 M  $\text{HNO}_3$ , before passing through two purifying columns containing AG1-X8 and Ln resins [17]. Neodymium isotope measurements were conducted in static mode using a Triton Plus (Thermo Scientific Triton™) at the Observatoire Midi-Pyrénées, using the  $^{146}\text{Nd}/^{144}\text{Nd}$  ratio value of 0.7219 to correct for instrumental

mass bias. Accuracy of the  $\epsilon_{\text{Nd}}$  measurement was established by repeated examination of La Jolla standards ( $^{143}\text{Nd}/^{144}\text{Nd} = 0.511838 \pm 0.000029$ , 1 sd., n = 5).

## Results

### *REE Concentrations in the waters of Van Uc and Cam-Nam Trieu estuaries*

The REE concentrations in the water samples are presented in Table 2, and the Post Archean Australian Shale (PAAS; [18]) normalized REE fractionation patterns are shown in Figure 2. The

summed concentrations of individual REEs range from 1.18 to 6.44 nmol/kg in the Cam-Nam Trieu estuary and from 10.5 to 23.6 nmol/Kg in the Van Uc estuary. The Van Uc estuary exhibits significantly higher REE concentrations than the Cam-Nam Trieu estuary, by approximately 5- to 10-fold. Despite the considerable difference in total REE concentrations, the proportional contributions of each REE group are remarkably similar between the two estuaries. Light REEs (La to Nd) dominate, accounting for the majority of the total REE concentration, while Middle REEs (Sm to Tb) and Heavy REEs (Dy to Lu) together contribute much smaller proportions, comprising 5–10% of the total concentration.

**Table 2.** Concentrations of dissolved REEs in surface water samples from the Van Uc and Cam-Nam Trieu estuaries. Light REEs are highlighted in dark red, medium REEs in dark blue, and heavy REEs in black.

