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The seasonal variations in the interactions between rare earth elements and organic matter in tropical rivers



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ABSTRACT

The escalation of global demands for critical minerals to facilitate the green energy transition creates emerging needs to better understand their environmental behaviours. Several nations recognize rare earth elements (REEs) as priority critical minerals and emphasize the necessity to evaluate their environmental mobility and potential effects on natural ecosystems and human health. Here, we investigated the seasonal variations in dissolved concentrations of REEs and their leachable fractions from suspended particles in samples collected bi-weekly from the Sai Gon and Dong Nai Rivers in Southern Vietnam. The investigation period extended over sixteen months, including a transition from wet to dry seasons. We reported significant mobility of REEs in the river waters during the wet season due to watershed runoff, especially in Sai Gon River with the occurrence of acid-sulphate soils. Dissolved REE concentrations in the dry season were significantly lower because of the interactions with organic-rich particles (up to 13% of particulate organic carbon, POC) mainly derived from phytoplankton materials. The conditional distribution coefficients ($\log K_D$ from 5 to 7 for Pr) were proportional to POC content. The scavenging capacity of particulate organic matter also led to affect the fractionation between light REEs and heavy REEs in solution, and the characteristic Middle REE-enrichment patterns for the leachable REEs fraction. We also reported significant Eu anomalies (Eu/Eu^* up to 7) in the Dong Nai River during the dry season and associated this observation with the decomposition of organic matter that previously accumulated Eu. However, further studies are required to confirm this hypothesis because of small reservoir effects; elevated Eu anomalies were observed in water samples with low dissolved Eu concentrations.

1. Introduction

Rare earth elements (REEs) are increasingly recognized as priority critical minerals by various nations and jurisdictions because of their implications in high-technologies, the low-carbon economy and renewable energy (e.g., [U.S. Department of the Interior, 2018](#); [European Commission, 2020](#); [Government of Canada, 2022](#)). Activities related to REE life cycles, including mining, processing, manufacturing and recycling, are expected to rise steeply to meet the global demand ([Binnemans et al., 2013](#); [Dutta et al., 2016](#); [Dang et al., 2021b](#); [Gaustad et al., 2021](#)). Therefore, knowledge of REE biogeochemistry is essential in further evaluating their potential environmental impacts, human exposure and

ecotoxicological effects ([Cobelo-García et al., 2015](#); [Dang et al., 2021a](#)).

The group of REEs consists of the lanthanide series ($_{57}\text{La}$ to $_{71}\text{Lu}$), $_{21}\text{Sc}$ and $_{39}\text{Y}$. Scandium is not commonly considered with other REEs in environmental studies because of its distinctly lower ionic radius relative to the group yielding to differential environmental behaviour ([Dang et al., 2022c](#) and references therein). Therefore, the lanthanides and Y are also often referred to as REYs or YREEs in the literature. Despite the coherent geochemical behaviours of the REEs, they can be further classified into light REEs (LREEs: La, Ce, Pr, Nd and Sm) and heavy REEs (HREEs: Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) in aquatic systems. The premise of such categorization is based on the slight differential behaviours between LREEs and HREEs, especially regarding

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biogeochemical processes and complexation affinity (Sholkovitz, 1995; Luo and Byrne, 2004; Garcia-Solsona and Jeandel, 2020). In biological and particulate samples, the middle REEs (MREEs: Nd and Sm, Eu, Gd, Tb, Dy, Ho) can be further fractionated from the lighter and heavier REEs (Dang et al., 2023 and references therein).

In areas unaffected by anthropogenic activities, various environmental parameters dictate REE geochemistry in aquatic systems; these factors include the geochemical backgrounds by weathering and pedogenetic processes (Tyler, 2004; Brioschi et al., 2013; Chapela et al., 2018), water chemistry including pH, redox conditions and complexing capacity (Kim and Kim, 2011; Paffrath et al., 2020; Floback and Moffett, 2021; Dang et al., 2022a), sorption processes and the interactions with humic substances (Davranche et al., 2004; Marsac et al., 2010; Pourret and Davranche, 2013; Bayon et al., 2015).

However, our understanding of the REE environmental behaviour remains fragmented; most studies focus on major rivers and logistically accessible field sites leading to sporadic snapshots of environmental processes (Gaillardet et al., 2003; Bayon et al., 2015; Rousseau et al., 2015). Seasonal studies are also scarce, leading to missed opportunities to document major changes in the environmental landscape, such as monsoons (Li et al., 2019; Hathorne et al., 2020) or ice-covered winters (Dang et al., 2022c; Laukert et al., 2022; Sattarova et al., 2023). Furthermore, the sources and sinks of REEs are not fully constrained at the global scale (Rousseau et al., 2015; Crockett et al., 2018). Consequently, the global marine budget of REEs remains unbalanced (Johannesson and Burdige, 2007; Garcia-Solsona and Jeandel, 2020). In this context, specific environmental systems such as mangrove forests (Bosco-Santos et al., 2017; Mandal et al., 2019; Dang et al., 2021c) or coastal acid-sulphate soils (Morgan et al., 2016) might have significant contributions and need further investigation.

Vietnam has the second-largest REE reserve globally with most of the REE ores located in the northwestern regions (Dang et al., 2021b), but data for dissolved REEs in aquatic systems remain unavailable. Here, we report the dissolved concentrations of REEs and leachable fractions from suspended particles in the Sai Gon and Dong Nai Rivers of Southern Vietnam, the third largest river basin in Vietnam with no reported REE ores or REE mining activities in the region. The biogeochemistry of the Sai Gon - Dong Nai Rivers is highly reactive to urban inputs from the megacity of Ho Chi Minh City (HCMC), resulting in a eutrophic status with seasonal algal blooms, elevated nutrients and organic carbon levels and intense mineralization and nitrification processes (Nguyen et al., 2019a, 2019b, 2021).

Here, we investigated the geochemistry of REEs related to water chemistry parameters, dissolved organic carbon (DOC), particulate organic carbon (POC), chlorophyll-a and the degraded forms (i.e., phaeopigments). Water and suspended particles were collected bi-weekly over sixteen months, including the transition from wet to dry seasons. It is also important to note that the ancillary parameters have been previously described (Nguyen et al., 2019b) to highlight the nutrient dynamics and eutrophication of the river systems. These data are reported in this study as supplementary figures and texts to support the discussion on the biogeochemistry processes of REEs. We further calculated the REE fractionation ratios (between LREEs, MREEs and HREEs), anomalies (Ce, Eu, Gd) and conditional distribution coefficients (K_D) to interpret their differential geochemical behaviours.

2. Materials and methods

1. The Sai Gon-Dong Nai River system

Southern Vietnam has a tropical monsoon climate, with two distinct wet and dry seasons. The wet season begins in May and ends in November, marked by an average annual rainfall of 1800 mm (Nguyen et al., 2019b).

