Anthropogenic Gd in urban river water: A case study in Guiyang, SW China

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As an emerging contaminant, rare earth elements (REEs) are becoming an environmental concern, especially in Chinese cities. This study investigated the distribution of REEs in river water and tap water samples in Guiyang, Southwest China. In all water samples, the concentrations of total dissolved REE (\(\sum\text{REE}\)) ranged from 15.1 to 53.3 ng L\(^{-1}\), with the heavy rare earth elements enriched than the light rare earth elements. Most of the water samples showed significant positive Gd anomalies, with the highest abnormal value calculated to be 29.23. The main reason for the positive Gd anomalies was found to be the release of medical wastewaters containing Gadopentetic acids (Gd-DTPA). Overall, anthropogenic Gd could contributed >60% of total Gd in river waters and tap waters. Because Gd-DTPA is commonly used in large Chinese hospitals, the results of this study implied that anthropogenic Gd release could be common in Chinese cities.

Keywords: Rare earth elements, Gd anomaly, Urban river water, Guiyang

1. Introduction

Rare earth elements (REEs) include the 15 lanthanide elements (atomic numbers ranging from 57 to 71) with extremely similar geochemical behaviors and combination rules in the geochemical processes (Cao et al., 2001; Ogata and Terakado, 2006; Tang et al., 2013; Gwenzi et al., 2018). Although the total content of REEs accounts for only 0.0153% of Earth’s crust, REEs are naturally enriched in phosphate minerals as well, which are widely used as agricultural fertilizers (Haley et al., 1965; Wang et al., 1998; Hu and Jin, 2000; Xiao, 2005). REEs have been widely used in industry and medical treatment (Wang et al., 1998; Xiao, 2005). With the increasing use of REEs, anthropogenic inputs will release elevated REEs to the environment. The REEs are mildy toxic and can cause adverse effects on human health (Liu and Qi, 2016). Excessive consumption of REEs may cause blood biochemical indices abnormality and cholesterol increase (Zhang et al., 2000). Consequently, the release of excess REEs becomes an environmental threat.

Many researchers studied the natural sources, distribution, and migration of REEs in watershed systems (Yang et al., 2002; Munksgaard et al., 2003; Xu and Han, 2009; Mao et al., 2011). Previous research also used REEs as an indicator of the provenance of sediments in river systems or as a proxy to understand climate/ocean changes by traditional methods including neutron activation analysis method, isotopic mass spectrometry, and plasma spectrum analysis, and so on (Fleet, 1984; Johannesson et al., 1997; Pattan et al., 2005; Kylander et al., 2007; Singh, 2009). With the improvement of detection technology, inductively coupled plasma mass spectrometry (ICP-MS) has become a general analysis and measurement technology for REEs at present (Wang and Liang, 2016; Wang et al., 2019). Through the separation and enrichment, dissolved REEs can further be monitored as an effective tracer and inversion tool because its sensitivity of environmental changes (Matherny and Macejko, 1991; Lin et al., 2017). There are also many scholars on the Yangtze River, Yellow River, and other systems of systematic research and made significant progress, such as the distribution and migration of REEs in different areas, water system evolution, weathering process, and their source (Yang et al., 2002; Munksgaard et al., 2003; Xu and Han, 2009; Mao et al., 2011). Moreover, REEs can be directly used to understand anthropogenic activities, for example, to trace anthropogenic REEs in the environment.

The first anthropogenic REEs anomaly was observed in Germany, 1996 (Bau and Dulski, 1996). After that, anthropogenic REE anomalies were reported in many densely populated areas, with Gd anomalies observed in developed medical areas (Müller et al., 2000; Sholkovitz and Szymczak, 2000; Song et al., 2017). The main source of Gd anomaly is...
Gadopentetic acids (Gd-DTPA), which is used in magnetic resonance imaging (MRI) in medical diagnostics (Bau and Dulski, 1996). During the MRI diagnostic process, a 70 kg adult needs to be injected the Gd-DTPA with 15 mL, and almost all of the Gd excreted outside the body in a few hours (Möller et al., 2002). As Gd-DTPA is unreactive with other substances, it is difficult to be metabolized by the human body or to be removed in wastewater treatment plants (WWTPs; Möller et al., 2002). It’s worth mentioning that, except for the use of REEs as a source tracer of natural water and sediment (Kamber et al., 2005; Liu et al., 2011), anthropogenic Gd has also been used to trace the source of wastewater in rivers and groundwater, especially in cities that have developed medical systems (Zhang et al., 1998; Möller et al., 2000; Hissler et al., 2014). China experienced rapid urbanization in the last decades, resulting in a large lease of REEs from various anthropogenic activities. However, the exact sources of anthropogenic REEs remain not well understood. This study investigated the distribution of Gd in the Nanming River, Guiyang, Southwest (SW) China. As a representative of ordinary Chinese cities, Guiyang has a population of >4.84 million. There are 130 large hospitals in Guiyang city, with MRI commonly used.

