



# Distribution, source and contamination of rare earth elements in sediments from lower reaches of the Xiangjiang River, China<sup>\*</sup>

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## ABSTRACT

Rare earth elements (REEs) are emerging micropollutants in aquatic environments. In this study, concentrations of REEs and major elements, and mineralogical compositions of sediments from lower reaches of the Xiangjiang River (China) were analyzed using ICP-MS technique. The results suggested that sediments were characterized by terrigenous compositions  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$  and  $\text{P}_2\text{O}_5$ , and contained high concentrations of REEs with mean total REE concentrations ( $\sum\text{REE}$ ) of 318.7 mg/kg. REEs were moderately enriched in upper river sediments, and slightly or less enriched in downriver sediments. The normalized REE distribution pattern for sediments was characterized by flat shakelike and Eu depleted V-shape REE patterns, which indicated REEs in sediments were lithologically contributed from sedimentary rocks and granites distributed in the watershed respectively. REEs in sediments were hosted mainly in Fe–Mn oxides, and sulfide and organic matters that were characterized by middle REEs (MREE) enrichments relative to light REEs (LREE) and heavy REEs (HREE), and the distribution and differentiation of REEs in sediments were controlled by clays, Fe–Mn oxides, organic matters and finer grains; and also by accessory minerals (e.g., zircon) from granite. The distribution features of REEs in sediments and BCR extraction results suggested that the sediment REE enrichment resulted from additional REE input from anthropogenic sources, including those in discharges from sulfide-ore smelting industries at Zhuzhou city and from phosphate fertilizer plants at Xiangtan city along the river. Thus, sediments were contaminated with REEs in moderate degree in upper river area, and REE contamination was then formed by superimposing anthropogenic REEs on lithological residues. Finally, concentrations of  $\text{Ce} > 100 \text{ mg/kg}$ ,  $\text{Gd} > 8.12 \text{ mg/kg}$ ,  $\sum\text{REE} > 274.9 \text{ mg/kg}$ ,  $\sum\text{LREE} > 252.3 \text{ mg/kg}$  and  $\sum\text{HREE} > 28.8 \text{ mg/kg}$  here were recommended as the REE contamination levels that represented as REE indices for identifying and rating REE contamination in this mining impacted river.

## 1. Introduction

Rare earth elements (REEs: La–Lu) are a group of chemically similar elements that are industrially important due to their use in modern commodities such as high technology, agricultural fertilization, medical techniques and also widely used as tracers in geoscience (Adeel et al., 2019; Shajib et al., 2020). They have been used to trace the provenance of sediments (Singh, 2009), interpret environmental change (Cao et al., 2019; Liu et al., 2021) and understand the earth's surface processes

(Nesbitt et al., 1990; Lafrenière et al., 2023). With the increasing application of REEs in modern industries, REEs have been recognized to be emerging micropollutants in environment and the distribution and fractionation, sources, and potential human health harm of REEs have been increasingly investigated (Mihajlovic and Rinklebe, 2018; Adeel et al., 2019; Li et al., 2020). Although REEs themselves can help to establish a sound screening procedure to tell contaminated from pristine environments (Kulaksız and Bau, 2007; Mihajlovic et al., 2019; Wang et al., 2019a), there is a paucity of study on using REEs themselves to

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evaluate and identify REE contamination in sediments from industry impacted rivers.

As river sediments naturally sample and average large areas of eroded continental crust (Garçon et al., 2014), and REEs are generally less mobile and minimally fractionated during processes from source to sink (Singh, 2009), REEs in river sediments thus represent their average value of weathering residues from a vast area with different source rocks. Therefore, river sediments usually display similarly uniform REE pattern being comparable to that of the upper continental crust, which is characterized by distinct enrichment of LREE (La to Eu) with weak or no Ce and Eu anomalies (Smith and Liu, 2018). However, as most great rivers pass through areas with intensive industrial activities (e.g., ore smelting), REE distribution in river sediments is altered by these anthropogenic inputs, and the anthropogenic REEs then lead to the elevated REE concentrations, anomalies and contamination in sediments. REE contamination has been identified in sediments from various rivers worldwide, such as those from Poyang Lake watershed (Wang et al., 2019a), North China Plain (Liu et al., 2021), Havel River system (Möller et al., 2014) and Wupper River (Mihajlovic et al., 2014a) in Germany, San Francisco Bay (USA) (Hatje et al., 2016), Santos estuary (Brazil) (De Oliveira et al., 2007), and Russian arctic area (Slukovskii et al., 2022). River sediments with REE contamination generally show REE patterns different from that of the pristine ones (e.g., Adeel et al., 2019; Munemoto et al., 2020), and concentrations of La > 80 mg/kg, Ce > 100 mg/kg, Nd > 85 mg/kg and Gd > 8.12 mg/kg in sediments are believed to be the REEs contributed from anthropogenic sources (Mihajlovic et al., 2019; Adeel et al., 2019). In addition, studies have described that the acid mining drainages and sediments deposited in mine drainage pits often show shale-normalized REE patterns with significant enrichment of MREE relative to LREE and HREE (Pérez-López et al., 2010; Delgado et al., 2012). However, such REE distribution pattern can change to be the flat shale-like pattern in sediments deposited along river-flow direction away from the mine pit due to the addition of rock weathering residues (Cao et al., 2019; Khorasanipour and Rashidi, 2020) that may hide signatures of anthropogenic REEs (Smith and Liu, 2018; Munemoto et al., 2020). Therefore, it is essential to understand the overall distribution, fractionation and contamination of REEs in sediments from mining impacted rivers.

The Xiangjiang River flows across Hunan province from south to north and finally enters in the Dongting Lake (Fig. 1a). The river watershed covers two thirds of total area of the province. Mining and metallurgical industries for exploring and exploiting for non-ferrous mineral resources were once highly concentrated and popularized in the watershed, thus the river sediments were seriously contaminated with heavy metals, which has attracted many researchers to study (e.g., Peng et al., 2011, 2022; Chai et al., 2017; Fang et al., 2019). In contrast, study on distribution and contamination of REEs in sediments is rare, except the analysis of REE concentrations in suspended particulates of the river (Gong et al., 2009). Thus, the present study contributes to this by analyzing REEs, major elements, and mineralogical compositions of sediments from Zhuzhou (ZZ), Xiangtan (XT), Changsha (CS), and Xiangyin (XY) sections (Fang et al., 2019) of the river, with purposes: 1) to examine REE distribution in sediments of the river; 2) to understand the sources of REEs and then the REE contamination in sediments; and 3) to set REE indices for identifying REE contamination in sediments from mining impacted rivers.

## 2. Materials and methods

### 2.1. Study area

The main channel of the river is 856 km in length, and the watershed is the major focus for agriculture and economic development in the province. Bedrock distributed in the upper and middle portions of the watershed includes Palaeozoic sedimentary rocks and Mesozoic-Cenozoic red clastic sedimentary rocks. The sedimentary rocks were mainly composed of sandstone and limestone, and they were frequently intruded with granites (Fig. 1a), where a remarkable array of ore deposits including lead, zinc, copper and REEs were exploited (Peng et al., 2011). Among these rocks, the limestones covered about 60% of the total area (Fig. 1a). Granites scattered throughout the watershed were sensitive to chemical weathering under the sub-tropical monsoon climate condition. The lower portion of the watershed was dominated by gravel and reticulated red soils of Quaternary (Fig. 1a). Industrial activities such as ore smelting and fertilizer producing were once concentrated along the middle and downriver channels such as those at