Both Sai Gon and Dong Nai Rivers are important hydrological systems in Southern Vietnam, especially for the megalopolis of HCMC. Two

dams were constructed upstream of these rivers creating major water reservoirs (Dau Tieng and Tri An, Fig. 1B), with capacities of 1.6×10^9 m³ and 2760×10^6 m³, respectively. The operational processes of these reservoirs are subject to stringent national protocols for flood and saline intrusion control and to provide irrigation water (Decision 471/QD-TTg, 2016). Accordingly, the dams should maintain a minimum discharge of $120\text{--}130$ m³ s⁻¹ (Tri An – Dong Nai River) and 36 m³ s⁻¹ (Dau Tieng – Sai Gon River) during the dry season. As the results of differential reservoir capacities and discharge minimum, the Sai Gon River has an average flow of 50 ± 20 m³ s⁻¹, significantly lower than that of the Dong Nai River (610 ± 220 m³ s⁻¹) (Nguyen et al., 2019b). The significant discharge fluctuations are also related to tidal influences and hydrological seasonality (Camenen et al., 2021).

Both rivers are natural boundaries between HCMC and neighbouring provinces (Fig. 1B). The Sai Gon River, however, meanders through the city and is connected to a system of urban canals conveying significant risks of contamination by domestic and industrial wastewaters, industrial discharges of hazardous waste, hospital effluent, floating litter and other xenobiotics associated with navigation, aqua- and agriculture (Strady et al., 2017; Lahens et al., 2018; Thanh-Nho et al., 2018; van Emmerik et al., 2018; Babut et al., 2019; Nguyen et al., 2019b, 2021; Caracciolo et al., 2023). The Dong Nai River is also subject to multiple sources of contamination, including the fast-growing population, gigantic industrial centres, and aquaculture (Nguyen et al., 2019b). The two rivers merge in the eastern HCMC, downstream of the Bach Dang Wharf, to form the Soai Rap River and discharge into the Vietnam Eastern Sea through the Can Gio Biosphere Reserve (Fig. 1B).

2. Sample collection and treatment

Water and suspended particles were collected bi-monthly from April 2015 to August 2016 from three stations: Phu Cuong (PC), Hoa An (HA) and Bach Dang (BD) (Fig. 1B). The first two stations are located on the upstream sections of the Sai Gon and Dong Nai Rivers, respectively, while the urban station BD is located near the Bach Dang Wharf in the highly urbanized area of HCMC.

The sampling and sample treatment protocols were carried out at the Centre Asiatique de Recherche sur l'Eau (CARE) and described in detail by Strady et al. (2017) and Nguyen et al. (2019a, 2019b). Briefly, surface water was taken using a 2.5 L Niskin bottle in the middle of the river. The samples were immediately filtered through either GF/F glass filters (0.7 µm, Whatman) for ancillary parameters and through PTFE filters (0.2 µm, Omnipore, pre-cleaned by 10% (v/v) HNO₃ Normapur) for REEs. The PTFE-filtered waters were stored in pre-cleaned polypropylene bottles, acidified to 10% (v/v) of HNO₃ (Normapur) and stored at 4 °C for dissolved REE analysis. The filters were later acid-leached for particulate REE analysis.

The particulate matters for REE analysis were subject to hot plate digestion according to the protocol detailed by Noncent et al. (2020). Briefly, the PTFE filter was digested into acid pre-cleaned 30 mL Savilex vessel using *aqua regia* (2 mL of 14-M HNO₃, Suprapur® and 4 mL of HCl 12 M Suprapur®) and placed on a heating plate at 120 °C for four hours. After cooling, the digested solution was evaporated until dryness, and the digestate was diluted to 10 mL using 0.5 mL HNO₃ (14 M, Suprapur®) and ultrapure water (Elga®) for 30 mins at 65 °C. After cooling and decantation, 3.5 mL of supernatant and 6.5 mL of ultrapure water (Elga®) were poured into 15 mL acid-pre-cleaned PP tubes. It is important to note that this protocol does not aim for total digestion but the *aqua regia*-leachable fraction of the elements; the concentrations will, therefore, be reported as leachable REEs from suspended particles rather than total or particulate REEs.

3. Elemental analysis and quality control

Concentrations of dissolved and particulate REEs were directly measured by an iCAPQ ICP-MS (Thermo Scientific) operating under the