To understand the source of anthropogenic Gd in the Nanming River, the REEs content of water samples were thoroughly measured by ICP-MS. The REEs results, together with the distribution of WWTPs and hospitals around rivers, enabled us to (1) identify the major sources of REEs in the Nanming river and (2) quantify the anthropogenic contribution of fluvial dissolved Gd.

2. Materials and methods
2.1. Study area
The Nanming River is the main receiving river of urban effluent in Guiyang, the capital of Guizhou province, SW China (Figure 1). The area has a subtropical monsoon humid climate, with an average annual temperature of 14°C–18°C and average annual precipitation of 1,100–1,300 mm (Li et al., 2012; Han et al., 2019; Zeng et al., 2020). The rainy season is from May to October and the dry season is from November to April (Zeng and Han, 2021). As the Qingshui River headstream of the Wujiang River system in the Yangtze River basin, the Nanming River is 118 km long, with 11 km passing through Guiyang. Along the way of the Nanming River in Guiyang, there are 28 hospitals, 4 tap water plants, and 3 large WWTPs. The hospitals are concentrated in the central city area, while the 3 WWTPs are outside the city. A large amount of domestic and medical wastewater is discharged from these WWTPs every year.

2.2. Sampling and analysis
Samples were collected in the dry season (March 2019), during which the anthropogenic REEs must be weakly affected by dilution due to the small runoff volume (Chen et al., 2001). Therefore, the variations of REEs concentrations are intensively influenced by human inputs and more reflective of the point sources inputs. Thirteen surface water and 3 outlets of WWTPs samples (10 cm under the surface) were collected from the Nanming River, and a total of 4 tap water samples were collected from
different sites in Guiyang. The sampling sites are shown in Figure 1.

Polyethylene bottles, precleaned with Milli-Q water (18.2 MΩ cm), were used to collect and preserve the samples. Electrical conductivity, pH, and temperature were measured at each sampling site, using a WTW Multi 3430 meter (WTW Company, Weilheim, Upper Bavaria, Germany). Samples were filtered by the cellulose-acetate membrane filter (0.22 μm, Whatman) in the field and then stored in precleaned polyethylene bottles. Purified HNO₃ was used to acidify samples to pH < 2 for conservation (Zhang et al., 2019).

The samples were analyzed at the Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. Chloride was analyzed by an ion chromatography system (DIONEX, ICS-1100, Sunnyvale, CA). Before determination, samples were spiked with Rhodium (Rh) as an internal standard. The concentrations of REEs were measured using an ICP-MS (NexION300X, Perkin Elmer, Waltham, MA), following a previously reported method (Smith and Liu, 2018). This method yielded an uncertainty of better than ± 3% relative standard deviation for all REEs, based on the measurement of SLRS-5 standard from the National Research Council Canada (Heimburger et al., 2013; Yeghicheyan et al., 2013). All samples showed high recoveries for the spiked Rh (97.5%–103.5%).

2.3. Calculation

Based on the atomic weights and radii, REEs are usually divided into 2 groups, including light rare earth elements (LREEs; La to Eu) and heavy rare earth elements (HREEs; Gd to Lu) (Gammons et al., 2005). To analyze the patterns of REEs, all REEs concentrations were normalized to the Post-Archaean Australian Shale (PAAS; Taylor et al., 1981). In this study, the third-order polynomial fitting method with the PAAS-normalized REEs pattern was chosen to calculate the REEs anomalies (Hatje et al., 2016). The ratios of CeSN/Ce*SN, EuSN/Eu*SN, and GdSN/Gd*SN were used to calculate the REEs anomalies (Hatje et al., 2016). The ratios of CeSN/Ce*SN, EuSN/Eu*SN, and GdSN/Gd*SN were used to calculate the REEs anomalies (Hatje et al., 2016).

$$Gd_{Anth} = \left( \frac{Gd_{SN}}{Gd_{PAAS}} \right) \times Gd_{PAAS}.$$  (6)

Positive or negative REEs anomalies are regarded as values of higher or lower than 1, respectively.