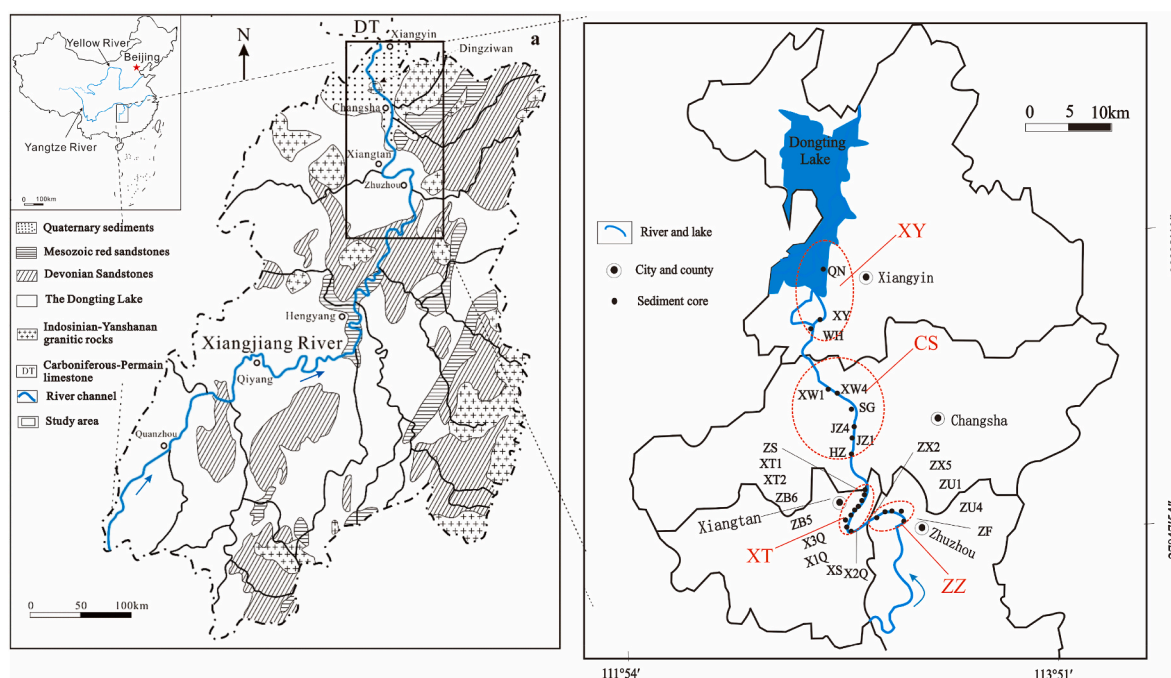


Fig. 1. Maps showing general geology of the Xiangjiang River watershed (a) and locations of sediment cores (b) for this study (after Fang et al., 2019).

Zhuzhou, and Xiangtan cities, and waste discharges from these industries then led to metal contamination in river sediments (Fang et al., 2019).

## 2.2. Sampling and sediment samples

Samples were obtained from sediment cores that were collected by drilling into sediments in the river channel running from the Zhuzhou, Xiangtan and Changsha cities, to Xiangyin county (Fig. 1b). Locations for collecting sediment cores were chosen on the base of field survey, and details for sampling were reported in Fang et al. (2019). Sediment cores generally consist of the upper light brownish layer and the lower dark or grey brownish layer of silty mud with grain size < 0.065 mm in diameter (Blair and McPherson, 1999) with length ranging from 25 cm to 86 cm. Samples were obtained by sub-sampling cores at an interval of 3 cm from top to bottom in the field. Due to the homogeneous lithological property of sediment cores, samples with odd numbers were selected for analysis in this study, which were grouped into four categories according to the sampling location, as follows, the ZZ, XT, CS, and XY sediments.

## 2.3. BCR sequential extraction

In order to elucidate the host components of REEs in sediments, the three-step BCR sequential extraction (Davranche et al., 2011) was carried out in 50 mL polyethylene acid washed centrifuged tubes. The extraction was applied to duplicate samples (0.5 g powders) and standard materials BCR-701 (0.5 g) that were used for quality control. The procedure and operating conditions for the BCR extraction were given elsewhere (Peng et al., 2022). Four chemical fractions including exchangeable (exchangeable ions and carbonates, S1), reducible (Fe–Mn oxides, S2), oxidizable (sulfides and organics, S3), and residual fraction (silicate minerals, S4) were obtained for REE analysis.

## 2.4. Analysis and quality control

Concentrations of REEs, and major elements of bulk samples (n = 347) were determined at the Key Laboratory of Isotopic Geochemistry, Chinese Academy of Sciences. For REEs, 50.0 mg of the powder sample was dissolved using a three-acid solution (HCl–HNO<sub>3</sub>–HF) in a disposable platinum crucible. The dissolved sample was then diluted using 2% HNO<sub>3</sub>, and the REEs were analyzed at a wide range of concentrations using inductively coupled plasma mass spectrometry (ICP-MS, Elan6000). Detail for analyzing can refer to Fang et al. (2019).

Details for major element analyzing can refer to Fang et al. (2021). Mineralogical compositions of the unheated powders (< 2 mm) from selected samples (n = 21) were measured on a Miniflex-600 diffractometer (XRD) at the Mineralogical Laboratory of Hunan University. The powders were mixed with known amounts of ZnO as an internal standard, and side-packed mounts were prepared for each sample. The XRD patterns were recorded between 5° and 90° at a scanning speed of 0.33°/s (2θ) with Cu Kα radiation (15 mA and 40 kV). Proportions (%) of minerals were determined using the Jade 6.0 program of Eberl (2003), which optimises a whole-pattern fit using previously scanned mineral standards.

## 2.5. Data treatment

### 2.5.1. Enrichment of REEs in sediments

To characterize the distribution of REEs in sediments, enrichment factors (EF) were calculated by normalizing REE concentration to Al<sub>2</sub>O<sub>3</sub> (using Al alone provided the same result) using Eq. (1) (Grygar and Popelka, 2016), after which the degree of REE enrichment was evaluated by criteria after Sutherland (2000).

$$EF = (C_{REE} / C_{Al_2O_3})_{Sample} / (C_{REE} / C_{Al_2O_3})_{Background} \quad (1)$$

where  $(C_{REE}/C_{Al_2O_3})_{Sample}$  represents the ratio of REE concentration to the reference element Al<sub>2</sub>O<sub>3</sub> in analyzed samples, and  $(C_{REE}/C_{Al_2O_3})_{Background}$  is the ratio of REE concentration to the reference element Al<sub>2</sub>O<sub>3</sub> in background sediments (Yan et al., 1997). Al<sub>2</sub>O<sub>3</sub> was selected as the reference element because it is homogeneously distributed in sediments, it is less mobile during sedimentation, and there is small anthropogenic input in sediments (Fang et al., 2019).

### 2.5.2. Normalization and REE anomalies calculation

The measured REEs were normalized to North American Shale Composition (NASC, Gromet et al., 1984) since NASC has been most frequently used in REE normalization procedures, facilitating the comparison with data in the literature as many other studies (Benabdelkader et al., 2019). Then, REE anomalies were calculated by the following equations (Eq. (2) - Eq. (6)) for La/La\* (Kulaksız and Bau, 2013), Ce/Ce\* (Hannigan et al., 2010), Sm/Sm\* (Kulaksız and Bau, 2013), Eu/Eu\* (Barrat et al., 2023), and Gd/Gd\* (Kulaksız and Bau, 2013).

$$La / La^* = 2\text{Log}Nd_N - \text{Log} Eu_N \quad (2)$$

$$Ce / Ce^* = 3Ce_N / (2La_N + Nd_N) \quad (3)$$

$$Sm / Sm^* = (2\text{Log}Eu_N + \text{Log}Nd_N) / 3 \quad (4)$$

$$Eu / Eu^* = \text{Log}[Eu_N / (0.67Sm_N + 0.33Tb_N)] \quad (5)$$

$$Gd / Gd^* = Gd_N / (0.33Eu_N + 0.67Tb_N) \quad (6)$$

where the subscript N denotes normalization to NASC (Gromet et al., 1984).

### 2.5.3. Assessment of REE contamination

The geoaccumulation index ( $I_{Geo}$ ) and pollution load index (PLI) here were employed to assess the degree of REE contamination in sediments (e.g., Shajib et al., 2020; Liu et al., 2021).