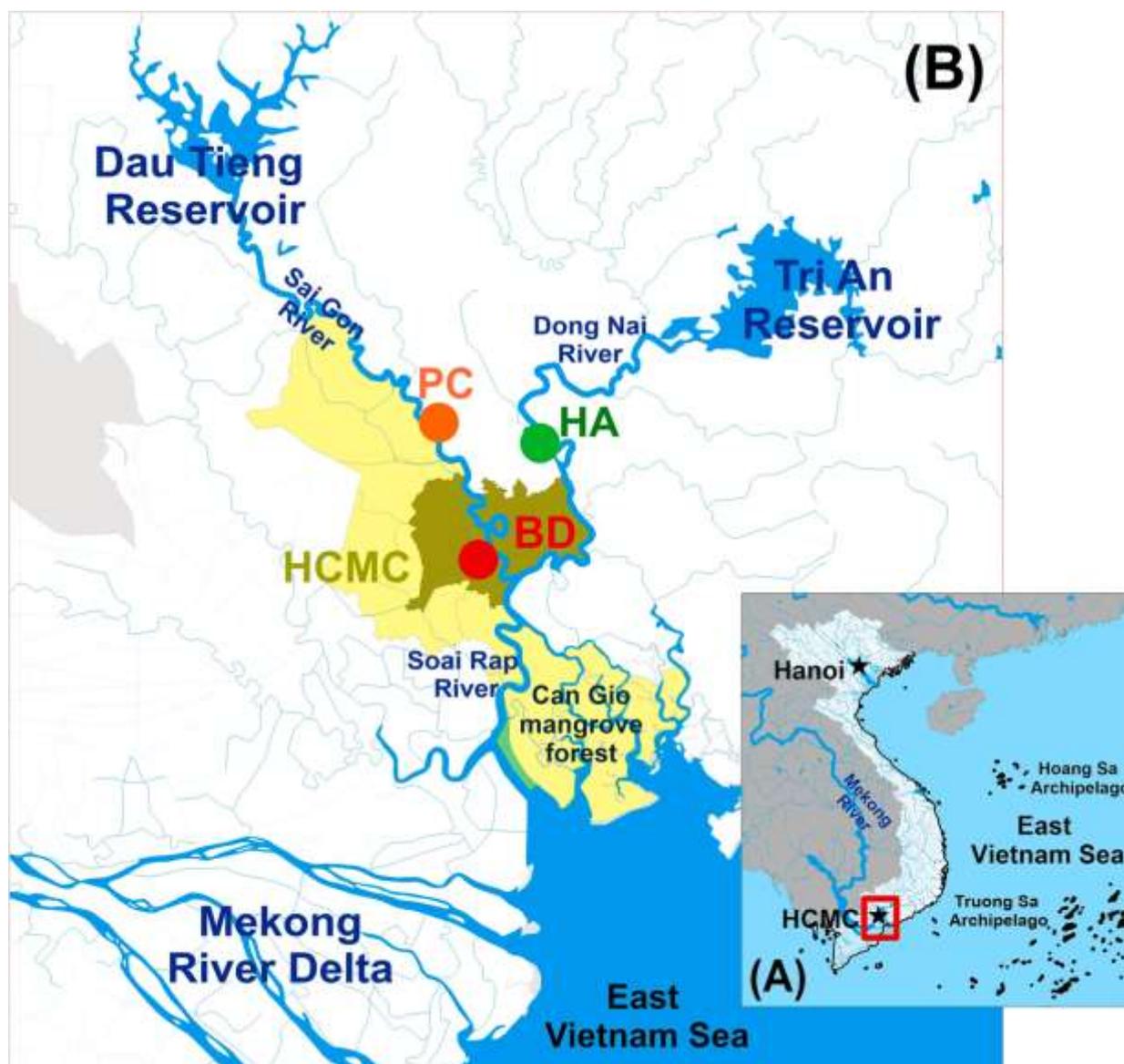


Fig. 1. Map of Vietnam (A) and the study region (B). The yellow area in B demarks Ho Chi Minh City (HCMC), while the dark yellow area shows the highly urbanized center of HCMC comprising sixteen urban districts. The three sampling stations include Phu Cuong (PC), Hoa An (HA) in the upstream sections of the Sai Gon and Dong Nai Rivers, respectively, and the urban station Bach Dang (BD) on the Sai Gon River. The dark blue lines show various river systems, and the fine blue straight lines highlight the dense canal systems of Southern Vietnam. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Kinetic Energy Discrimination mode and Argon Gas Dilution technique (Kutscher et al., 2016) at the AETE-ISO platform, OSU-OREME/Universite de Montpellier. More precisely, the monitored m/z were ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{151}Eu , ^{160}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb , ^{175}Lu and we used ^{74}Ge , ^{103}Rh , ^{193}Ir as internal standards. The ^{136}Ba isotope was also monitored for potential polyatomic interferences ($^{135}\text{Ba}^{16}\text{O}^+$) for ^{151}Eu .

Certified reference materials (CRMs) from the National Research Council of Canada for river water (SLRS-6) and marine sediment (MESS-3), as well as blank filters, were used for QA/QC. The measured dissolved REE concentrations in SLRS-6 were in agreement with the values reported by an interlaboratory comparison campaign (Table S1, Yeghicheyan et al., 2019). The blanks for filter digestion were also three orders of magnitude lower than the *aqua regia* digested samples. For the solid CRM MESS-3, the concentrations of leachable REEs from particles were constantly at 50% of total REEs (12 replicates, Table S1). This comparable recovery obtained from multiple batches of digestion

indicates a consistent fraction of REEs being leached from the solid environmental samples. The lower recovery is expected given that we did not use HF for complete digestion of the solid matrix. The range of recovery approximated the values reported by other studies for sediments (e.g., Amyot et al., 2017).

2.4. Normalization of REE concentrations, REE fractionation and anomalies

The REE concentration patterns are characterized by zig-zag variations due to the Oddo-Harkins effects. Therefore, we normalized the REE concentrations against the upper continental crust (UCC, Rudnick and Gao, 2003). The UCC-normalized concentrations are hereafter referred to as REE_{UCC} .

To evaluate the trend of UCC-normalized REE concentration patterns, we computed the ratios of $\text{Pr}_{\text{UCC}}/\text{Er}_{\text{UCC}}$ as representatives for LREEs and HREEs, respectively. Any increase or decrease in this ratio

indicate processes that fractionate LREEs and HREEs, a phenomenon often observed in aquatic systems (Nozaki et al., 2000; Lawrence and Kamber, 2006; Dang et al., 2022c). Furthermore, MREEs can also be fractionated relative to the lighter and heavier neighbours in particulate or biological systems; this is often associated with organic matter complexation or diagenetic and biogenic phosphate (Marsac et al., 2013; Auer et al., 2017). For this purpose, we computed the ratios of Tb_{UCC}/La_{UCC} and Lu_{UCC}/La_{UCC} . A biplot of these ratios allows the identification of three types of normalized patterns: dissolved (seawater-like or HREE enrichment), particulate (LREE enrichment) or MREE enrichment (Dang et al., 2023).

We also computed Ce, Eu and Gd anomalies according to the following equations described by Dang et al. (2022b).

$$Ce \quad Ce^* = \frac{Ce_{UCC}}{\frac{1}{2} \times La_{UCC} + \frac{1}{2} \times Pr_{UCC}} \quad (1)$$

$$Eu \quad Eu^* = \frac{Eu_{UCC}}{\frac{1}{2} \times Nd_{UCC} + \frac{1}{2} \times Tb_{UCC}} \quad (2)$$

$$Gd \quad Gd^* = \frac{Gd_{UCC}}{\frac{1}{2} \times Sm_{UCC} + \frac{1}{2} \times Dy_{UCC}} \quad (3)$$

3. Results

1. Variations in REE concentrations

Because of similar concentration variations of the lanthanides series, we selectively presented the seasonal variations in the concentrations of Pr and Er as representative LREE and HREE (Fig. 2, A and B). The concentrations of both elements gradually increased during the 2015 wet season but significantly dropped and remained low during the dry season at upstream stations (HA and PC). The concentrations of Pr and Er varied from 0.8 to 25 $ng L^{-1}$ and 0.5 to 10.7 $ng L^{-1}$, respectively. This variation was less noticeable at station BD, but we did not have data on dissolved REE concentrations during the dry season because of the increasing salinity during this period (Fig. S2C), introducing a high matrix effect on the analysis.

Despite the significant seasonal variations in dissolved REE concentrations, the leachable REE concentrations remained constant over the wet and dry seasons and for all stations, e.g., the concentrations of leachable Pr and Er were $4.5 \pm 1.0 mg kg^{-1}$, and $1.6 \pm 0.3 mg kg^{-1}$, $n = 74$ (Fig. S3, A-B).

3.2. REEs fractionation and anomalies

As an indication of potential fractionation between LREEs and HREEs, the Pr_{UCC}/Er_{UCC} ratios vary between the two seasons, with higher ratios observed during the wet season of 2015 (Fig. 2C). For example, at station HA, Pr_{UCC}/Er_{UCC} was significantly higher ($p < 0.001$) during the wet season (0.60 ± 0.06 , $n = 12$) than in the dry season (0.44 ± 0.09 , $n = 9$). However, the Pr_{UCC}/Er_{UCC} in leachable REEs were similar for all stations and seasons, 0.9 ± 0.1 , $n = 74$ (Fig. S3C).