3. Results and discussion

3.1. Concentrations of ∑REEs

The REEs results in our samples are presented in Table 1 and their distributions are plotted in Figure 2. Notably, samples from WWTPs (e.g., NM-1, NM-6) and areas downstream displayed significantly higher ∑REE concentrations than river samples collected upstream from WWTPs (e.g., XH-2, NM-5), suggesting WWTPs were a potential source of anthropogenic REEs in the Nanming River.

The concentrations of ∑REEs of river water samples ranged from 15.07 ng L⁻¹ (HX-1, Huaxi Reservoir) to 53.33 ng L⁻¹ (XH-1, downstream of the Huaxi WWTP). Generally, urban samples (NM-1, NM-2, NM-3) displayed higher REEs levels than those collected from rivers before they flowed through the city (HX-1, HX-2, and HX-3) and the suburban sample (SHX), which was collected from an area with a smaller population density. The concentrations of ∑REEs were found to range from 40 to 60 μg L⁻¹ in the Wujiang River, while the average concentration of dissolved ∑REEs was 78.45 μg L⁻¹ in the upstream portion of the Wujiang River (Han et al., 2009). The Nanming River, who shares a similar environment, also exhibits slightly lower ∑REEs concentrations, indicating that there may be similar factors influencing the presence of REEs in the Nanming River.

In general, colloids and particles have a negative charge and adsorb cations in the water. A large proportion of REEs in the river existed in alkaline water in the form of complex ions (Goldstein and Jacobsen, 1988). As the pH of the water increases, the negative electricity of the colloids will increase, and the adsorption of the colloids to REEs will be enhanced (Zhu et al., 2005). Therefore, the content of dissolved REEs in alkaline water is low. The high pH in the Nanming River is another reason for the low ∑REE levels, as studies have shown that a higher pH would decrease ∑REEs contents in several rivers (Byrne and Li, 1995; Jiang and Ji, 2012).

The concentrations of ∑REEs in tap water samples ranged from 11.87 ng L⁻¹ to 33.67 ng L⁻¹ and varied among sites (Figure 2c). These differences in tap water
REEs contents may have been due to different water supplies. The REE concentrations of tap water plant in the northern suburbs (NJSC) were several times higher than those of other tap water plants. The source of the NJSC facility is the Aha Reservoir, where positive Gd anomalies have been reported in an inflow river (Zhang et al., 2019), while the water sources of the other tap water plants are far from urban areas without distinct anthropogenic influences. Delivery processes may also have contributed to the noticeable variability in REE concentrations among the 4 investigated tap water plants. Furthermore, the different concentrations of REE might be correlated with the flow of water. Additionally, the river material may be recharged to groundwater through bank filtration, which would have an impact on the chemical composition of raw water (Schmidt et al., 2019). This phenomenon has also been found in Germany and Berlin (Birka et al., 2016; Schmidt et al., 2019).

The HREEs content of river, tap, and WWTP water ranged within 5.42–42.68 ng L⁻¹, 2.12–4.19 ng L⁻¹, and 19.20–107.09 ng L⁻¹, respectively, representing 31%–87%, 11%–34%, and 36%–87% of the ∑REEs. The high fractions of HREEs in our samples were mainly related to the high Gd concentration, which accounted for 22%–92% of the HREEs. The concentrations of HREEs and Gd followed the linear relation: HREE = 1.0074 × Gd + 7.4978 (R² = 0.911, P < 0.01). The high HREEs in the Nanming River may be also be caused by a large amount of domestic effluent in the Nanming River, which results in high organic matter concentrations and converts the HREEs in suspended particulate matter (SPM) to the soluble state (Wang et al., 2003; Zeng and Han, 2020). Organic matter is honeycombed with a large surface area and has a large number of coordination groups on its surface, resulting in strong electrical adsorption capacity for heavy metal ions (Meng and Fu, 2006). The content of dissolved REEs is largely controlled by organic colloids, which could increase the solubility of REEs (Banner et al., 1989; Perret et al., 1994). Additionally, HREEs are more likely to form complex soluble complexes in water than LREEs (Zhong and Mucci, 1995). The organic complexation of HREEs is stronger than that of LREEs, and the stability of HREE-humic acid is greater than that of LREE-humic acid (Byrne and Li, 1995; Astroem and Corin, 2003).