Sample	CNT-1	CNT-2	CNT-3	CNT-4	VU-1	VU-2	VU-3	VU-4
	(nmol/kg)							
La	1.25 $\pm$ 0.03	0.18 $\pm$ 0.01	0.90 $\pm$ 0.01	0.45 $\pm$ 0.01	3.27 $\pm$ 0.05	1.90 $\pm$ 0.03	2.12 $\pm$ 0.03	4.73 $\pm$ 0.11
Ce	2.80 $\pm$ 0.05	0.48 $\pm$ 0.01	1.74 $\pm$ 0.03	0.87 $\pm$ 0.01	6.52 $\pm$ 0.22	4.27 $\pm$ 0.06	4.56 $\pm$ 0.08	10.38 $\pm$ 0.23
Pr	0.30 $\pm$ 0.01	0.04 $\pm$ 0.01	0.14 $\pm$ 0.01	0.12 $\pm$ 0.01	0.77 $\pm$ 0.01	0.50 $\pm$ 0.01	0.50 $\pm$ 0.01	1.11 $\pm$ 0.03
Nd	1.15 $\pm$ 0.03	0.18 $\pm$ 0.01	0.83 $\pm$ 0.01	0.34 $\pm$ 0.01	3.22 $\pm$ 0.19	2.37 $\pm$ 0.05	1.89 $\pm$ 0.03	4.18 $\pm$ 0.15
Sm	0.21 $\pm$ 0.01	0.05 $\pm$ 0.01	0.12 $\pm$ 0.01	0.07 $\pm$ 0.01	0.61 $\pm$ 0.03	0.37 $\pm$ 0.01	0.33 $\pm$ 0.02	0.78 $\pm$ 0.04
Eu	0.04 $\pm$ 0.01	0.01 $\pm$ 0.01	0.03 $\pm$ 0.01	0.02 $\pm$ 0.01	0.15 $\pm$ 0.01	0.08 $\pm$ 0.01	0.08 $\pm$ 0.01	0.19 $\pm$ 0.01
Gd	0.17 $\pm$ 0.01	0.05 $\pm$ 0.01	0.14 $\pm$ 0.01	0.07 $\pm$ 0.01	0.68 $\pm$ 0.02	0.37 $\pm$ 0.01	0.35 $\pm$ 0.01	0.85 $\pm$ 0.02
Tb	0.03 $\pm$ 0.01	0.01 $\pm$ 0.01	0.02 $\pm$ 0.01	0.01 $\pm$ 0.01	0.10 $\pm$ 0.01	0.06 $\pm$ 0.00	0.05 $\pm$ 0.01	0.12 $\pm$ 0.01
Dy	0.14 $\pm$ 0.01	0.04 $\pm$ 0.01	0.10 $\pm$ 0.01	0.06 $\pm$ 0.01	0.46 $\pm$ 0.02	0.28 $\pm$ 0.01	0.29 $\pm$ 0.01	0.62 $\pm$ 0.03
Ho	0.03 $\pm$ 0.01	0.01 $\pm$ 0.01	0.02 $\pm$ 0.01	0.01 $\pm$ 0.01	0.08 $\pm$ 0.01	0.05 $\pm$ 0.01	0.05 $\pm$ 0.01	0.11 $\pm$ 0.01
Er	0.07 $\pm$ 0.01	0.02 $\pm$ 0.01	0.06 $\pm$ 0.01	0.03 $\pm$ 0.01	0.22 $\pm$ 0.02	0.14 $\pm$ 0.01	0.15 $\pm$ 0.01	0.30 $\pm$ 0.02
Tm	0.01 $\pm$ 0.01	0.01 $\pm$ 0.01	0.01 $\pm$ 0.01	0.01 $\pm$ 0.01	0.03 $\pm$ 0.01	0.02 $\pm$ 0.01	0.02 $\pm$ 0.01	0.04 $\pm$ 0.01
Yb	0.05 $\pm$ 0.01	0.02 $\pm$ 0.01	0.04 $\pm$ 0.01	0.02 $\pm$ 0.01	0.16 $\pm$ 0.01	0.09 $\pm$ 0.01	0.10 $\pm$ 0.01	0.22 $\pm$ 0.01
Lu	0.01 $\pm$ 0.01	0.01 $\pm$ 0.01	0.01 $\pm$ 0.01	0.01 $\pm$ 0.01	0.02 $\pm$ 0.01	0.01 $\pm$ 0.01	0.02 $\pm$ 0.00	0.03 $\pm$ 0.00
$\Sigma\text{REE}$	6.44	1.18	4.16	2.15	16.3	10.5	10.5	23.6
Gd*/Gd	1.1	1.1	1.1	1.1	1.2	1.1	1.2	1.3
$\epsilon_{\text{Nd}}$	-11.3	-11.3	N/A	N/A	-10.6	-10.8	N/A	N/A

The PAAS-normalized pattern displays a positive anomaly for MREEs and a slight negative anomaly for HREE. Ce shows no depletion, typical for river and estuarine water. Specifically, water from CNT-2 shows a

negative La anomaly. The small positive Gd anomaly characterizes all the water samples, ranging from 1.1 to 1.3 (Table 2). This anomaly was slightly higher in Cam River than in Van Uc River.

