Due to the rapid urbanization process, the consumption of trace and rare earth elements has dramatically increased. Although some elements have been extensively studied due to their high biological toxicity, most elements are ignored and taken seriously in recent years. Here, we investigated the urban geochemistry, source, and anthropogenic responding factor for 15 trace elements (Cd, Pb, Co, Sn, Cu, Ni, V, As, Mo, Sb, Al, Li, Fe, Zn, and Sr) and rare earth elements in surface water of the Suzhou city. The percentage of anthropogenic gadolinium vary from 46.9% (YCH-2) to 92.8% (WS-2), while the analysis of variance shows that human activities may affect the distribution of Cd, Co, Sn, Ni, As, Li, Fe, and Sr. Three clusters are obtained from the correlation and cluster analysis. The Cluster 1 with a significant positive correlation of Pb, Cd, Gd, Li, Sr, Co, Fe, Ni, and Sn reflecting these elements are dominantly influenced by urban sewage and industrial activities. The Cluster 2 (Zn, Cu, and Al) can be attributed to geologic sources, while the Cluster 3 (V, Mo, As, and Sb) indicate the combined action of agricultural and urban activities. The Gd versus Li plot showed a significant positive correlation, which can be used as a new indicator to trace the anthropogenic impact on urban waters. Overall, this study provides clear evidence that the content and distribution of Gd and Li are deeply affected by human activities in a high-tech industrial city (Suzhou), which can be regarded as emerging elements contaminations.

Keywords: Trace elements, Rare earth elements, Urban geochemistry, Anthropogenic Gd, Anthropogenic Li

1. Introduction
With the intensification of industrial and urban development, increasing concentration of trace elements profoundly influence the aquatic ecosystem and human beings (Islam et al., 2015; Zeng et al., 2019). Although some trace elements are essential for humans, their non-biodegradability, bioaccumulation, persistent, ubiquitous, and toxic nature can pose various potential risks for human health and ecological security (Chi et al., 2018). More and more population face severe water pollutions, notably in urban areas (Chanpiwat and Sthiannopkao, 2014; Xiao et al., 2019; Zhou et al., 2021), where the densely population, developed industry, and advanced medical (Vörösmarty et al., 2010) are relatively intense. Previous studies have shown that anthropogenic sources can be the primary contribution for trace elements in a specific area (Schmidt et al., 2019; Wang et al., 2020; Zeng et al., 2020). Despite receiving considerable global attention to some trace element pollution in aquatic environments, the application and consumption of trace elements keep changing accompanied by the rapid development of high-tech and emerging industries (Choi et al., 2019; Itoh et al., 2021). Thus, emerging trace element contaminations, such as Gd and Li contaminations (Bau and Dulski, 1996; Choi et al., 2019), are reported in succession in recent years and should be in deep concern.

Here, to explore the urban geochemistry and anthropogenic responding factor, we sampled and analyzed trace elements and rare earth elements (REEs) in surface water of the Suzhou city. Suzhou is an important national high-tech industrial base in the Yangtze River Delta. It drains a population of about more than 10 million and the majority of people (more than 76.05%) live in urban areas. Thus, Suzhou offers a unique opportunity to examine the emerging concerns of trace elements and REEs in...
a high-tech industrial city. However, the distribution, source, and contaminations of dissolved trace elements in Suzhou surface water have not been investigated systematically.

This study investigates the urban geochemistry and anthropogenic responding factor of dissolved trace elements and REEs, facilitating a survey on emerging element contaminations in Suzhou surface water. The aims are to (1) analyze the distribution of 15 dissolved trace elements and REEs in Suzhou city, (2) identify the anthropogenic sources of selected elements, and (3) explore possible unconventional contaminations of the high-tech trace elements in urban waters. The results would greatly help manage the urban water resources and provide a reference for trace elements and REEs pollution prevention policy.

2. Materials and methods

2.1. Study site

Suzhou City is in the Yangtze River Delta of China (30°45′–32°02′N; 120°11′–121°16′E; Figure 1), with a population of more than 10 million. As a central regional city and national high-tech industrial base, the urbanization rate is as high as 76.05%. The study area has a subtropical humid monsoon climate with a mean annual temperature of about 15.7°C. The average annual rainfall is 1,086.3 mm, while the average annual rainfall days are about 150 days. In 2019, there are 3,720 medical and health institutions, including 221 hospitals. The high-tech industry, such as aerospace, new energy, and biomedicine, has formed agglomeration effect in Suzhou National High-Tech District.