There is also no change in Eu anomalies at station PC during both wet and dry seasons ($Eu/Eu^* = 1.5 \pm 0.2$, $n = 27$) and at station BD during the wet season (1.9 ± 0.2 , $n = 11$) (Fig. 2D). However, Eu anomalies at station HA significantly increased during the dry season (up to 7.1) compared to the background values of 1.7 ± 0.2 , $n = 12$ during the 2015 wet season. Besides, the seasonal variations in Gd anomalies were similar at station HA and PC, with constant values during the wet season (1.26 ± 0.04 , $n = 12$ at HA and 1.46 ± 0.06 , $n = 12$ at PC), which later decreased during the dry season (minimum Gd/Gd^* of 0.8). At the urban station BD, there is an increasing trend for Gd/Gd^* during the wet

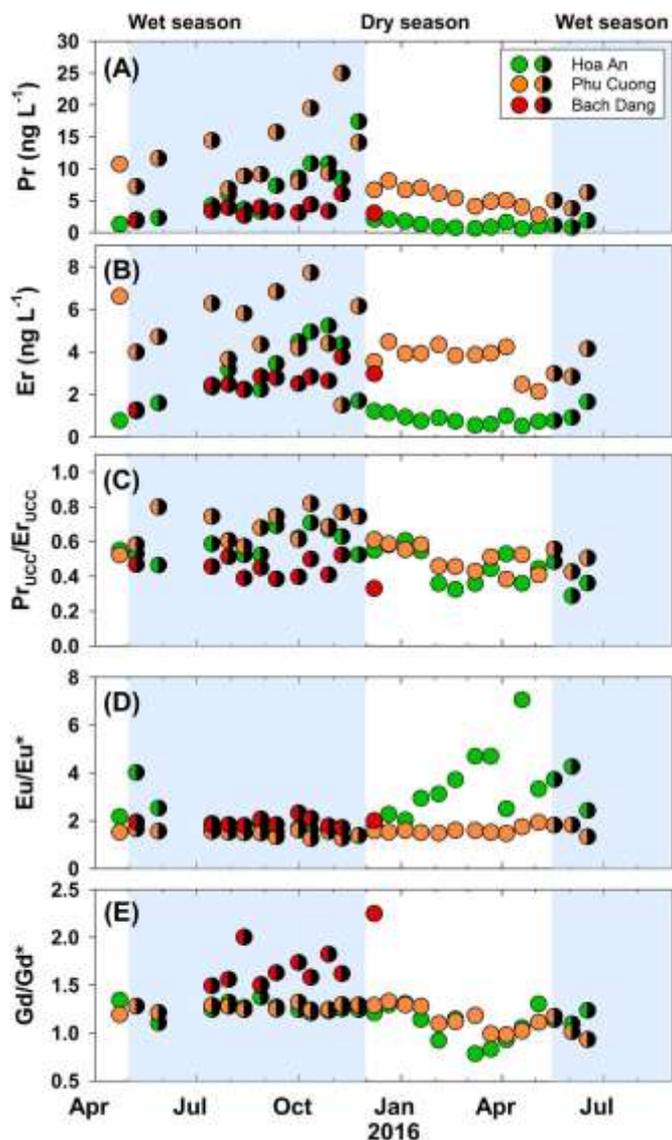


Fig. 2. The seasonal variations of dissolved Pr (A) and Er (B) concentrations, their normalized ratios (C), and anomalies of Eu (D) and Gd (E) at stations HA (green circles), PC (orange circles) and BD (red circles). The half-filled symbols show the samples taken during the wet season (blue area), while the open symbols represent the samples of the dry season (white area). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

season, with maximum values recorded at 2.3 (Fig. 2E).

However, there are no variations in Eu and Gd anomalies in the leachable fractions of REEs; $Eu/Eu^* = 1.1 \pm 0.1$, $n = 74$ and $Gd/Gd^* = 1.1 \pm 0.1$, $n = 74$ (Fig. S3, D-E). Similarly, we did not observe Ce anomalies in the entire dataset ($Ce/Ce^* = 0.97 \pm 0.08$, ranging from 0.97 to 1.17).

4. Discussion

1. Seasonal variations in REE geochemistry

The significant seasonal and spatial variations in dissolved REE concentrations could be related to different water chemistry of the three stations across the seasons. The upstream section of the Sai Gon River was slightly more acidic than the Dong Nai River (6.3 ± 0.2 vs. 7.0 ± 0.3 , Fig. S2B), contained higher DOC ($3.7 \pm 0.4 mg L^{-1}$ vs. $2.2 \pm 0.6 mg L^{-1}$, Fig. S2E), but less organic-rich suspended particles during the dry

season (Fig. S2F). The acidic water upstream of the Sai Gon River was assigned to the interactions with acid sulphate soils within its watershed (Nguyen et al., 2011; Strady et al., 2017). Despite a mesotrophic status in the Saigon river compared to an oligotrophic one in the Dong Nai (Nguyen et al., 2019b), the POC in both river systems was mainly associated with allochthonous organic matter, e.g., from untreated wastewater, rather than the autochthonous phytoplankton. This is more noticeable during the wet season as the dry season typically presents an algal bloom with significant phytoplankton density (Fig. S4) (Nguyen et al., 2021); a significant correlation between chlorophyll-a and POC ($r^2 = 0.69$, Fig. S5) was observed at the two upstream stations (HA and

PC). High dissolved REEs and low POC characterized the wet season; the opposite was observed during the dry season (Fig. 3, A and B). The wet season samples also had lower pH (Fig. 3, C and D) and dissolved oxygen (Fig. S6) due to the decomposition of organic matter, nitrification processes (Nguyen et al., 2019b) and enhanced leaching from acid sulphate soils (Nguyen et al., 2011). The REE geochemistry in two river systems is regulated by either their sorption on organic-rich particles (scavenging effects during the dry season) or their release from particles because of the acidity of the water column as observed during the wet season. The enhanced mobility of REEs under acidic conditions has been widely