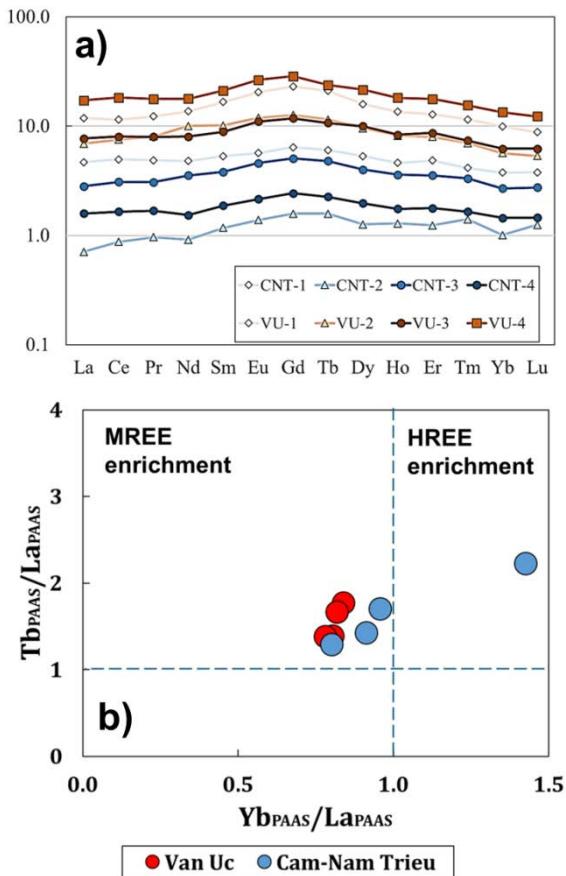


Figure 2. a) PAAS-normalized patterns of the two sample groups. See Figure 1 for sampling site locations, with darker colors indicating higher salinity b) Biplot of  $Tb_{PAAS}/La_{PAAS}$  as a function of  $Yb_{PAAS}/La_{PAAS}$

#### *Van Uc and Cam-Nam Trieu estuaries $\epsilon_{Nd}$*

Neodymium isotope values differ between the two estuaries. The Cam-Nam Trieu estuary exhibits a value of  $-11.3 \pm 0.1$ , while the Van Uc estuary shows a more radiogenic value of  $-10.7 \pm 0.1$ . Neodymium isotopes provide an additional tracer for identifying sediment and water mass provenance within estuarine systems. The  $\epsilon_{Nd}$  values obtained from the Cam-Nam Trieu and Van Uc estuaries exhibit a narrow range, from  $-11.3$  at CNT-1 and CNT-2 to  $-10.6$  to  $-10.8$  at VU-1 and VU-2, indicating broadly similar lithogenic sources across the two systems. The slightly less negative  $\epsilon_{Nd}$  signatures in the Van Uc estuary suggest a

greater contribution of materials derived from more radiogenic lithologies upstream, consistent with the higher dissolved Nd concentrations observed at these stations (up to  $4.18 \text{ nmol kg}^{-1}$  at VU-4). In contrast, the more negative values at the Cam-Nam Trieu stations reflect a stronger influence of older, more weathered continental sources. The absence of  $\epsilon_{Nd}$  data for several mid-estuarine samples limits the ability to fully resolve mixing processes along the salinity gradient; however, the existing measurements nonetheless highlight that both estuaries deliver dissolved REEs with distinct but overlapping isotopic fingerprints to the coastal zone. This pattern underscores the utility of Nd isotopes in distinguishing terrestrial inputs and tracing geochemical pathways of REEs in complex estuarine environments.

#### Discussion

Within the LREE group, individual LREE concentrations in the Van Uc water were at least twice as high as those in the Cam-Nam Trieu water. Since LREE, such as neodymium (Nd), are primarily used in the magnetic industries and given that Cam-Nam Trieu receives water inputs from surrounding industrial areas, the lower LREE concentrations observed in Cam-Nam Trieu may indicate minimal anthropogenic influence. Instead, the natural geochemical context appears to play a more important role, as evidenced by the Van Uc estuary, which has been described as a less impacted system than the Cam-Nam Trieu.

The Neodymium isotope results from the Cam-Nam Trieu estuary highlight distinct isotopic compositions between the two adjacent systems, suggesting differences in the underlying rock types that dominate these estuaries. Both estuaries are part of the Red River Basin [19], where the outcropping rocks, predominantly formed during the Quaternary period, consist mainly of conglomerates, sandstones, and gravel stones. However, the lack of  $\epsilon_{Nd}$  data for these outcropping rocks in the study area prevents further conclusions. Additionally, the concentrations of neodymium in both rivers were found to vary, with

significantly higher concentration found for Van Uc River.