The  $I_{Geo}$  index was applied in the assessment of REE contamination by eliminating the influence of geological contributions. For this, the background concentration of individual REEs and a correction coefficient K were included in the assessment, as follows:

$$I_{Geo} = \text{Log}_2[C_M / K \times B_M] \quad (7)$$

where  $C_M$  is the concentration of the evaluated REE in a sample and  $B_M$  is the background concentration of that REE. Thus, the most important step for the assessment is the definition of K. Here, K value was determined by normalizing the concentration of Al<sub>2</sub>O<sub>3</sub> in the samples  $(C_{Al_2O_3})_{Sample}$  to the background concentration (12.8% for Al<sub>2</sub>O<sub>3</sub>) for the watershed (Yan et al., 1997), as shown in Eq. (8).

$$K = (C_{Al_2O_3})_{Sample} / (C_{Al_2O_3})_{Background} \quad (8)$$

The PLI index is an integrated index used to assess the sediment quality (Islam et al., 2015) by calculating the contamination factor (CF) of all REEs presenting in a sample using Eq. (9). A sample pollution index ( $PLI_{sample}$ ) was then calculated by taking the CF values and deriving the 15th root of the fifteen factors, multiplied together, using Eq. (10). Such sample indices could be treated in exactly the same way to give a site pollution index ( $PLI_{site}$ ) using Eq. (11) (Tomlinson et al., 1980).

$$CF_M = C_M / B_M \quad (9)$$

$$PLI_{site} = (CF_{La} \times CF_{Ce} \times \dots \times CF_{Lu})^{1/15} \quad (10)$$

$$PLI_{Zone} = (PLI_{sample-1} \times PLI_{sample-2} \times \dots \times PLI_{sample-n})^{1/n} \quad (11)$$

where  $C_M$  and  $B_M$  are the same as for Eq. (7), and  $n$  is the number of sampling sites (i.e., sediment cores). The index is effective for evaluating watershed scale spatial trends of REE contamination in sediments according to Tomlinson et al. (1980).

#### 2.5.4. Statistical analysis

Principal component analysis (PCA) was utilized to reduce the complexity of analyzing relationships among observed variables. Briefly, the Kaiser-Meyer-Olkin (KMO value > 0.5) and Bartlett sphericity tests ( $P < 0.001$ ) were performed to examine the validity of PCA outputs and a covariance matrix was built based on the measured concentrations of REEs, major elements, and metals Cs and Zr as well as ratios of Si/Al, Ce/Ce\* and Eu/Eu\* of the sediments (Fang et al., 2019). Then, Pearson's correlation analysis was used to measure the correlations among REEs and major elements within the sediments. All statistical analyses were performed using SPSS 18.0 for Windows.

### 3. Results and discussions

Data of concentrations of REEs and major elements, and mineralogical composition were reported in STable 1, in which those of the upper continental crust (UCC), granite rocks (GR), Yangtze River sediments (YZ), Soil of China (CSA) (Yan et al., 1997), and NASC (Gromet et al., 1984) were included for comparison. They are discussed as follows.

#### 3.1. Chemical composition of sediment

The river sediments were dominated by terrigenous components  $TiO_2$ ,  $SiO_2$ ,  $Al_2O_3$ ,  $K_2O$ ,  $Na_2O$  and  $P_2O_5$ , with total proportion of > 81%, which were comparable to that of many other rivers (e.g., Saputro et al., 2022; Zhang et al., 2022). However, ZZ sediments displayed major element compositions different from that of other (XT, CS and XY) sediments, for which (1) concentrations of major elements in ZZ

sediments were more variable than in other sediments. For example, concentrations of  $SiO_2$  and  $Fe_2O_3$  in ZZ sediments varied from 27 to 78 and 4.39 to 44.5 (%) respectively. In comparison, those of the other sediments varied from 53.3 to 83.9 and 2.12 to 10.9 (%) respectively; and (2) concentrations of  $TiO_2$  (0.74% – 5.87%),  $Fe_2O_3$  (4.39% – 44.1%) and CaO (0.66% – 12.53%) in ZZ sediments were significantly higher than those in other sediments that had  $TiO_2$ ,  $Fe_2O_3$  and CaO concentrations varying from 0.41 to 1.18, 2.12 to 10.9 and 0.2 to 2.4 (%) respectively.

The mineralogical compositions (STable 1) of sediments were also dominated by terrigenous minerals including detrital (quartz + microcline + albite = 23% – 97%) and clay (mica + illite + kaolinite + chlorite + hydrargillite = 1.5% – 28.7%) minerals, with variable contents of carbonates (calcite + dolomite + oulopholite = 0.38% – 19.7%) and Fe-bearing minerals (pyrite + hematite + magnetite + goethite = 0.13% – 15.3%). Such mineralogical compositions of sediments (except ZZ sediments) were consistent with the above major element compositions. The contents of carbonates (6.9% – 26.8%) and Fe-bearing minerals (0.44% – 15.4%) in ZZ sediments were significantly higher than those (ranging from 0.3 to 7.78 and 0.13 to 2.36%) respectively in other sediments. This was probably due to additional inputs of carbonates and Fe oxides dispersed from discharges from ore smelting plants therein at sites of ZZ samples (Fang et al., 2019).

#### 3.2. Distribution of REEs in sediments

##### 3.2.1. Concentrations and enrichment of REEs in sediments

REE concentrations in ZZ, XT, CS and XY sediments were variable as shown by these of La, Ce, Nd and Gd (Fig. 2a–d). Among the REEs, Ce had concentrations higher than others, and its highest concentration was 305 mg/kg (Fig. 2b). The total REE concentrations ( $\sum REE$ ) in ZZ, XT, CS and XY sediments ranged from 198 to 503, 196 to 689, 128 to 480 and 95 to 356 (mg/kg) respectively, with mean values of 305, 295, 256 and 250 (mg/kg) respectively, showing that REE concentrations decreased significantly from upper river ZZ through XT and CS to downriver XY

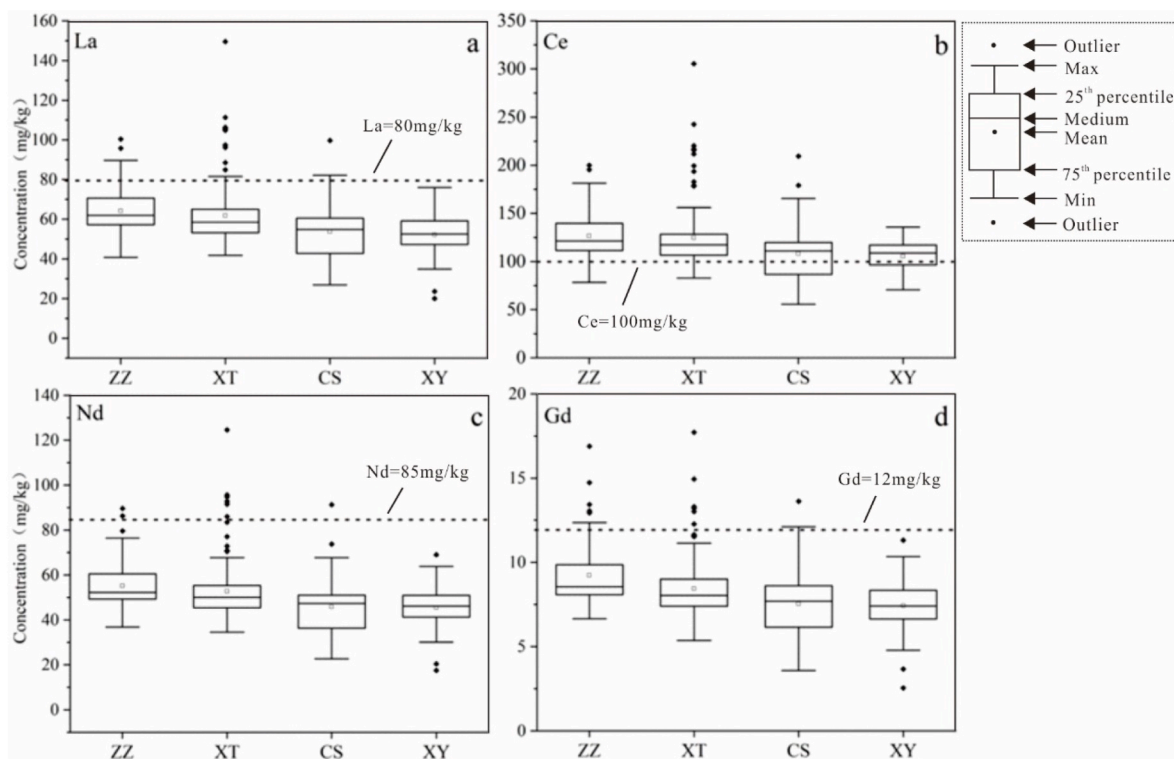


Fig. 2. Box-plots of concentrations of La (a), Ce (b), Nd (c) and Gd (d) in sediments of Zhuzhou (ZZ), Xiangtan (XT), Changsha (CS) and Xiangyin (XY) sections in lower reaches of the Xiangjiang River in China. The horizontal dash lines represent REE contamination levels after Mihajlovic et al. (2019) and Adeel et al. (2019).