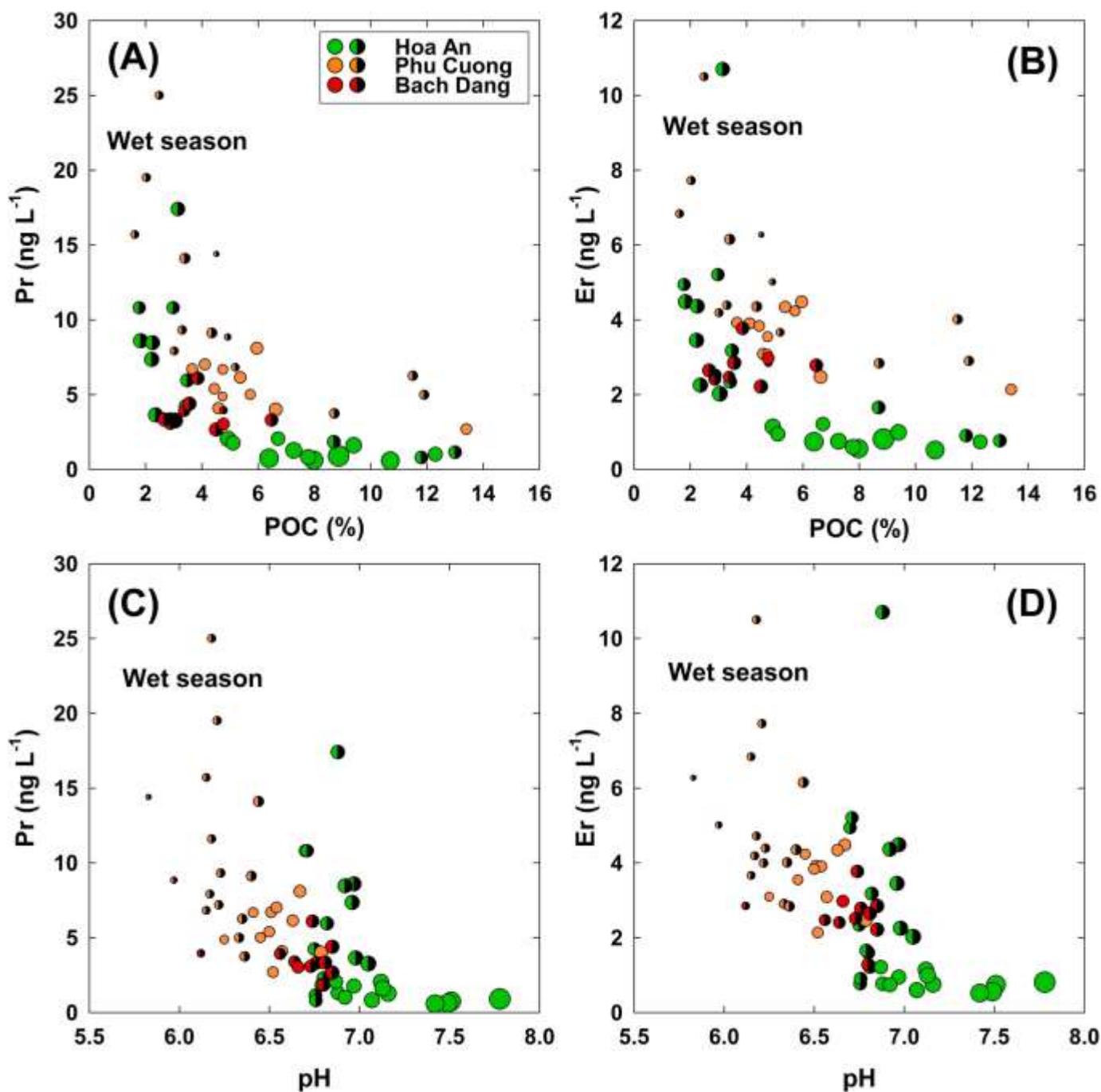


Fig. 3. The relationships of Pr and Er vs. particulate organic matter (A and B) and pH (C and D) at stations HA (green circles), PC (orange circles) and BD (red circles). The half-filled symbols show the samples taken during the wet season, while the open symbols represent the dry season samples. The symbol sizes in all four panels are proportional to pH values of the water samples (pH range from 5.83 to 7.78). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reported for surface waters and led to unique accumulation patterns in the Australian intertidal mangrove sediments receiving coastal acid sulphate soil drainage (Morgan et al., 2016).

4.2. REE fractionation affected by organic-rich particles

Seasonal effects were also reflected in the fractionation between LREEs (e.g., Pr) and HREEs (e.g., Er). Pr_{UCC}/Er_{UCC} decreased with increasing POC concentrations, indicating preferential sorption of LREEs on organic-rich particles, especially during the dry season (Fig. 4A). Such preferential removal of LREEs by sorption has been documented in natural ecosystems; dissolved LREEs exist as free ions in a greater proportion than HREEs, thus, are more susceptible to surface reactions, while the HREEs are mainly bound in dissolved carbonate complexes (Sholkovitz, 1995; de Baar et al., 2018; Garcia-Solsona and Jeandel, 2020; Dang et al., 2022c). The variations in pH could be an important factor leading to a change in REEs' chemical speciation as it dictates the bicarbonate-carbonate equilibrium and, thus, the proportion of REE-carbonate complexes (Och et al., 2014). However, we did not observe a significant variation trend between Pr_{UCC}/Er_{UCC} and pH, mainly

because of a limited variation range of pH (average of 6.8 ± 0.4 , $n = 125$ and range from 5.83 to 7.78, Fig. S2B). Therefore, these results highlight the significance of particulate organic complexes in immobilizing REEs and inducing the fractionation between LREEs and HREEs in fluvial systems.

To further elucidate the role of organic-rich particles in fractionating REEs, we evaluate the fractionation ratios between LREEs, MREEs and HREEs, given that organic matter and biogenic phosphate tend to induce an enrichment of MREEs relative to the lighter and heavier REEs (Pourret et al., 2007; Auer et al., 2017). This feature has also been demonstrated in plankton samples from the St. Lawrence River and Estuary (Dang et al., 2023). Therefore, we plotted the ratios of Tb_{UCC}/La_{UCC} as the function of Lu_{UCC}/La_{UCC} (Fig. 5) to identify the three categories of REE patterns corresponding to the enrichment of LREEs, MREEs and HREEs, respectively.

All dissolved REEs patterns are categorized in the HREE enrichment (Fig. 6A), commonly referred to as the “seawater-like” pattern, as the results of LREEs being removed by sorption processes (Pourret and Tuduri, 2017; Dang et al., 2023). These linear REE patterns differ the Sai Gon and Dong Nai Rivers from other major tropical rivers (e.g., Amazon, Orinoco Rivers) as the latter display an MREE enrichment because of stronger binding with humic substances or organic-coated colloids (Osborne et al., 2014; Rousseau et al., 2015). However, this observation could be associated with different operational procedures as we filtered our samples through 0.2- μ m filters while previous studies used the 0.45 μ m cutoff. Variance in particle size cutoffs directly affects the data interpretation, especially for chemical species with high affinity to colloidal fractions and for the definition of the “truly dissolved” phase (Dang et al., 2022b). Therefore, we expected that the smaller particle size cutoff of 0.2 μ m had eliminated most of the coarse colloids and the “dissolved” REEs patterns included mainly the carbonate complexes displaying linear HREE enrichment shapes.