The concentrations of rare earth elements (REEs) in both riverine and estuarine waters of the Van Uc estuary are significantly higher than those observed in the Cam-Nam Trieu estuary. This likely reflects differences in geological settings and hydrodynamic conditions between the two estuaries. The Van Uc estuary is characterized by significant freshwater input and potentially higher contributions of REEs from weathering processes. In contrast, the Cam-Nam Trieu estuary, with its more diluted inputs, maintains comparatively lower REE concentrations. This difference also suggests that anthropogenic activities, which are more prevalent in the Cam-Nam Trieu estuary, do not appear to significantly alter the natural REE background in these estuarine systems.

Additionally, Gadolinium (Gd)-based compounds, widely used in hospitals as contrast agents for Magnetic Resonance Imaging, have been introduced into the aquatic environment through disposal in sewage systems. These compounds persist in water as conventional wastewater treatment systems are ineffective at removing them [20–23]. Several studies have highlighted Gd as an emerging contaminant in rivers and estuaries [24–26]. In this study, the Gd anomaly shows slight enrichment, with a peak value of 1.3, but does not provide conclusive evidence of contamination from hospitals. Two potential factors explain this finding: (1) the dilution factor in the water may be too high to observe a clear Gd signal, or (2) the use of Gd for MRI in Vietnam may not be widespread, or the signal could be too weak to detect due to the dominance of other medium REE (MREE) anomalies, as shown in Figure 2b.

Although Gd is widely used in hospital wastewater studies to trace effluent discharge, the absence of clear Gd contamination in our samples is most plausibly explained by the potentially limited use of Gd-based MRI contrast agents in Vietnam, which would substantially reduce anthropogenic Gd inputs to the system. The  $\epsilon_{Nd}$  data also support this hypothesis, showing clear differences between the two estuaries, likely reflecting differences in the composition of geological material. However,

the geological setting does not provide clear evidence for this observation, as Quaternary material dominates the Red River basin.

## Conclusion

This study highlights significant differences in REE concentrations between the Van Uc and Cam-Nam Trieu estuaries, with higher levels observed in the Van Uc estuary, likely due to differences in the hydrological and geological characteristics of these two systems. The Gd anomaly shows no clear evidence of anthropogenic impact on the riverine and estuarine waters, suggesting that the widespread use of cutting-edge diagnostic technology, such as MRI systems, may not be prevalent in Vietnam. Additionally, the lack of REE data from the Gulf of Tonkin Bay prevents further calculations of REE fluxes to the ocean from these two estuarine systems, highlighting the challenge in tracing emerging contaminants and assessing their potential impacts on the ecosystem.

**Acknowledgments:** The authors acknowledge the funding support from the funding support from the Vingroup Innovation Foundation (VINIF) for project VINIF.2022.STS.26. This study was supported by the VAST-IRD collaboration, QTFR02.02/24–25 project. We would like to thank the researchers and technicians of the Institute of Marine Environment and Resource (IMER), VAST for their insightful comments and encouragement.

## References

- [1] V. Piton, S. Ouillon, V. D. Vinh, G. Many, M. Herrmann, and P. Marsaleix, "Seasonal and tidal variability of the hydrology and suspended particulate matter in the Van Uc estuary, Red River, Vietnam," *Journal of Marine Systems*, vol. 211, 103403, 2020. DOI: 10.1016/j.jmarsys.2020.103403.
- [2] V. D. Vinh, S. Ouillon, T. D. Thanh, and L. V. Chu, "Impact of the Hoa Binh dam (Vietnam) on water and sediment budgets in the Red

River basin and delta," *Hydrology and Earth System Sciences*, vol. 18, no. 10, pp. 3987–4005, 2014. DOI: 10.5194/hess-18-3987-2014.

[3] V. D. Vinh and S. Ouillon, "The double structure of the Estuarine Turbidity Maximum in the Cam–Nam Trieu mesotidal tropical estuary, Vietnam," *Marine Geology*, vol. 442, 106670, 2021. DOI: 10.1016/j.margeo.2021.106670.