sediments. The lowest REE concentration was observed in sample XY39 from XY sediments, which had  $\sum\text{REE}$  of 105.9 mg/kg. While the highest was in sample ZB5-36 from XT sediments, which had  $\sum\text{REE}$  of 774.8 mg/kg (STable 1). Moreover, there were 95.4% samples that had  $\sum\text{REE}$  > 200 mg/kg, being higher than those of the CAS (198 mg/kg), YZ sediments (203 mg/kg) and UCC (163.8 mg/kg) (Yan et al., 1997). Such high REE concentrations of sediments from this river were comparable to those of Xiamen Bay ( $\sum\text{REE}$ s of 245.9 mg/kg, Hu et al., 2019), Jiu-long River (245.3 mg/kg, Yu et al., 2018), and North China Plain (227 mg/kg, Liu et al., 2021). It was noted that REE concentrations of core sediments of this study were distinctly higher than those of surface sediments from this river ( $\sum\text{REE}$ s of 145.6 mg/kg) (Gong et al., 2009; Mao et al., 2014) and also higher than those of surface sediments from Dongting Lake ( $\sum\text{REE}$ s of 197 mg/kg) (Wang et al., 2019b), as observed in many other rivers (e.g., Di Leonardo et al., 2009; Liu et al., 2017, 2021). This suggested that core sediments could be whole representative for REEs in sediments of the river. Anomalies of La, Ce, and Gd were less significantly observed, while negative Eu anomalies were significant in sediments (STable 1).

REEs in sediments were moderately enriched ( $2 = \text{EF} < 5$ ) in ZZ and XT sediments, slightly enriched ( $1 < \text{EF} < 2$ ) in CS sediments, and less significantly enriched in XY sediments, as shown by box plots of EF values (Figs. S1a–d). This spatial variation of REE enrichment was similar with that of heavy metals Pb, Zn and Cu, but different from that of Mn and Cd in sediments (Chai et al., 2017; Fang et al., 2019). Moreover, the significant correlation coefficients between concentrations of REEs and Cu (0.79), Zn (0.63), Pb (0.72), and Cd (0.42) was observed in XY sediments, but not in other (ZZ, XT and CS) sediments. This suggests that REEs in sediments behaved differently from heavy metals, and probably had different sources from heavy metals (e.g., Munemoto et al., 2020; Slukovskii et al., 2022).

### 3.2.2. REE distribution patterns and source implications

The NASC normalized REE distribution patterns of sediments displayed the typical shale-like REE patterns (Fig. 3) with ratios of  $(\text{La}/\text{Yb})_{\text{N}}$ ,  $(\text{Gd}/\text{Yb})_{\text{N}}$  and  $(\text{La}/\text{Sm})_{\text{N}}$  for ZZ, XT, CS and XY sediments similarly around 1.32, 1.14 and 1.13 respectively. Ratios of  $\text{Nd}/\text{Sm}$  for ZZ, XT, CS and XY sediments ranged similarly and consistently from 4.9 to 6.1, and those of  $\text{Y}/\text{Ho}$  ranged from 22.7 to 30,  $(\text{Pr}/\text{Tb})_{\text{N}}$  from 0.69 to 1.43 and  $\text{Ce}/\text{Ce}^*$  from 0.59 to 1.02 (STable 1). This suggested that sediments from different section displayed roughly similar REE patterns. Such REE distribution pattern was similar to that of suspended particulates and surface sediments (Gong et al., 2009; Mao et al., 2014; Wang et al., 2019b) of this river, which could be observed in many other river sediments (e.g., Yang et al., 2002; Hu et al., 2019; Munemoto et al., 2020). As REE concentrations were distinctly variable, the REE distribution patterns were less uniform but dispersive. This might suggest that REEs of different sources were less completely mixed within sediments, and thus the maturity of river sediments was lower as indicated by major elements (Fang et al., 2021).

More interestingly,  $\text{Eu}/\text{Eu}^*$  values ranging from  $-0.53$  to  $-0.03$  could be referred as to group sediments into two groups: sediments that had  $\text{Eu}/\text{Eu}^*$  values ranging from  $-0.11$  to  $-0.03$  with an average of  $-0.04$  displayed the typical flat shale-like REE patterns (shale-like sediments, Fig. 3a); and sediments that had  $\text{Eu}/\text{Eu}^*$  values ranging from  $-0.53$  to  $-0.07$  with an average of  $-0.18$  displayed significantly Eu depleted V-shape REE patterns (V-shape sediments, Fig. 3b). As REE distribution in sediments resulted from complex factors such as lithological sources, rock weathering, host minerals, anthropogenic input, hydrological sorting, and sediment maturity (Balistreri et al., 2007; Delgado et al., 2012; Mihajlovic et al., 2014a and b, 2017), the two types of REE patterns could shine lights on sources of REEs in sediments.

The classic sedimentary rocks distributed in the watershed generally displayed shale-like REE patterns (Liang et al., 2014), and the granites scattered in the area were characterized by Eu depleted V-shape REE pattern (Mao et al., 2014). It was seen that sediments with low REE

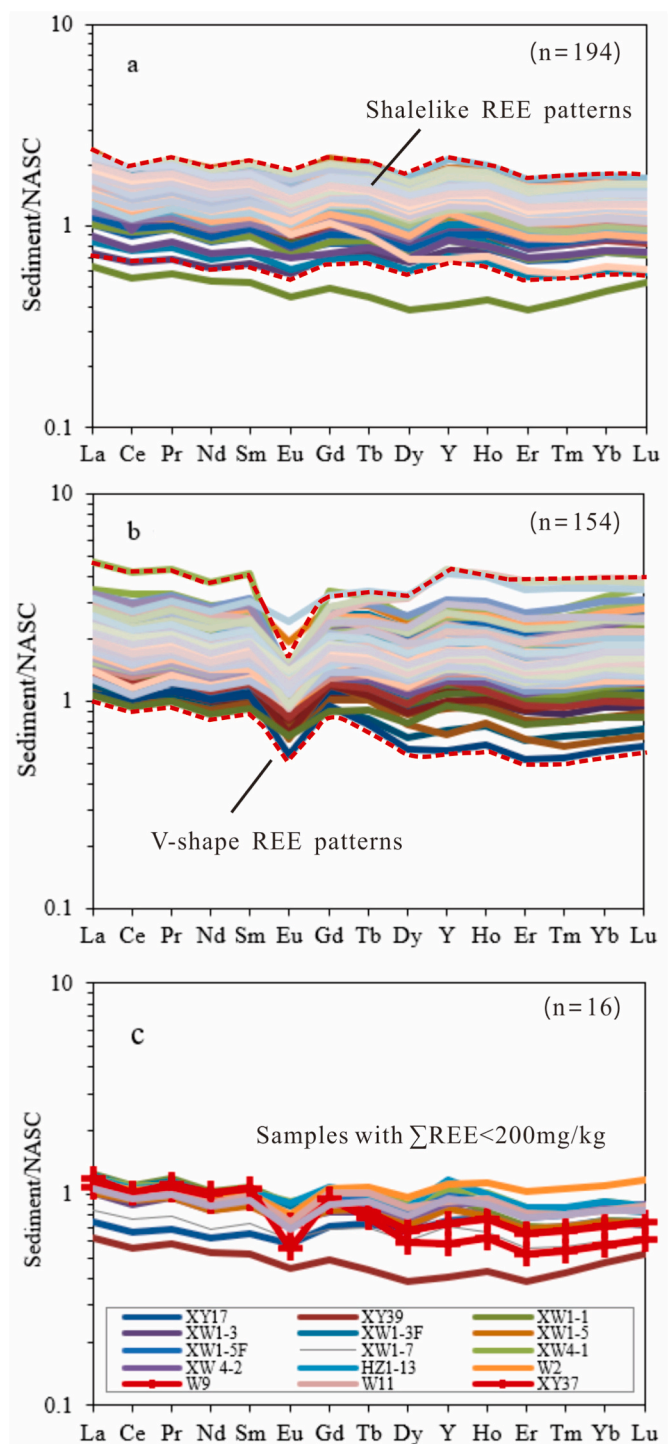


Fig. 3. NASC normalized REE patterns of sediments, showing two types of REE patterns: shale-like (a) (with  $\text{Eu}/\text{Eu}^*$  value around  $-0.04$ ), and Eu depleted (b) (with  $\text{Eu}/\text{Eu}^*$  value around  $-0.18$ ) REE patterns; and REE patterns (c) of samples ( $n = 16$ ) with lower REE concentrations ( $\sum\text{REEs} < 200 \text{ mg/kg}$ ).