According to the method of Jenks Natural Breaks by ArcGIS 10.7, three levels of population density are obtained: high population density (HPD; 0–2,230 persons per 4 km²), medium population density (MPD; 2,230–9,357 persons per 4 km²), and low population density (LPD; 9,357–30,601 persons per 4 km²).

2.2. Sampling and analysis

Considering the population, land use and human/industrial activities of the Suzhou urban area, 30 water samples were sampled in September 2019 (low flow season; Figure 1). The pH and electrical conductivity values were measured in the field using the WTW Multi 3430 (WTW Company, Weilheim, Upper Bavaria, Germany). Waters were instantly filtered by 0.22-µm acetate
cellulose-acetate membrane after collection. Then, the samples were acidified with ultrapurified HNO₃ (pH < 2) and sealed in precleaned polyethylene bottles and stored at 4°C in refrigerator before measurement.

Fifteen trace elements (Cd, Pb, Co, Sn, Cu, Ni, V, As, Mo, Sb, Al, Li, Fe, Zn, and Sr) and REEs were detected by an inductively coupled plasma optical emission spectrometry (ICP-MS NexION300X, PerkinElmer, Waltham, MA) at the Institute of Geochemistry, Chinese Academy of Sciences. Quality assurance and quality control were performed by standard reference materials (GSB 04-1767-2004 for trace elements; SLRS-5 for REEs). Relative standard deviations for trace elements were approximately ±5%, and recovery percentage ranged from 80% to 110%. Otherwise, the samples were detected again until the data reach the standard (Han et al., 2020).

2.3. Quantification of REE anomalies
The concentrations of anthropogenic Gd were adapted from Kulaksız and Bau (2013) and references therein. The anthropogenic gadolinium (Gdanth) can be quantified by the following equations:

$$\text{Gd}_{\text{anomaly}} = \frac{Gd_{\text{SN}}}{Gd_{\text{SN}} + 2Pr_{\text{SN}} + 5Dy_{\text{SN}}}$$

$$\text{Gd}_{\text{anth}} = Gd - Gd^*.$$  

where Gd, Pr, and Dy are the measured concentrations of the samples, Gd* is the calculated natural concentration. The SN means that the concentration is normalized to the international reference Post Archean Australian Shale.

2.4. Statistical analysis
The statistics were performed using SPSS 24.0 (IBM SPSS Statistics, Origin 2018 (OriginLab Corporation, Northampton, MA), and R software. Two-tailed Spearman correlation analysis (with significance levels at $P < .05$ and $P < .01$) and hierarchical cluster analysis were performed for the trace elements using R software. Differences between the trace element concentrations for 3 levels of population density were estimated by one-way analysis of variance (ANOVA) using SPSS 24.0.

3. Results and discussion
3.1. General characteristics in surface water
The K–S test was used to check the normal distribution of all trace elements. The test results show that only Cd, Sn, Cu, As, Mo, and Fe contents are normally distributed (significance > 0.1), which means the mean values are influenced by outliers, so the median values of each trace element are comparable. According to the median contents of dissolved trace elements, the abundance of them in Suzhou surface water can be divided into 3 groups (Tables 1 and S1): (1) Sr was the most abundant element, with a median concentration of >100 μg/L; (2) concentration of Cu, Ni, V, As, Mo, Sb, Al, Li, and Fe were all ranging from 1 to 100 μg/L, which were the moderate elements; and (3) the content of Cd, Pb, Co, and Sn were <1 μg/L, which were belonged to low abundant elements. For different population density in Suzhou surface water, Cd, Pb, Co, Sn, Cu, Ni, Mo, Li, Fe, and Sr contents in MPD are higher than that in LPD and HPD, Sb and Zn contents in MPD are below that in LPD and HPD. Notably, none of the lowest values of 15 trace elements appear in LPD.

The comparison of trace elements in Suzhou surface water with global rivers has shown in Table S2. Pb and Cu contents in Suzhou surface water were close to the average content of global river, Fe and Al contents were far below average content of global river, while the Ni, V, and Zn contents were several folds higher than that of global river (Gaillardet et al., 2003). Owing to the differences in urban development process and industrial structure, human activities were quite diverse in urban aquatic environment, so the contents of dissolved trace element were various all over the world. As a distinct comparison, the Zn, As, Pb, Cu, and Cd contents in Xiangjiang River were much greater than that of Suzhou surface water (Zeng et al., 2015), while those elements content in Tarim River were close to Xiao et al. (2014). In such a high-tech industrial leading district with a large population in Suzhou, the potential emission intensity of mining and agriculture trace element pollutants were much weaker, such as Zn, As, Cu, and Cd.