[4] K. Binnemans, P. T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton, and M. Buchert, "Recycling of rare earths: a critical review," *Journal of Cleaner Production*, vol. 51, pp. 1–22, 2013. DOI: 10.1016/j.jclepro.2012.12.037.

[5] H. J. de Baar, C. R. German, H. Elderfield, and P. Van Gaans, "Rare earth element distributions in anoxic waters of the Cariaco Trench," *Geochimica et Cosmochimica Acta*, vol. 52, no. 5, pp. 1203–1219, 1988. DOI: 10.1016/0016-7037(88)90275-X.

[6] A. H. Osborne, B. A. Haley, E. C. Hathorne, Y. Plancherel, and M. Frank, "Rare earth element distribution in Caribbean seawater: Continental inputs versus lateral transport of distinct REE compositions in subsurface water masses," *Marine Chemistry*, vol. 177, pp. 172–183, 2015. DOI: 10.1016/j.marchem.2015.03.013.

[7] A. E. Floback and J. W. Moffett, "Rare earth element distributions in the Arabian Sea reveal the influence of redox processes within the oxygen deficient zone," *Chemical Geology*, vol. 577, 120214, 2021. DOI: 10.1016/j.chemgeo.2021.120214.

[8] Z. Qudsi, A. O. Mucci, H. Dang, Y. Gélinas, and G. Chaillou, "Contrasting rare earth element concentrations and mixing behaviors in the St. Lawrence Estuary and Saguenay Fjord," *Marine Chemistry*, vol. 258, 104336, 2024. DOI: 10.1016/j.marchem.2023.104336.

[9] J. Schijf and R. H. Byrne, "Speciation of yttrium and the rare earth elements in seawater: Review of a 20-year analytical journey," *Chemical Geology*, vol. 584, 120479, 2021. DOI: 10.1016/j.chemgeo.2021.120479.

[10] G. Bayon, C. R. German, K. W. Burton, R. W. Nesbitt, and N. Rogers, "Sedimentary Fe–Mn oxyhydroxides as paleoceanographic archives and the role of aeolian flux in regulating oceanic dissolved REE," *Earth and Planetary Science Letters*, vol. 224, no. 3–4, pp. 477–492, 2004. DOI: 10.1016/j.epsl.2004.05.033.

[11] H. T. Nguyen, L. Gourdon, H. V. Bui, D. T. Dao, H. Mai, H. M. Do, T. V. Nguyen, and S. Ouillon, "Ecological responses of meiofauna to a saltier world—A case study in the Van Uc River Continuum (Vietnam) in the dry season," *Water*, vol. 15, no. 7, 1278, 2023. DOI: 10.3390/w15071278.

[12] V. D. Vinh, S. Ouillon, and D. Van Uu, "Estuarine Turbidity Maxima and variations of aggregate parameters in the Cam–Nam Trieu estuary, North Vietnam, in early wet season," *Water*, vol. 10, no. 1, 68, 2018. DOI: 10.3390/w10010068.

[13] M. Lagarde, V. Q. Pham, P. Lherminier, M. Belhadj, and C. Jeandel, "Rare earth elements in the North Atlantic, part I: Non-conservative behavior reveals margin inputs and deep waters scavenging," *Chemical Geology*, vol. 664, 122230, 2024. DOI: 10.1016/j.chemgeo.2024.122230.

[14] V. Q. Pham, M. Grenier, S. Cravatte, S. Michael, S. Jacquet, M. Belhadj, Y. Nachez, C. Germineaud, and C. Jeandel, "Dissolved rare earth elements distribution in the Solomon Sea," *Chemical Geology*, vol. 524, pp. 11–36, 2019. DOI: 10.1016/j.chemgeo.2019.05.012.