More interestingly, the samples with lower POC display more substantial fractionation (i.e., higher ratios of Tb_{UCC}/La_{UCC} and Lu_{UCC}/La_{UCC}) than those with higher POC (Fig. 5A). This observation suggests that POC also attenuates the extensive fractionation between these LREE, MREE and HREE, as it has been observed for inorganic surfaces. The difference in the stability constants between inorganic forms of La and Lu for hydrous manganese oxides often is across one order of magnitude (Pourret and Davranche, 2013). However, the presence of humic substances significantly modifies the sorptive properties as REEs bind to the particles mainly through REE-humate complexes (Davranche et al., 2005). There is also evidence from natural samples where significantly different $\log K_D$ values were observed between the LREEs, MREEs and HREEs for suspended particles in the estuary and gulf of St. Lawrence, while there was no difference in the organic-rich water of the

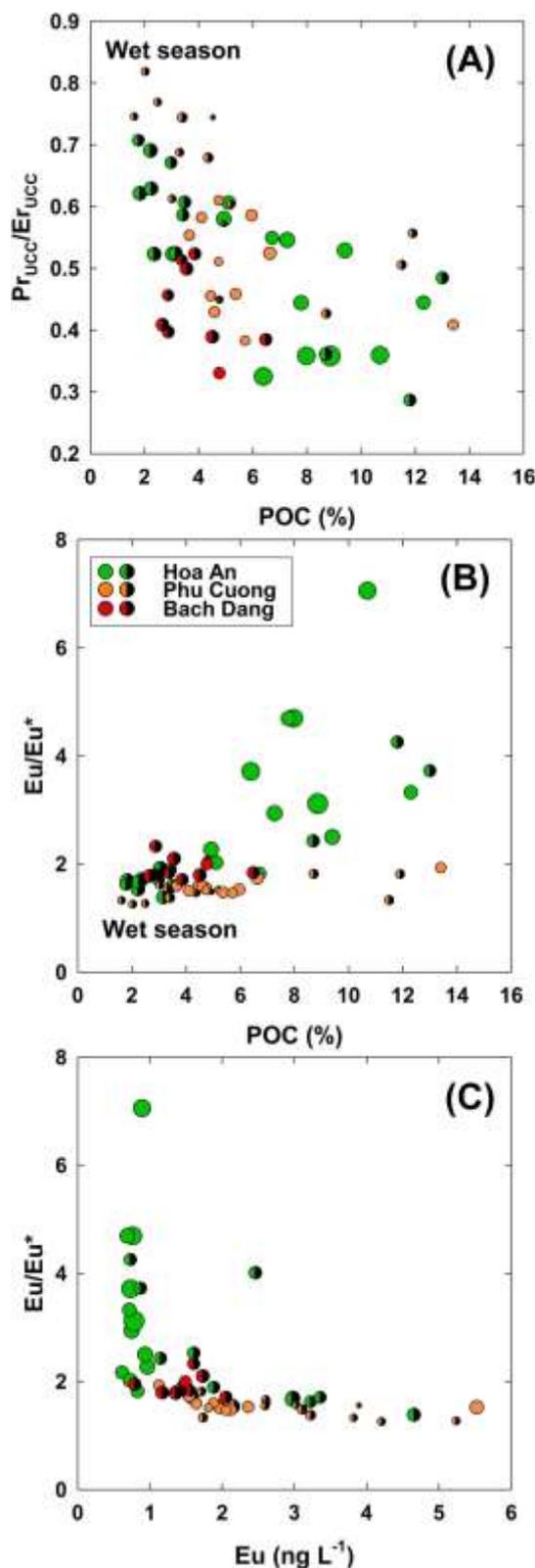


Fig. 4. The relationship between dissolved Pr/Er ratios (A) and Eu anomalies (B) with particulate organic carbon at stations HA (green circles), PC (orange circles) and BD (red circles). The half-filled symbols show the samples taken during the wet season, while the open symbols represent the dry season samples. Panel C shows the biplot of Eu anomalies as the function of dissolved Eu concentrations. The symbol sizes are proportional to pH values of the water samples (pH range from 5.83 to 7.78). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