concentrations ( $\sum\text{REE} < 200 \text{ mg/kg}$ ,  $n = 16$ ) also displayed the above two types of REE patterns (Fig. 3c), suggesting they represented REE patterns of the pristine sediments of the river. Here, the PCA was performed on sediments to determine associations between REEs and major elements, and then to characterize the REE sources of sediments. The Kaiser–Meyer–Olkin (KMO) value for the PCA was 0.951 and the associated probability of the Bartlett sphericity test was 0. That indicates that PCA could be applied to the dimensionality decompositions. The

PCA results revealed that the variability of REEs can be expressed as three principal components (PC1, PC2, and PC3) that explained 78.354% of the total variance. These data were plotted in PC1 vs. PC2 vs. PC3 plots for shale-like and V-shape sediments separately (Fig. 4a and b) to visualize the REE controlling factors. It is seen that REEs in shale-like sediments were associated with elements  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{LOI}$ , and  $\text{Cs}$  (Group I in Fig. 4a), with the Pearson correlation coefficients ( $r$ ) mostly  $>0.55$  ( $p < 0.01$ ) (STable 1). Such associations of REEs with major elements were also observed in samples with lower REE concentrations ( $\sum \text{REE} < 200$  mg/kg, STable 1). That suggested that REEs in sediments were hosted in and controlled by clay minerals, Fe–Mn oxides, organic matters (represented by  $\text{LOI}$ ), and finer grains as indicated by  $\text{Si}/\text{Al}$  ratios and  $\text{Cs}$  concentrations (Négre et al., 2018), which were similar with that concluded by Mihajlovic et al. (2014a and b, 2017). The above REE distribution patterns and their associations with other elements as shown in Fig. 4a suggested that REEs in sediments were contributed from sedimentary rocks through weathering (e.g., Nesbitt et al., 1990; Lafrenière et al., 2023).

However, the PCA results showed that REEs in V-shape sediments were hosted in and controlled by mineral phases different from that of shale-like sediments, for which REEs and elements  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$  and  $\text{Zr}$  were loaded in the same group (Group I in Fig. 4b), and the significant correlations were observed between REEs and  $\text{Zr}$  ( $r > 0.48$ ,  $p < 0.01$ ) as well as others (e.g.,  $\text{U}$ ,  $\text{Th}$  and  $\text{Sc}$ ), and between HREEs and  $\text{TiO}_2$  ( $r > 0.45$ ,  $p < 0.01$ ) (STable 1). As concentrations of  $\text{Zr}$  in V-shape sediments (mean concentration of 678.7 mg/kg) were distinctly higher than in shale-like sediments (mean concentration of 297.3 mg/kg) (STable 1), and  $\text{Zr}$  as well as  $\text{U}$ ,  $\text{Th}$  and others were generally enriched within granite as accessory minerals (e.g., zircon, titanite, monazite, etc.) in which REEs were hosted and enriched (Garçon et al., 2014), it is concluded that REEs in sediments were also contributed from granites distributed in the watershed through weathering. Moreover, the  $\text{Eu}/\text{Eu}^*$  values were less significantly correlated with  $\text{CIA}$  values and  $\text{Si}/\text{Al}$  ratios of the sediments (Fig. 4), and this suggested chemical weathering and hydrological sorting could have less effect on  $\text{Eu}/\text{Eu}^*$  values in sediments. Therefore, the two types of REE patterns (Fig. 3) indicated the lithological sources of REEs, being those from sedimentary rocks and granites in the watershed. More importantly, it is found that accessory minerals such as zircon, titanite and monazite from granites represented an important factor that controlled the distribution and differentiation of REEs in sediments.

However, concentrations of REEs in sediments (with mean  $\sum \text{REE}$  of

318.7 mg/kg) were distinctly higher than those of sedimentary rocks ( $\sum \text{REE} = 170.8$  mg/kg) and granites ( $\sum \text{REE} = 202.7$  mg/kg) (STable 1). It was also noted that the coarser V-shape sediments (as shown by higher mean  $\text{Si}/\text{Al}$  ratio of 4.7) could contain REE concentrations (mean  $\sum \text{REE} = 355.3$  mg/kg) higher than the finer ( $\text{Si}/\text{Al}$  ratio of 3.6) shale-like sediments (mean  $\sum \text{REE} = 290.5$  mg/kg) (STable 1). Correlations of REE concentrations to major elements  $\text{Al}_2\text{O}_3$  (representing clays, e.g., kaolinite),  $\text{Fe}_2\text{O}_3$  (Fe oxides, e.g., hematite),  $\text{CaO}$  (carbonates, e.g., calcite), and  $\text{P}_2\text{O}_5$  (P-bearing minerals, e.g., apatite) were hardly observed in V-shape sediments (Fig. 4, STable 1). All these suggested that there was the additional inputs of REEs probably from anthropogenic sources (e.g., Fiket et al., 2017; Li et al., 2022).

### 3.2.3. BCR speciation and REE anthropogenic sources

The BCR extraction results of selected samples (STable 1) suggested that REEs in sediments (except sample ZZ2-3) were dominated by those in reducible (S2) and oxidizable (S3) fractions, with proportion ranging from 42.0% to 63.0% (S2, reducible) and 9.7% to 28.4% (S3, oxidizable) ( $n = 11$ ) (Fig. S2). That is to say that REEs were hosted mainly in reducible Fe–Mn oxides, and oxidizable sulfide minerals and organic matter in sediments, as observed in Aquia aquifer sediments (Willis and Johannesson, 2011), and Erdenet mining area sediments (Munemoto, et al., 2020). However,  $\sum \text{REE}$  in exchangeable (S1) and residual (S4) fractions were extremely low, ranging from 0.95 to 3.3 and 4.0 to 30.6 (mg/kg) respectively (except sample ZZ2-3), with proportion of  $< 10\%$  (Fig. S2), which was quite different from those observed in many other river sediments (e.g., Song and Choi, 2009; Yan et al., 2022). In order to confirm such a difference of REEs in BCR extractions, the BCR extraction procedure was repeated using the same samples and similar results were obtained. Thus, the BCR extraction results reported here were reproducible, and the very low proportion of REEs in residual fraction (S4) might be due to the REE-host minerals such as zircon, titanite and apatite (STable 1, Fig. 4a and b) that were hard to be dissolved during the three steps of the BCR extraction processes (Marx and Kamber, 2010; Davranche et al., 2011).