### Table 1. Concentrations of rare earth elements and Cl⁻, pH, and electric conductivity (EC) in Nanming River and 4 tap water plants. DOI: https://doi.org/10.1525/elementa.2020.00147.t1

<table>
<thead>
<tr>
<th>Sample</th>
<th>La (ng/L)</th>
<th>Ce (ng/L)</th>
<th>Pr (ng/L)</th>
<th>Nd (ng/L)</th>
<th>Sm (ng/L)</th>
<th>Eu (ng/L)</th>
<th>Gd (ng/L)</th>
<th>Tb (ng/L)</th>
<th>Dy (ng/L)</th>
<th>Ho (ng/L)</th>
<th>Er (ng/L)</th>
<th>Tm (ng/L)</th>
<th>Yb (ng/L)</th>
<th>Lu (ng/L)</th>
<th>pH</th>
<th>EC (µS/cm)</th>
<th>Cl⁻ (mg/L)</th>
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</thead>
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<tr>
<td>NM-1</td>
<td>1.64</td>
<td>1.01</td>
<td>0.69</td>
<td>3.05</td>
<td>7.28</td>
<td>2.53</td>
<td>7.83</td>
<td>0.34</td>
<td>2.23</td>
<td>1.26</td>
<td>2.72</td>
<td>0.66</td>
<td>4.49</td>
<td>0.88</td>
<td>7.82</td>
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<td>15.08</td>
</tr>
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<td>0.76</td>
<td>4.39</td>
<td>2.49</td>
<td>4.3</td>
<td>2.06</td>
<td>1.36</td>
<td>23.71</td>
<td>0.34</td>
<td>0.96</td>
<td>0.07</td>
<td>0.64</td>
<td>0.16</td>
<td>12.9</td>
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<td>0.93</td>
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<td>2.43</td>
<td>4.71</td>
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<td>2.12</td>
<td>3.51</td>
<td>2.71</td>
<td>4.2</td>
<td>0.2</td>
<td>1.17</td>
<td>0.57</td>
<td>1.28</td>
<td>0.38</td>
<td>2.99</td>
<td>0.64</td>
<td>7.96</td>
<td>444</td>
<td>14.86</td>
</tr>
<tr>
<td>NM-5</td>
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<td>0.78</td>
<td>0.85</td>
<td>1.37</td>
<td>3.9</td>
<td>1.53</td>
<td>6.81</td>
<td>0.21</td>
<td>0.78</td>
<td>0.3</td>
<td>1.1</td>
<td>0.39</td>
<td>2.2</td>
<td>0.48</td>
<td>7.92</td>
<td>431</td>
<td>14.05</td>
</tr>
<tr>
<td>SHX</td>
<td>1.28</td>
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<td>0.71</td>
<td>0.76</td>
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<td>3.8</td>
<td>3.94</td>
<td>0.49</td>
<td>0.71</td>
<td>0.5</td>
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<td>0.4</td>
<td>1.26</td>
<td>0.41</td>
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<td>1.72</td>
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<td>1.59</td>
<td>30.27</td>
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<td>0.67</td>
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<td>2.04</td>
<td>20.61</td>
<td>0.4</td>
<td>1.8</td>
<td>0.82</td>
<td>2.16</td>
<td>0.78</td>
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<td>8.05</td>
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<td>4.94</td>
<td>3.49</td>
<td>8.3</td>
<td>0.28</td>
<td>1.8</td>
<td>0.67</td>
<td>2.82</td>
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<td>4.64</td>
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<tr>
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<td>0.54</td>
<td>1.17</td>
<td>1.94</td>
<td>2.05</td>
<td>0.88</td>
<td>0.15</td>
<td>0.41</td>
<td>0.2</td>
<td>0.53</td>
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<td>NJSC</td>
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<td>3.86</td>
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<td>3.07</td>
<td>6.18</td>
<td>0.22</td>
<td>1.38</td>
<td>0.32</td>
<td>0.6</td>
<td>0.14</td>
<td>0.48</td>
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<td>XJSC</td>
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<td>5.08</td>
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<td>2.07</td>
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<td>2.46</td>
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<td>0.44</td>
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<td>0.45</td>
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<td>0.09</td>
<td>0.37</td>
<td>0.14</td>
<td>0.31</td>
<td>0.16</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

HX = Huaxi River; XH = Xiaohuang River; NM = Nanming River; SX = Shixi River; SHX = Wenquan Road; DJSC = tap water plant in the eastern suburbs; NJSC = tap water plant in the northern suburbs; XJSC = tap water plant in the western suburbs; BJSC = tap water plant in the southern suburbs.
Moreover, samples of WWTPs water had pH values of 7.8–8.6, and LREEs are more easily adsorbed and precipitated by colloids in alkaline water (Wang et al., 1995; Jiang and Ji, 2012).