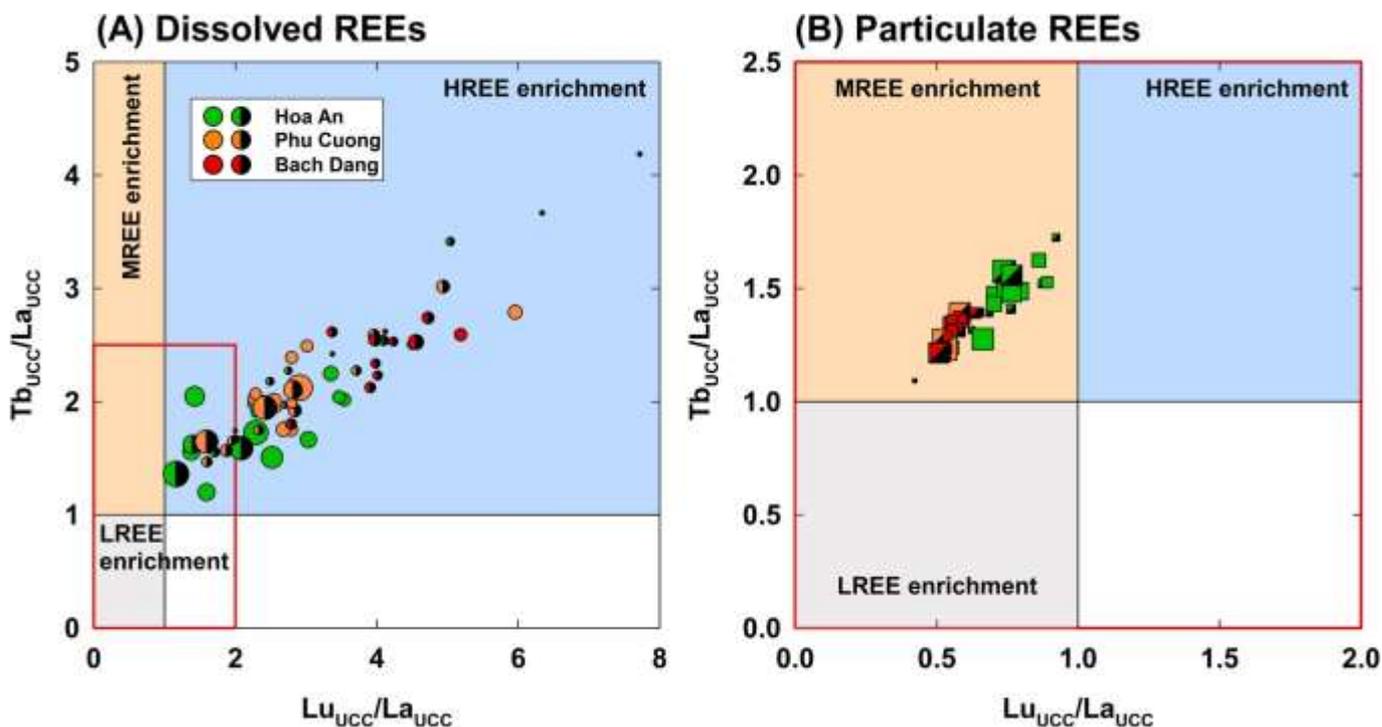


Fig. 5. Biplots of Tb_{UCC}/La_{UCC} as the function of Lu_{UCC}/La_{UCC} for dissolved (A) and particulate (B) fractions at stations HA (green circles), PC (orange circles) and BD (red circles). The half-filled symbols show the samples taken during the wet season, while the open symbols represent the dry season samples. The colored areas demark REE pattern types in environmental samples, i.e., the enrichment of LREEs, MREEs and HREEs. The symbol sizes are proportional to POC concentrations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

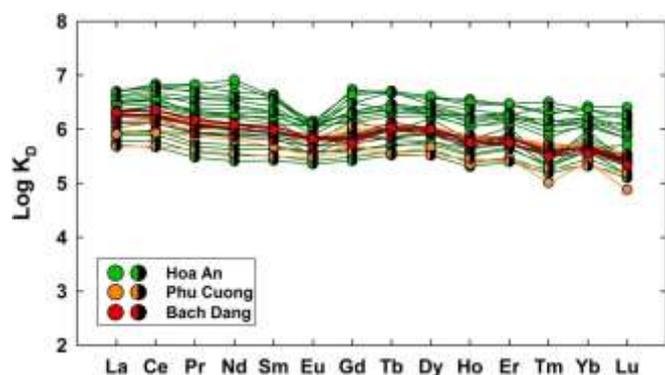


Fig. 6. The variations in $\log K_D$ patterns across the lanthanide series at stations Hoa An (green circles), Phu Cuong (orange circles) and Bach Dang (red circles). The half-filled symbols show the samples taken during the wet season, while the open symbols represent the dry season samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Saguenay Fjord (Dang et al., 2022c). Therefore, we hypothesize that the increasing POC concentrations on suspended particles of the Sai Gon and Dong Nai Rivers significantly scavenge dissolved REEs (Fig. 3, A and B) while attenuating the extreme fractionation between LREEs, MREEs and HREEs, leading to decreasing Tb_{UCC}/La_{UCC} and Lu_{UCC}/La_{UCC} (Fig. 5A) in the dissolved fractions.

Furthermore, the scavenging effects of POC for dissolved REEs led to a specific signature on the particulate matters; the particulate REE patterns show enrichment of MREEs (Fig. 5B). This pattern is a common feature of REE-humic complexes, organic-coated colloids, organic sediments and authigenic/biogenic phosphate and plankton samples (Rousseau et al., 2015; Auer et al., 2017; Pourret and Tuduri, 2017; Adebayo et al., 2018; Dang et al., 2023). The consistent MREE-

enrichment pattern observed for all samples demonstrates the significance of organic complexes governing the mobility of REEs in the Sai Gon and Dong Nai River systems.

4.3. The conditional solid/liquid distribution of REEs

We computed the distribution coefficient K_D by dividing the leachable REE concentrations (mg kg^{-1}) by the dissolved REE concentrations (mg L^{-1}). It is important to note that this parameter is conditional, given that our method yields partial digestion of the suspended particles, and thus, our calculated K_D might be lower than the values based on the total concentrations in suspended particles (Turner et al., 1993).

There was no significant difference between the average $\log K_D$ values for the three stations, which gradually decreased from 6.3 ± 0.3 ($n = 34$) for La to 5.6 ± 0.4 ($n = 34$) for Lu (Fig. 6). The $\log K_D$ values of Eu were also lower than the neighbouring REEs due to its anomalies; this is especially noticeable at station HA. The decreasing $\log K_D$ pattern reflects the differential affinities between LREEs and HREEs for sorptive surfaces, see Section 4.2. The $\log K_D$ values, although reported for partial digestion of suspended particles, were a few orders of magnitude higher than values reported for REE sorption onto ferromanganese oxides ($\log K_D \sim 3-4$, (Davranche et al., 2004, 2005) and the St. Lawrence River and Estuary and the Saguenay Fjord ($\log K_D \sim 2.5$ to 4.5, (Dang et al., 2022c). This high range of $\log K_D$ observed in the Sai Gon and Dong Nai Rivers suggested the occurrence of highly reactive surfaces to effectively scavenge REEs; this is particularly noticeable during the dry season, where dissolved REE concentrations decreased significantly compared to the wet season (Fig. 3).

We previously associated such highly reactive surfaces with the phytoplankton-derived organic matter of the river systems (Nguyen et al., 2019b, 2021), this hypothesis is further supported by a good correlation between $\log K_D$ of REEs and the POC content (Fig. 7). Note that a few water samples at station PC upstream of the Sai Gon River were excluded from the regression because of their lower pH associated

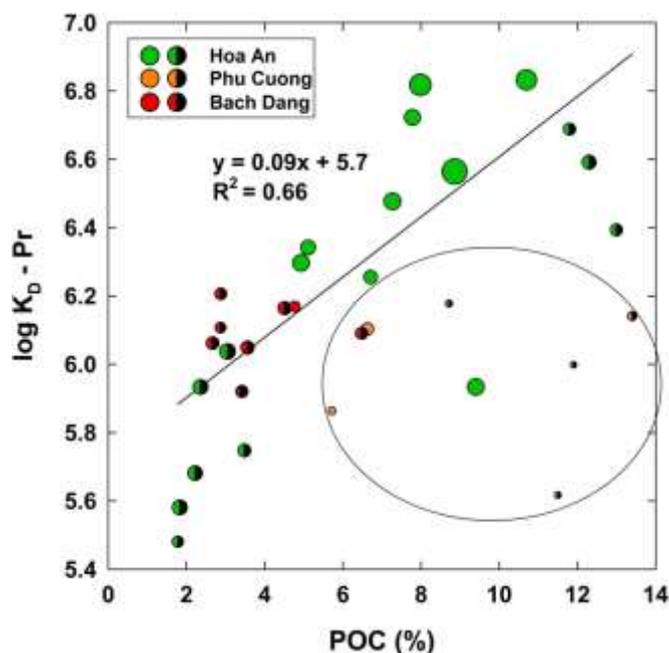


Fig. 7. The relationship between $\log K_D$ of Pr and POC at stations HA (green circles), PC (orange circles) and BD (red circles). The half-filled symbols show the samples taken during the wet season, while the open symbols represent the dry season samples. The samples in the circles are excluded from the regression line. The symbol sizes are proportional to pH values of the water samples (pH range from 5.83 to 7.78). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with the local geochemical backgrounds, e.g., acid-sulphate soils or local groundwater discharges (Tu et al., 2022). Besides these outliers, the $\log K_D$ -POC correlation confirms the role of particulate organic matter in scavenging REEs from solutions. The POC contents were relatively high (up to 13%) and rich in chlorophyll-a and algal decomposition materials (e.g., phaeopigments) (Fig. S5).