Given the low proportion of REEs in residual fraction (S4) and only two samples having REE concentrations of total BCR fractions ( $\text{S1} + \text{S2} + \text{S3} + \text{S4}$ ) ( $\sum \text{REE}$  of 73.9 mg/kg for sample XY17 and 64.6 mg/kg for XY39) comparable with that of analyses of bulk sediments ( $\sum \text{REE}$  of 105.0 mg/kg for XY17 and 94.0 mg/kg for XY39) (STable 1), REE distribution in extracted fractions (S1, S2 and S3) (Fig. 5) could provide important information on sources of REEs in sediments. The NASC-

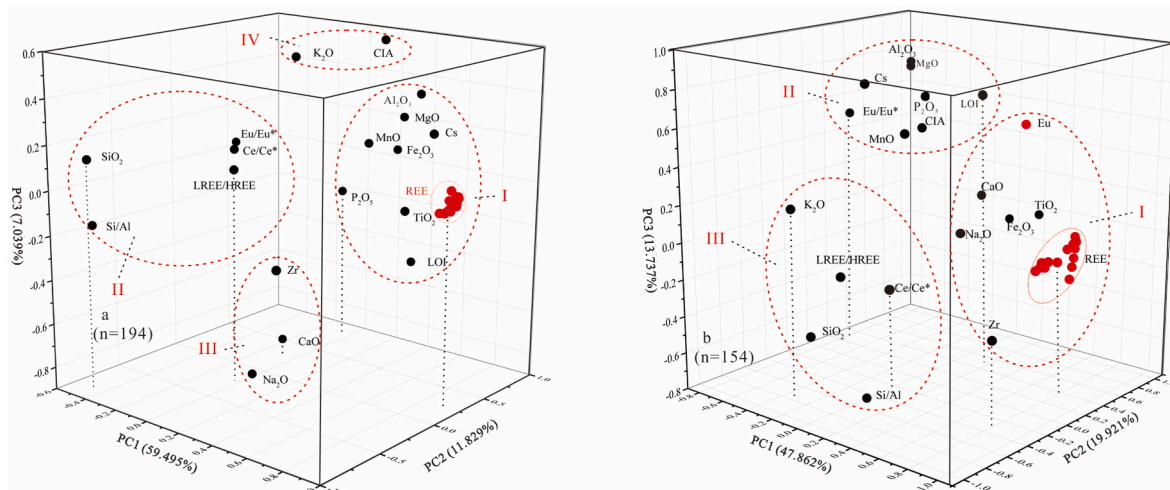


**Fig. 4.** Principal components PC1 vs. PC2 vs. PC3 plots showing element groups and different associations of REEs with major elements in shale-like (a) and Eu depleted V-shape (b) REE sediments. For shale-like sediments, there four groups of elements: Group I, II, III, and IV. REEs were associated with  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{LOI}$ , and  $\text{Cs}$  in group I, and were less associated with  $\text{Eu}/\text{Eu}^*$  in group II,  $\text{Zr}$  in group III and  $\text{CIA}$  in group IV. While, REEs of V-shape sediments were associated with  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ , and  $\text{Zr}$  in group I, and less associated  $\text{Eu}/\text{Eu}^*$  and  $\text{CIA}$  in group II.

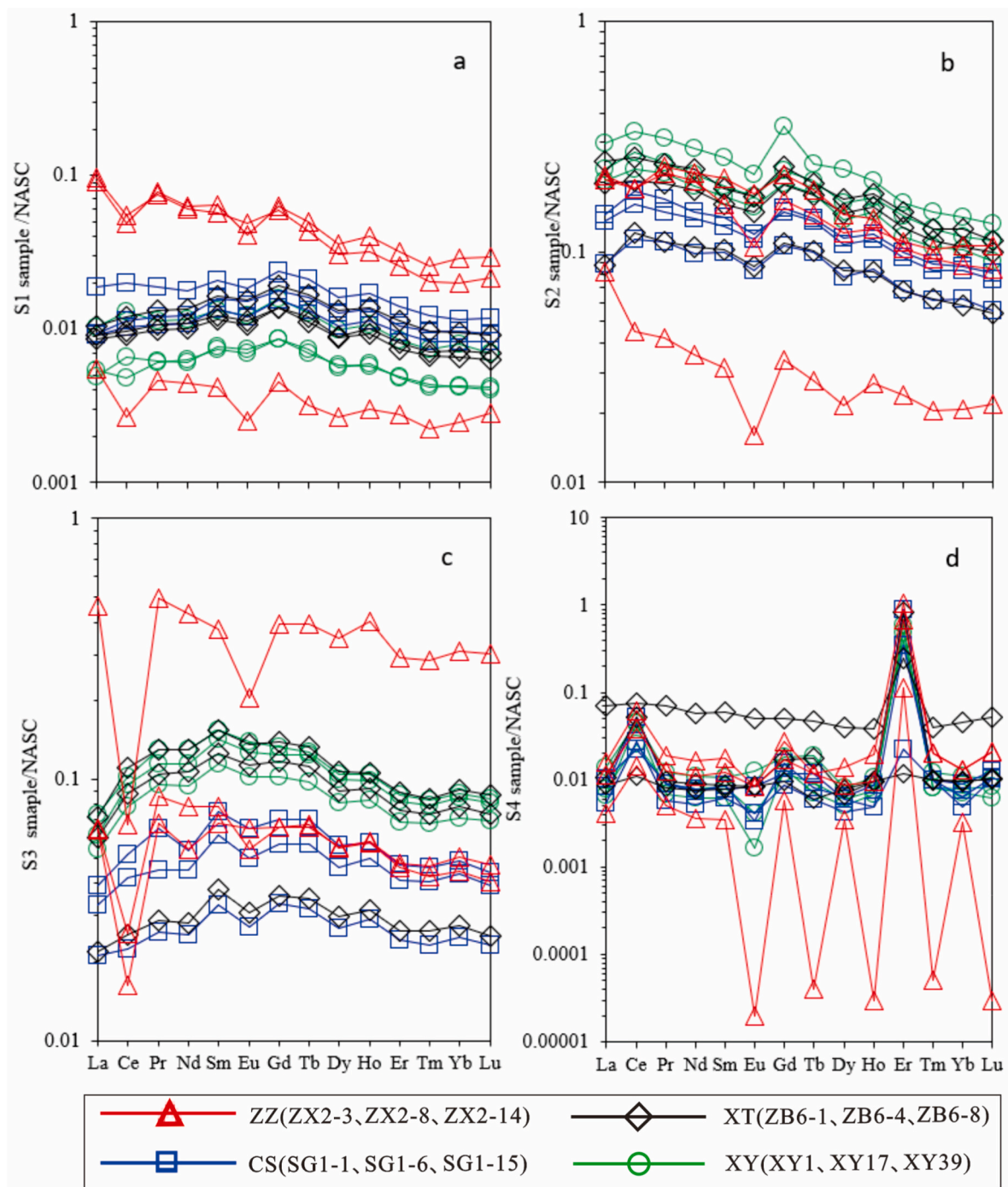


**Fig. 5.** REE distribution patterns in BCR fractions of selected samples from the Xiangjiang River, China. a, b, c and d represent REEs in exchangeable (S1), reducible (S2), oxidizable (S3) and residual (S4) fractions in sediments respectively.

normalized REE patterns for S1, S2 and S3 fractions showed significant enrichment of MREE with concave or 'hat' patterns (Fig. 5a–c), for which enrichment of Gd was observed in S2 and S3 fractions (except sample ZX 2–3, Fig. 5b and c). As MREEs (Gd) could be more effectively sorbed onto Fe–Mn oxide, organic matter and clay when acidic mining discharges were neutralized (Mihajlovic and Rinklebe, 2018) during mixing with the river water, they could be higher enriched in S1, S2 and S3 fractions than other REEs (e.g., Yu et al., 2018; Liu et al., 2021). Ratios of  $(La/Gd)_N$  and  $(La/Sm)_N$  in S1 (0.53 – 0.79 and 0.64 – 0.77 respectively), S2 (0.83 – 1.04 and 0.88 – 1.23 respectively), and S3 (0.49 – 0.61 and 0.43 – 0.54 respectively) (except ZZ sediments) were mostly < 1.0, being similar to that of sulfide-mining discharges (e.g., Morgan et al.,

2012; Delgado et al., 2012) and agricultural phosphate fertilization discharges (e.g., Geagea et al., 2007; Valetich et al., 2022). In addition, negative Ce anomalies in S1 and S3 fractions ( $Ce/Ce^* = 0.26$ ) of ZZ samples (Fig. 5a, c) suggested reductive dissolution of insoluble Ce(IV) to soluble Ce(III) in sediments. This indicated that REEs were from discharges of ore smelting industries, because ore smelting could release reductive dissolution due to sulfide minerals included in smelting processes and ZZ samples were from sites where such industries were once concentrated therein at the Zhuzhou City.