3.2. The PAAS-normalized REE pattern

The PAAS-normalized REE distribution patterns of 16 samples in the mainstream are presented in Figure 3, which shows the enrichment of HREEs relative to LREEs. The ratio of (La/Yb)\textsubscript{SN} is often used to indicate the fractionation between LREEs and HREEs (Sholkovitz et al., 1994; Mihajlovic et al., 2019). As shown in Table 2, all of the (La/Yb)\textsubscript{SN} in this study showed ratios of <1 (0.02–0.12) in the present study, which can be explained by the complexations of REEs in the Wujiang River system. The complex of REE in the study area location is dominated by REE-carbonate ions, and HREEs preferentially complex with carbonate ions, sulfate, and organic ligands in alkaline aquatic systems (Elderfield, 1988; Johannesson et al., 1996a; Johannesson et al., 1996b; Tang and Johannesson, 2003; Han and Liu, 2004). The \( \sum \)HREEs concentration downstream of the Xinzhuang WWTP (NM-6) was more than double that of the concentration upstream (NM-5) of the facility (Figure 2a). Wastewater from Guiyang is mainly discarded into the Nanming River, resulting in a large release of organic matter. Because organic matter is adsorbed onto the particulate matter, its presence can increase the adsorption capacity of SPM, and LREEs tend to precipitate because of their preferential adsorption (Goldstein and Jacobsen, 1988). Therefore, these findings suggest that wastewater discharge played an important role in controlling the fractionation of REEs in the Nanming River.

3.3. Ce and Eu anomalies

The Ce\textsubscript{SN}/Ce\textsuperscript{*}\textsubscript{SN} ratios of our samples are presented in Table 2. All of samples showed negative Ce anomalies (0.06–0.55), and the Ce\textsubscript{SN}/Ce\textsuperscript{*}\textsubscript{SN} gradually increased from upstream to downstream. During redox reactions, the Ce valence states usually change (Elderfield, 1988; Feng, 2010). The Nanming River has alkaline and oxidation conditions. Under such conditions, Ce\textsuperscript{3+} is easily oxidized to Ce\textsuperscript{4+} to form less soluble CeO\textsubscript{2}, which further absorbs to Fe-Mn oxides or other substances (Braun et al., 2018), thereby causing negative Ce anomalies in the river. Indeed, negative Ce anomalies have been observed in many rivers in Guizhou Province, including the Xijiang, Youyu, Baiyan, and Jinzhong rivers, and are considered to be affected by local rock weathering and redox conditions in aquatic environments (Han et al., 2009; Zhang et al., 2019). Wang et al. (2013) observed a similar phenomenon in Aha and Hongfeng Lakes in Guiyang City and demonstrated that Ce anomalies in the lake and river were dominated by redox reactions with Mn. Thus, we suggest that the significant negative Ce anomalies observed were mainly derived from natural sources.

Our samples showed positive Eu anomalies, with the Eu\textsubscript{SN}/Eu\textsuperscript{*}\textsubscript{SN} values varying from 5.85 to 16.18 (Table 2). Positive Eu anomalies in water samples have mainly been attributed to natural origins (Zhang et al., 2019). According to the previous studies, there are slight positive Eu anomalies founded in the natural rivers in Guizhou.
Province. Jiang and Ji (2012) found an Eu/SN/Eu*SN of 0.9–1.2 in multiple rivers in central Guizhou Province. Wang et al. (2013) did not find positive Eu anomalies in Hongfeng Lake, Aha Lake, and their tributaries. However, positive Eu anomalies usually occur in regions that have been affected by human activities (especially medically developed cities) like Sakai River (Itoh et al., 2017) and Cotonou’s Watershed (Atinkahoun et al., 2020). In addition to natural sources, anthropogenic activities may contribute to these anomalies. Given that Eu has been widely used as an activator for the barium fluoride in X-ray sensitizing screens for medical applications (Xiao, 2005), medical wastewater discharge might be a potential source of the elevated Eu concentrations that were observed in the Nanming River.