4.4. REE anomalies

We did not observe significant negative Ce anomalies associated with the oxidation of Ce(+III) to the less soluble Ce(+IV) as observed in aquatic systems, especially in seawater (de Baar et al., 2018). However, this is a common feature of freshwater systems as it was recently suggested that the formation of dissolved complexes (e.g., carbonate) stabilizes Ce(+III) and prevents it from oxidative transformations in river waters (Dang et al., 2022a).

Europium anomalies at station PC (upstream of the Sai Gon River) and the urban station BD remained low ($\text{Eu}/\text{Eu}^* = 1.5 \pm 0.2, n = 27$ and $1.9 \pm 0.2, n = 11$, respectively) (Figs. 4B and S7B), compared to station HA (upstream of the Dong Nai River), especially during the dry season (Eu/Eu^* up to 7.05, Fig. 2D). These ranges of values are, however, higher than most river systems, including the Mekong River Delta (upstream section in Cambodia), where Eu/Eu^* in the clay fraction approximates 1.2 (Bayon et al., 2015). There is increasing evidence that unusually high Eu anomalies could be an analytical artifact in ICP-MS analysis because of interferences with Ba (Pourret et al., 2022). However, there is no correlation between the dissolved Ba concentrations and Eu/Eu^* ; the variations in Ba concentrations remained limited, i.e., 11 to 14 $\mu\text{g L}^{-1}$ during the dry season of 2016 when elevated Eu/Eu^* were recorded. Also, Ba concentrations reached up to 45 $\mu\text{g L}^{-1}$ (station BD during the dry season) without an increased in Eu/Eu^* . Therefore, the possibility of analytical interferences could be eliminated.

Such high values of Eu anomalies were only reported for the St. Lawrence River with a correlation between Eu/Eu^* and Ca/Al ratios,

indicating cation exchange processes or the competition of the divalent ions on clay particles releasing Eu into the dissolved fraction (Dang et al., 2022a). However, we did not observe any change in conductivity at station HA, while PC and BD showed large variations in conductivity values but constant Eu/Eu^* (Fig. S7B). Therefore, the hypothesis of cation exchange dislocating Eu from particles might be excluded. However, there is a similar variation trend between Eu/Eu^* and POC at station HA (Fig. 4B), which might indicate processes involving the biogeochemistry of organic matter, including its decomposition releasing Eu. In estuarine and marine plankton samples, slightly positive Eu anomalies have been associated with preferential enrichment of Eu than the neighbouring REEs because of the analogy to Ca into microalgal cells or invertebrate's chitin shell (Dang et al., 2023). The decomposition of this plankton-derive organic matter, which prevails at station HA on the Dong Nai River, might release the previously-incorporated Eu. This station also exhibited a peak of chlorophyll-a in February 2016 and a delayed peak of phaeopigment in March 2016 (dry season, Fig. S4), suggesting the degradation of algal chlorophyll pigment into phaeopigments during this period.

Nevertheless, such interpretation should be cautiously considered as the elevated Eu anomalies were observed at minimum REEs concentrations during the dry season (Fig. 4C). We calculated the excess concentrations of Eu ($\text{Eu}_{\text{excess}}$) that would be released into the solutions as the difference between the measured Eu concentrations ($\text{Eu}_{\text{measured}}$) and the geogenic Eu.

$$\text{Eu}_{\text{excess}} = \text{Eu}_{\text{measured}} - \text{Eu}_{\text{geogenic}} = \text{Eu}_{\text{measured}} - \frac{\text{Eu}_{\text{measured}}}{\text{Eu}/\text{Eu}^*} \quad (4)$$

Accordingly, the excess concentrations of Eu were lower during the dry season ($0.5 \pm 0.1 \text{ ng L}^{-1}$) than the wet season ($1.0 \pm 0.3 \text{ ng L}^{-1}$) at station HA. In other words, the elevated Eu/Eu^* values recorded at HA (up to 7.0) could be exacerbated by the small reservoir effect.

Lastly, Gd anomalies were only observed at the urban station BD (Fig. 3E). The Gd/Gd* maximum of 2.3 is slightly higher than the threshold of natural Gd anomaly of 1.4 (de Baar et al., 2018; Dang et al., 2022c). Therefore, the emissions of anthropogenic Gd associated with its medical sources are present at this urban station but might not be as significant as in other major cities, e.g., Seoul or Berlin (Knappe et al., 2005; Song et al., 2017). However, there might be a significant dilution effect as station BD is 15–20 km downstream of a wastewater treatment plant (Fig. S8).

5. Conclusion

This study provides additional insight into the aquatic geochemistry of REEs in tropical and anthropogenically-impacted systems of Southern Vietnam. The seasonal discrepancy was associated with differential hydrological regimes where watershed runoff significantly elevated dissolved REE concentrations in the wet season. However, there is limited REE mobility during the dry season as the suspended particles are enriched with organic matter derived from phytoplanktonic activities, thus with stronger complexing capacities. This seasonality in the river discharge of REEs is particularly striking; it calls for more comprehensive consideration of such phenomenon in affecting the dissolved REE riverine loadings to the oceans from tropical systems, especially those with high REE leachability from river basins. The fates of REE-loaded and organic-rich particles in coastal waters should also be taken into consideration, as REEs could be further released upon decomposition of the organic coating or geochemical interactions with saline matrices (Rousseau et al., 2015). These future studies will therefore help constrain the global marine budget of REEs, which is currently unbalanced.

We provided robust evidence of increasing REE distribution coefficients (K_D) with increasing POC contents on suspended particles. The interactions between REE and particulate organic matter also affect the fractionation between LREEs and HREEs in the dissolved fraction while

inducing an enrichment of MREEs in the suspended particles. While there are no Ce anomalies in the dissolved and particulate samples of the freshwater systems, we observed increasing Eu anomalies during the dry season, for which hypotheses of analytical artifacts or cationic exchange processes might be excluded. We associated such Eu anomalies with the decomposition of phytoplanktonic organic matter, which might previously enrich Eu as an analog for Ca. However, this interpretation should be cautiously considered given the small reservoir effect (increasing Eu anomalies but decreasing Eu concentrations in solutions).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data is included as a supplementary file

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Appendix A. Supplementary Material

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