The MREE enrichment in extracted fractions (S1, S2 and S3) of XT sediments (samples ZB6-1, ZB6-4 and ZB6-8) provided information on REE sources from discharges from phosphate fertilizer plants

(Mihajlovic and Rinklebe, 2018; Valetich et al., 2022) since such industries were once concentrated in Zhubugang district of the Xiangtan City where XT sediments were obtained (Fang et al., 2019). The higher REE concentrations in XT samples with the highest in sample ZB5-36 that had  $\sum\text{REE}$  of 774.8 mg/kg (STable 1) also implied REEs contributed from fertilizer plants therein.

The above signatures of anthropogenic REE sources were hidden in bulk sediments probably by mixing with lithological REEs.

### 3.3. REE contamination in sediments

#### 3.3.1. Contamination levels of REEs

REEs have been widely used as environmental tracers of contamination by acid mine drainage (Delgado et al., 2012; Hu et al., 2019; Munemoto et al., 2020), phosphate fertilization (e.g., Möller et al., 2014; Valetich et al., 2022), and hospital discharge (Kulaksız and Bau, 2007; Hatje et al., 2016). However, there are few studies on assessing contamination of REEs themselves in sediments (Benabdelkader et al., 2019). As having reduced knowledge regarding REE toxicology and bioavailability, REE contaminant limit-values in sediments lack a consistent guideline (Lim and Ottosen, 2021). Thus, here REE contamination levels for La > 80 mg/kg, Ce > 100 mg/kg, Nd > 85 mg/kg and Gd > 8.12 mg/kg (Mihajlovic et al., 2019; Adeel et al., 2019) were referred to at first for rating REE contamination in sediments. As there were less than 5.5% samples having La > 80 mg/kg and/or Nd > 85 mg/kg in sediments of this river, the contamination with La and Nd in sediments was insignificant. However, there were 94.2% samples in ZZ, 90.1% in XT, 63.7% in CS, and 72.2% in XY sediments having concentrations of Ce > 100 mg/kg, and 76.9%, 56.1%, 38.5%, and 33.3% of samples respectively having concentrations of Gd > 8.12 mg/kg (STable 1), the contamination with Ce and Gd was significant in sediments. Thus, concentrations of Ce > 100 mg/kg and Gd > 8.12 mg/kg were here referred to as REE contamination levels (Mihajlovic et al., 2019; Adeel et al., 2019).

Based on contamination levels of Ce and Gd, the contamination levels for  $\sum\text{REE}$  could be estimated using the linear regression correlations of Ce concentrations to  $\sum\text{REE}$ , as shown by Eq. (12) and Eq. (13) respectively.

$$\sum\text{REE} = 2.6208 \times \text{Ce} + 12.818 \quad (R^2 = 0.9647) \quad (12)$$

$$\sum\text{REE} = 39.572 \times \text{Gd} - 2.14 \quad (R^2 = 0.9539) \quad (13)$$

The calculated contamination levels for  $\sum\text{REE}$  could be 274.9 mg/kg by Eq. (12) and 319.2 mg/kg by Eq. (13). As more than 90% samples had concentration of Ce > 100 mg/kg, this calculated by using Ce concentration (Eq. (12)) was recommended as contamination level for  $\sum\text{REE}$

(274.9 mg/kg). Then, the contamination levels for  $\sum\text{LREE}$  were estimated to be 252.3 mg/kg, and  $\sum\text{HREE}$  (Y not included) were estimated to be 28.8 mg/kg using the similar methods.

As ratios of  $(\text{La}/\text{Gd})_N$  and  $(\text{La}/\text{Sm})_N$  were mostly >1.0 in bulk sediments, REE ratios of bulk sediments were less informative on REE contamination in sediments since anthropogenic REE signatures were hidden by lithological REE input (Delgado et al., 2012; Munemoto et al., 2020). Thus, REE contamination levels were here recommended as REE indices for identifying and rating REE contamination in sediments.

#### 3.3.2. Distribution of REE contamination

The REE contamination of sediments from Xiangjiang River has seldom been assessed by previous studies (e.g., Mao et al., 2014; Wang et al., 2019b). The  $I_{\text{Geo}}$  values of REEs (STable 1, Fig. 6) showed that REE contamination in XY and CS sediments was less significant because approximately less than 4.4, 5.5, 6.5, 5.5 and 9.9 (%) of samples had a  $I_{\text{Geo}} > 1.0$  for La, Ce, Nd, Gd and Yb respectively. While, there were about 10.6% samples for La, 14.4% for Ce, 6.8% for Nd, 12.9% for Gd and 20.5% for Yb in XT sediments had a  $I_{\text{Geo}} > 1.0$ ; and about 17.3, 23.1, 21.2, 26.9 and 28.7 (%) samples for La, Ce, Nd, Gd and Yb respectively in ZZ sediments had a  $I_{\text{Geo}} > 1.0$ . Thus, ZZ and XT sediments of the river were contaminated with REEs and HREEs in light to moderate degree, with LREEs in light degree ( $0.7 < I_{\text{Geo}} < 2.0$ , Fig. 6).

The  $\text{PLI}_{\text{site}}$  values for REEs in sediments from 20 sampling sites were summarized in Fig. S3. Sediments from ZF, ZU1, XZ5 and ZX2 cores of ZZ sediments; from 2Q, XS, X1Q, X3Q, ZB6, ZB5, XT2 and ZS cores of XT sediments; from JZ4, JZ1 and SG cores of CS sediments; and from QN core of XY sediments had  $\text{PLI}_{\text{site}}$  values > 1.5 and < 2.5, suggesting that sediments were moderately contaminated with REEs (Tomlinson et al., 1980). The  $\text{PLI}_{\text{site}}$  values for REEs in other samples ranged between 0.8 and 1.2, displaying less REE contamination. The averaged  $\text{PLI}_{\text{site}}$  values of REEs in ZZ, XT, CS, and XY sediments decreased in order of  $1.82 > 1.71 > 1.46 > 1.43$  respectively, showing REE contamination degree decreasing significantly from upper river ZZ to downriver XY sediments, being consistent with that identified by  $I_{\text{Geo}}$  index (Fig. 6).

#### 3.3.3. Formation of REE contamination

Up to date, no country has imposed limit-values of REEs in sediments (Lim and Ottosen, 2021), and there is no consensus on REE risk to human health (Hirano and Suzuki, 1996; Lim and Ottosen, 2021). Thus, the formation of REE contamination might result from REEs of both lithological and anthropogenic sources. Generally, the weaker bound REEs from lithological sources might be easily transported away from the weathering rocks by water, and REEs in river water were transported as ions ( $\text{REE}^{3+}$ ), suspended particulates such as clay minerals, Fe–Mn oxides and accessory minerals (e.g., zircon), and organic complexes (e.g., Gong et al., 2009; Mihajlovic and Rinklebe, 2018). As river water of