3.4. Gd anomalies and anthropogenic Gd contribution

The Gd/SN/Gd*/SN ratios are shown in Table 2, and their spatial variation is shown in Figure 4. The values ranged from 0.70 to 29.23. Moreover, all of the river samples displayed positive Gd anomalies, except for HX-1. In general, the enrichment of Gd did not occur in natural rivers (Hannigan and Sholkovitz, 2001; Leybourne and Johannesson, 2008). Therefore, the significant positive Gd anomalies are likely related to local anthropogenic activities such as urban domestic emissions and industrial and agricultural emissions rather than to natural sources. As shown in Figure 4b, anthropogenic Gd was the main source of Gd in the Nanming River. Anthropogenic Gd (GdAnth.) was found to increase slightly from upstream to downstream, but to sharply rise to 29.13 ng L⁻¹ in NM-6, which received effluent from WWTPs. When compared with the concentrations of Gd in other urban rivers located in metropolitan areas such as the Rhine River (mean: 41.35 ng L⁻¹; Kulaksız and Bau, 2011), San Francisco Bay (mean: 171.40 ng L⁻¹; Hatje et al., 2016), and Han River (mean: 110.67 ng L⁻¹; Song et al., 2017), the concentrations of Gd in the Nanming River (mean: 10.9 ng L⁻¹) are lower.

Previous studies have shown that the main cause of Gd anomalies in river waters was the use of Gd-DTPA contrast agents for MRI in hospitals (Rabiet et al., 2009; Song et al., 2017). When patients are injected with Gd-DTPA contrasting agents during MRI examinations, 80% of the injected reagent is excreted in its original form (Lerat-Hardy et al., 2019). Generally, the excrement of patients is not defined as medical waste and directly enters municipal WWTPs as domestic wastewater (including daily wastewater of resident and hospital domestic wastewater). However, the Gd-DTPA in wastewater also mostly remained after treatment by WWTPs because of the excellent stability and water solubility of Gd-DTPA (Møller et al., 2003; Hatje et al., 2016).

Moreover, Møller et al. (2002) illustrated that hospital discharged Gd-DTPA could account for more than 95% of the total Gd in some river water samples (Møller et al., 2002). Large hospitals in Guiyang are mostly located in...
urban areas, and the positive Gd anomalies in urban area samples were significantly higher than in samples collected from rivers before they entered urban areas (Figure 4a). A detailed analysis of our data revealed that urban sites with high Gd anomalies were closely related to hospitals. For instance, samples from WWTP outlets (NM-1, NM-6) having WWTPs discharge at their upstream (XH-1 and SX-1) exhibit high \((\text{GdSN}/\text{Gd*SN})\) values. Moreover, the Gd concentrations in rivers always increased after WWTPs discharge, which was consistent with the results of previous studies (Morteani et al., 2006). Furthermore, the ratios of \(\text{Gd}/\sum \text{REEs} \) exceeded 30% in almost all samples and exceeded 60% at 3 sites (XH-1, XH-2, and NM-6). Taken together, these findings indicated that the positive Gd anomaly observed in river water in this study was related to the distribution of WWTPs which release medical effluent.

Chloride (Cl\(^-\)) is an inorganic ligand that has a great influence on the behavior of Gd in water, and chloride complexes of Gd are highly soluble (Byrne and Sholkovitz, 1996; Wells and Wells, 2001). The highest contents of Cl\(^-\) and Gd in the Nanming River were detected at the 2 WWTPs outlet and downstream of the Huaxi WWTP (XH-1, Cl\(^-\) = 40.9 mg/L, Gd = 35.42 ng/L). Moreover, the concentrations of Gd and Cl\(^-\) gradually decrease following the direction of the river. However, the concentrations of Cl\(^-\) and Gd at the Xiaohe WWTP outfall (NM-1) were not remarkably high, similar as the contents of samples collected from portions of the river in the central part of the city (NM-2 and NM-3). Comparison of the Gd concentrations of XH-1, XH-2, and NM-1, which are speculated to contain higher Gd concentrations discharged from the Huaxi WWTP, exert a vital influence. Furthermore, comparisons of the Gd concentrations in the