[15] D. Yeghicheyan, D. Aubert, M. Bouhnik-Le Coz, J. Chmeleff, S. Delpoux, I. Djouraev, G. Granier, F. Lacan, J. L. Piro, T. Rousseau, C. Cloquet, A. Marquet, C. Menniti, C. Pradoux, R. Freydier, E. V. da Silva-Filho, and K. Suchorski, "A new interlaboratory characterisation of silicon, rare earth elements and twenty-two other trace element concentrations in the natural river water certified reference material SLRS-6 (NRC-CNRC)," *Geostandards and Geoanalytical Research*, vol. 43, no. 3, pp. 475–496, 2019. DOI: 10.1111/ggr.12268.

[16] A. Bouvier, J. D. Vervoort, and P. J. Patchett, "The Lu–Hf and Sm–Nd isotopic composition of CHUR: constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets," *Earth and Planetary Science Letters*, vol. 273, no. 1–2, pp. 48–57, 2008. DOI: 10.1016/j.epsl.2008.06.010.

[17] V. Q. Pham, C. Jeandel, M. Grenier, S. Cravatte, G. Eldin, M. Belhadj, C. Germineaud, and T. V. Vu, "Neodymium isotopic composition and rare earth element concentration variations in the

Coral and Solomon Seas," *Frontiers in Environmental Chemistry*, vol. 3, 803944, 2022. DOI: 10.3389/fenvc.2022.803944.

[18] S. M. McLennan, "Rare earth element geochemistry and the 'tetrad' effect," *Geochimica et Cosmochimica Acta*, vol. 58, no. 9, pp. 2025–2033, 1994. DOI: 10.1016/0016-7037(94)90282-8.

[19] H. Khuong The, P. Nguyen, T. C. Nguyen, N. S. Pham, and D. T. Nguyen, "Identifying correlation of coal seams in the Tien Hai Area, Northern Vietnam by using multivariate statistic methods," *Inżynieria Mineralna*, no. 2, pp. 129–148, 2021. DOI: 10.29227/IM-2021-02-11.

[20] A. M. Amorim, F. F. Sodré, T. C. Rousseau, and P. D. Maia, "Assessing rare-earth elements and anthropogenic gadolinium in water samples from an urban artificial lake and its tributaries in the Brazilian Federal District," *Microchemical Journal*, vol. 148, pp. 27–34, 2019. DOI: 10.1016/j.microc.2019.04.055.

[21] V. Hatje, K. W. Bruland, and A. R. Flegal, "Determination of rare earth elements after pre-concentration using NOBIAS-chelate PA-1® resin: Method development and application in the San Francisco Bay plume," *Marine Chemistry*, vol. 160, pp. 34–41, 2014. DOI: 10.1016/j.marchem.2014.01.006.

[22] V. Hatje, K. W. Bruland, and A. R. Flegal, "Increases in anthropogenic gadolinium anomalies and rare earth element concentrations in San Francisco Bay over a 20 year record," *Environmental Science & Technology*, vol. 50, no. 8, pp. 4159–4168, 2016. DOI: 10.1021/acs.est.5b04322.

[23] N. Tepe, M. Romero, and M. Bau, "High-technology metals as emerging contaminants: Strong increase of anthropogenic gadolinium levels in tap water of Berlin, Germany, from 2009 to 2012," *Applied Geochemistry*, vol. 45, pp. 191–197, 2014. DOI: 10.1016/j.apgeochem.2014.04.006.

[24] M. Bau and P. Dulski, "Anthropogenic origin of positive gadolinium anomalies in river waters," *Earth and Planetary Science Letters*, vol. 143, no. 1–4, pp. 245–255, 1996. DOI: 10.1016/0012-821X(96)00127-6.

[25] S. Kulaksız and M. Bau, "Anthropogenic gadolinium as a microcontaminant in tap water used as drinking water in urban areas and megacities," *Applied Geochemistry*, vol. 26, no. 11, pp. 1877–1885, 2011. DOI: 10.1016/j.apgeochem.2011.06.011.

[26] L. Ma and W. X. Wang, "Dissolved rare earth elements in the Pearl River Delta: Using Gd as a tracer of anthropogenic activity from river towards the sea," *Science of the Total Environment*, vol. 856, 159241, 2023. DOI: 10.1016/j.scitotenv.2022.159241.