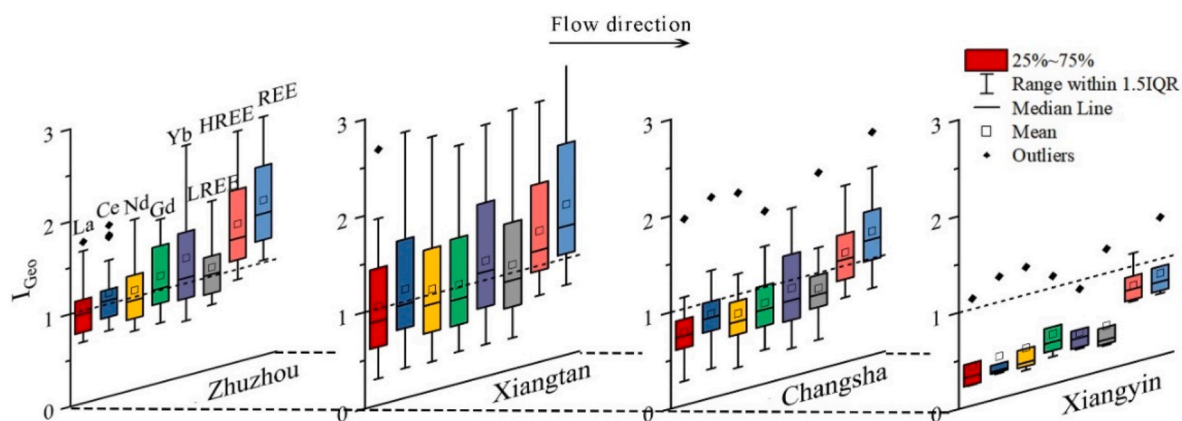


**Fig. 6.** Box-plots of  $I_{\text{Geo}}$  values of La, Ce, Nd, Gd, Yb,  $\sum\text{LREE}$ ,  $\sum\text{HREE}$  and  $\sum\text{REE}$  in ZZ, XT, CS and XY sediments from lower reaches of the Xiangjiang River (China). The  $I_{\text{Geo}}$  values of  $\sum\text{LREE}$ ,  $\sum\text{HREE}$  and  $\sum\text{REE}$  represent the average values of those of individual LREEs, HREEs and REEs respectively.

the lower reaches was alkaline with pH value of 7.2, and usually was under condition of weak hydrodynamics (Peng et al., 2011; Fang et al., 2019), REEs from lithological sources could be sunk by co-precipitating with organic matter and carbonates, absorbing onto clays and amorphous Fe–Mn oxides, and ion exchanging with other metal ions (e.g., Delgado et al., 2012; Mihajlovic and Rinklebe, 2018) due to change of physical chemical conditions (e.g., neutralization) of the aquatic system. The heavy accessory minerals with REEs could be deposited directly when hydrodynamics decreased. While REEs from anthropogenic sources could be sunk quickly because the acidic discharges were neutralized immediately when they were discharged into the alkaline (pH = 7.2) river water from ore smelting industries at Zhuzhou City and P fertilizer plants at Xiangtan City. Thus, the formation processes of REE contamination in sediments of the Xiangjiang River could be summarized in Fig. 7.

#### 4. Conclusions

The results of this study presented concentrations of REEs in bulk sediments and BCR extractions from sediments of lower reaches of the Xiangjiang River (China) to understand the distribution, source and contamination of REEs in river sediments. They support the following conclusions:

- (1) The river sediments were characterized by terrigenous components  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$  and  $\text{P}_2\text{O}_5$ , and contained high concentrations of REEs with mean  $\sum\text{REE}$  of 318.7 mg/kg. These REEs were moderately enriched in upper river sediments, and slightly or less enriched in downriver sediments;
- (2) Sediments displayed two types of REE distribution patterns: the shale-like and Eu-depleted V-shape REE patterns, which suggested that sediment REEs were lithologically contributed from sedimentary rocks and granites in the watershed through weathering. The REE enrichment feature in sediments and the BCR extraction results suggested that there was additional input of REEs from anthropogenic sources, and these anthropogenic REEs were from discharges dispersed from ore smelting industries at the Zhuzhou city and from phosphate fertilizer plants at the Xiangtan city;
- (3) REEs in sediments were hosted mainly in Fe–Mn oxides and sulfide and organic matters, and they were characterized by

enrichment with MREE relative to LREE and HREE. The distribution and differentiation of REEs in sediments were controlled by clay minerals, Fe–Mn oxides, organic matters and finer grains; and by accessory minerals (e.g., zircon) from granites through weathering;

- (4) Sediments were contaminated with REEs in moderate degree in upper river area, and REE contamination was formed by superimposing anthropogenic REEs onto lithological residues. The contamination levels of  $\text{Ce} > 100 \text{ mg/kg}$ ,  $\text{Gd} > 8.12 \text{ mg/kg}$ ,  $\sum\text{REE} > 274.9 \text{ mg/kg}$ ,  $\sum\text{LREE} > 252.3 \text{ mg/kg}$  and  $\sum\text{HREE} > 28.8 \text{ mg/kg}$  were here recommended as indices for identifying and rating the REE contamination in this mining impacted river.

#### Author statement

All authors of this research paper have directly participated in the planning, execution, or analysis of the study. I am sure that the manuscript is original, not under consideration for publication elsewhere right now, and that all authors are aware of the submission and agree to its publication.

#### Authorship contribution

Xiaohong Fang (First Author): Conceptualization, Field investigation, Lab analysis, Figure design, Formal analysis, and Writing original draft; Bo Peng (Corresponding Author): Whole research processes, Funding acquisition, Supervision, Data Curation, Writing and reviewing; Xintong Guo: Data treatment, Figure design; Sicheng Wu: Figure design, Data curation; Shurong Xie: Data Curation, Cooperation in lab analysis; Jing Wu: Data curation, Figure design; Xia Yang: Data curation, Figure design; Haisheng Chen: Data curation, Figure design; Yanan Dai: Field work, Part of lab work, Data curation.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Bo Peng reports financial support was provided by Construction Program for First-Class Disciplines (Geography) of Hunan Province. Bo Peng reports a relationship with Hunan Normal University that includes:

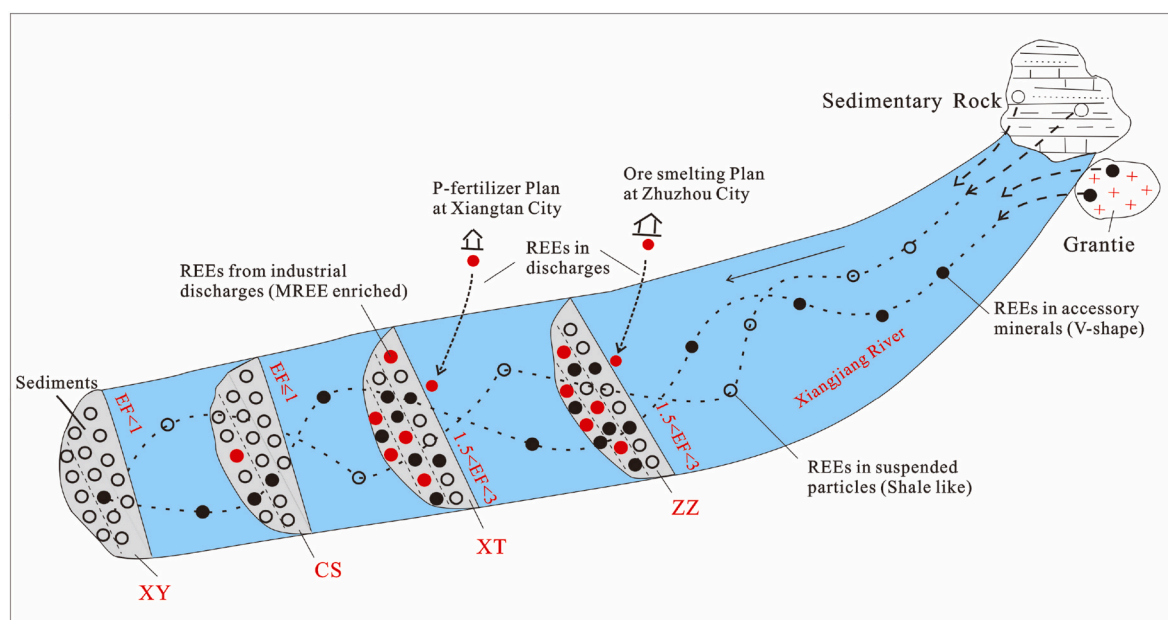


Fig. 7. Sketch showing formation processes of REE contamination in bed sediments of the Xiangjiang River (China). For details see the text.

consulting or advisory, employment, and funding grants. Bo Peng has patent Construction Program of Hunan Province issued to First-Class Disciplines (Geography). The Innovative Research Team in Higher Educational Institutions of Hunan Province (2014), China; the Scientific Research Fund of Hunan Provincial Education Department (18A012 to B Peng, 21A0433 to X H Fang); and grants (Grant No. 2022JJ30030 to B Peng, 2022JJ40014 to XH Fang) from Department of Science and Technology of Hunan province (China).

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2023.122384>.

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