### Table 2. The elements anomalies of the samples in Nanming River and 4 tap water plants. DOI: https://doi.org/10.1525/elementa.2020.00147.t2

| Sample | \(\sum \text{REE} \) | LREE | HREE | La/Yb | Ce/Ce\(^*\) | Eu/Eu\(^*\) | Gd/Gd\(^*\) | Gd\(_{\text{Anthr.}}\) | Gd\(_{\text{Anthr.}}\)(%\(^*) | 
|--------|----------------|------|-------|--------|-------------|------------|--------------|----------------|----------------|----------------|
| HX-1   | 15.07          | 9.66 | 5.42  | 0.12   | 0.54        | 9.33       | 0.7          | —              | —              |
| HX-2   | 21.1           | 13.81 | 7.29  | 0.09   | 0.55        | 9.34       | 1.25         | 0.26           | 12.22          |
| XH-1   | 53.33          | 10.64 | 42.68 | 0.02   | 0.49        | 5.85       | 18.07        | 33.26          | 93.91          |
| HX-3   | 20.69          | 14.38 | 6.32  | 0.11   | 0.44        | 12.19      | 1.2          | 0.11           | 8.05           |
| XH-2   | 34.3           | 6.93 | 27.36 | 0.05   | 0.2         | 8.31       | 15.54        | 22.03          | 92.92          |
| NM-1   | 36.61          | 16.2 | 20.41 | 0.03   | 0.22        | 7.78       | 4.43         | 5.89           | 75.18          |
| NM-2   | 24.36          | 12.77 | 11.59 | 0.05   | 0.17        | 10.36      | 2.78         | 1.89           | 60.44          |
| SX-1   | 36.03          | 12.62 | 23.41 | 0.03   | 0.35        | 9.11       | 6.34         | 8.98           | 82.65          |
| SX-2   | 39.54          | 16.59 | 22.94 | 0.05   | 0.24        | 14.27      | 6.59         | 8.28           | 83.30          |
| NM-3   | 20             | 9.82 | 10.16 | 0.04   | 0.3         | 11.87      | 3.91         | 3.38           | 71.85          |
| NM-4   | 22.98          | 11.55 | 11.43 | 0.03   | 0.23        | 16.18      | 4.2          | 3.1            | 73.83          |
| NM-5   | 22.25          | 9.96 | 12.27 | 0.05   | 0.16        | 8.38       | 6.42         | 5.64           | 82.87          |
| SHX    | 19.35          | 11.17 | 8.17  | 0.07   | 0.19        | 15.87      | 1.79         | 1.52           | 38.50          |
| NM-6   | 43.71          | 8.43 | 35.27 | 0.06   | 0.1         | 11.16      | 29.23        | 29.13          | 96.42          |
| NM-7   | 44.18          | 12.72 | 31.44 | 0.04   | 0.11        | 8.51       | 11.1         | 18.57          | 90.09          |
| NM-8   | 34.99          | 15.42 | 19.56 | 0.04   | 0.06        | 14.83      | 5.93         | 6.76           | 81.44          |
| DJSC   | 11.87          | 7.77 | 4.09  | 0.07   | 0.25        | 20.03      | 1.23         | 0.09           | 10.78          |
| NJSC   | 33.67          | 24.15 | 9.53  | 0.53   | 0.76        | 13.71      | 5.3          | 4.9            | 79.23          |
| XJSC   | 21.54          | 19.09 | 2.45  | 0.78   | 0.77        | 13.38      | 0.81         | —              | —              |
| BJSC   | 13.38          | 11.78 | 2.12  | 0.33   | 0.33        | 14.76      | 0.78         | —              | —              |

HREE = heavy rare earth elements; LREE = light rare earth elements; REE = rare earth elements; HX = Huaxi River; XH = Xiaohuang River; NM = Nanming River; SX = Shixi River; SHX = Wenquan Road; DJSC = tap water plant in the eastern suburbs; NJSC = tap water plant in the northern suburbs; XJSC = tap water plant in the western suburbs; BJSC = tap water plant in the southern suburbs.

\(a\) \(\text{CeSN}/\text{Ce*SN} = \text{CeSN}/(\text{LaSN} \times \text{PrSN})^{0.5}\) (Section 2.2).

\(b\) \(\text{EuSN}/\text{Eu*SN} = \text{EuSN}/(\text{SmSN}^{0.67} + \text{TbSN}^{0.33})\) (Section 2.2).

\(c\) \(\text{GdSN}/\text{Gd*SN} = \text{GdSN}/(0.33\text{SmSN} + 0.47\text{TbSN})\) (Section 2.2).

\(d\) \(\text{Gd}_{\text{Anthr.}} = (\text{Gd}_{\text{Anthr.}}/\text{Gd}_{\text{Measured}}) \times 100\%\) (Section 2.2).

\(e\) \(\text{Gd}_{\text{Anthr.}} = \text{Gd}_{\text{Measured}} - \text{Gd}^*\) (Section 2.2).
Xiaohuang river (XH-1 and XH-2), the Huaxi river (HX-1, HX-2, and HX-3), and NM-1 revealed that the concentration of Gd in NM-1 (7.83 ng/L) was higher than in HX-1 (1.22 ng/L), HX-2 (2.13 ng/L), and HX-3 (1.38 ng/L) but lower than in XH-1 (35.42 ng/L) and XH-2 (23.71 ng/L). The NM-1 receives the confluence of the Xiaohuang River and Huaxi River. It is likely that the Huaxi WWTP, which is located at the upstream portion of the Xiaohuang River, may be the dominant source for the higher Gd concentration in NM-1. Except for sample sites that were affected by effluent discharge outlets (XH-1, XH-2, NM-6, and NM-7), the Gd concentrations were less than 11 ng/L. Moreover, the concentrations of Gd and Cl⁻ were found to be positively correlated (Figure 5), suggesting they shared similar anthropogenic sources. Unlike urban rivers, effluent discharge is the main source of chloride (Minhui et al., 1982; Yang, 2004). Gd and Cl⁻ readily form a complex that is discharged after treatment by the WWTP (Song et al., 2017). Chlorine-containing antibiotics were previously found in domestic and medical wastewater discharged into the Namming River (Liu et al., 2009).

Because Gd mainly comes from anthropogenic sources, we estimated the contributions of anthropogenic Gd using Equation 6. The values of Gd_Anthr. and Gd_Measured for the Namming River are summarized in Table 2 and shown in Figure 4. Overall, 13 samples were found to have the ratios of Gd_Anthr./Gd_Measured >60%, while 4 samples (XH-1, XH-2, NM-6, and NM-7) showed Gd_Anthr./Gd_Measured ratios of >90%. Additionally, the Gd_Anthr./Gd_Measured of 2 WWTPs effluent outlet samples (NM-6 and NM-7) were both higher than 90%. The percentage of Gd_Anthr./Gd_Measured for the Shixi River was higher than 80%. As mentioned above, the high Gd_Anthr./Gd_Measured may be attributed to wastewater discharge from the hospitals in urban areas in Guiyang. The average value of Gd_Anthr. in the Namming River was 69.6%, which was slightly higher than results previously reported for other systems such as the Adige River (Gd_Anthr./Gd_Measured = 61.2%; Fuganti et al., 1996), the Rhine River (Gd_Anthr./Gd_Measured = 63.6%; Kulaksız and Bau, 2013), and the Han River (Gd_Anthr./Gd_Measured = 68.3%; Song et al., 2017), suggesting that there was severe Gd pollution in the Namming River.

A significant positive Gd anomaly (Gd_sn/Gd_sn* = 5.30) was found in one of the tap water samples from the NJSC, which was closest to the urban area. Based on Equation 6, the percentage of Gd_Anthr./Gd_Measured was 79.23% for the tap water sample from the NJSC. Similar phenomena have been observed in several regions with developed medical systems in Germany, France, and Japan (Nozaki et al., 2000; Elbaz-Poulichet et al., 2002; Hennebrüder et al., 2004). These findings indicate Gd-DTPA may enter into groundwater through riverbank filtration and then affect the Gd content of source water used in tap water plants (Schmidt et al., 2019).

4. Conclusions

In this study, we discovered anthropogenic REEs in river water and tap water in Guiyang city for the first time. Based on our findings, the following conclusions were drawn: (1) The ratio of (La/Yb)_SN was higher than 1 in the Namming River because of the local WWTPs discharge, (2) the Namming river water was associated with positive Gd
anomalies because of the discharge of medical wastewater from hospitals, and (3) significant negative Ce anomalies and positive Eu anomalies observed in water samples were mainly attributed to natural origins, although there might be an anthropogenic Eu contribution as well. Overall, our study indicated that anthropogenic REEs pollution may be common in Chinese cities. In addition, anthropogenic REEs have the potential to be used as an efficient tracer of anthropogenic discharge in urban water systems accurately due to their stability and sensitive chemical properties, which will enable more detailed analyses of the degree of pollution in urban water systems.

Data accessibility statement
Data summaries are reported in Tables 1 and 2.

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Competing interests
The authors declare no conflict of interest.

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Contributed to conception and design: RH, ZW, QW.
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Contributed to analysis and interpretation of data: RH, ZW, YS, CC, QW.
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