The dissolved REE concentrations in Suzhou surface water are presented in Figure 2 and Table S3. The abundance of REEs exhibited extensive variation, varying from 0.06 to 26.50 ng/L. The mean and median contents of Gd were the highest among REEs, while Tb was the least abundant REE. La, Ce, Pr, Nd, Sm, Gd, Tb, and Ho had one or more outliers, demonstrating a noticeable variability of those REEs.

3.2. Identification of anthropogenic responding factor
3.2.1. Presence of anthropogenic Gd
Since the first report of positive Gd anomalies caused by anthropogenic input in 1996 (Bau and Dulski, 1996), such anomalies have been described from all over the world (Nozaki et al., 2000; Möller et al., 2002; Kulaksız and Bau, 2011; Merschel et al., 2015; Song et al., 2017; Zhang et al., 2019). Anthropic Gd in urban water is mainly from the contrast agents in magnetic resonance imaging (MRI) in hospitals (Lerat-Hardy et al., 2019), thus the contents can be impacted by local population and the levels of medical services. The Gdanth and its contributions (Gdanth%) has shown in Table S3. It was noteworthy that the Gdanth% vary from 46.9% (YCH-2) to 92.8% (WS-2), showing the quite high Gdanth percentage in Suzhou surface water. Especially in WC-6 and WS-2, which were the samples downstream of wastewater treatment plants (WWTP), contents and percentages of Gdanth were obvious higher than other elements. Thus, it was obvious that anthropogenic Gd input are present in Suzhou.

3.2.2. ANOVA
The ANOVA was performed to explore the relationship between the selected elements and population density (Table 1). The population density can reflect the intensity of human activities, so the content of trace elements may
Table 1. Trace element (µg/L) and gadolinium (ng/L) contents, and the results of one-way ANOVA in Suzhou surface water. DOI: https://doi.org/10.1525/elementa.2020.00151.t1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>LPD (n = 16)</th>
<th>MPD (n = 7)</th>
<th>HPD (n = 7)</th>
<th>Levene Test</th>
<th>One-Way ANOVA</th>
</tr>
</thead>
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<td>Range</td>
<td>Mean</td>
<td>Median</td>
<td>Range</td>
<td>Mean</td>
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<td></td>
<td>7.16–9.10</td>
<td>7.99</td>
<td>7.80</td>
<td>6.67–8.12</td>
<td>7.39</td>
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<tr>
<td>EC</td>
<td>362–720</td>
<td>514</td>
<td>520</td>
<td>371–677</td>
<td>566</td>
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<tr>
<td>Cd</td>
<td>0.006–0.023</td>
<td>0.014</td>
<td>0.012</td>
<td>0.015–0.032</td>
<td>0.023</td>
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<tr>
<td>Pb</td>
<td>0.001–0.147</td>
<td>0.037</td>
<td>0.025</td>
<td>0.014–0.296</td>
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<tr>
<td>Co</td>
<td>0.031–0.117</td>
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<td>0.053</td>
<td>0.079–0.238</td>
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<tr>
<td>Sn</td>
<td>0.018–0.088</td>
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<td>0.057</td>
<td>0.050–0.107</td>
<td>0.085</td>
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<tr>
<td>Cu</td>
<td>0.45–2.18</td>
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<td>0.97</td>
<td>1.16–1.78</td>
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<td>Ni</td>
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<td>2.53</td>
<td>2.45</td>
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<tr>
<td>V</td>
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<td>3.16</td>
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<td>Sb</td>
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<td>6.74–8.99</td>
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<td>5.85</td>
<td>3.59–149.00</td>
<td>28.66</td>
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<tr>
<td>Sr</td>
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<td>219.93</td>
<td>218.12</td>
<td>218.20–251.74</td>
<td>238.32</td>
</tr>
<tr>
<td>Gd</td>
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<td>6.95</td>
<td>5.34</td>
<td>3.62–11.52</td>
<td>7.16</td>
</tr>
</tbody>
</table>

ANOVA = analysis of variance; LPD = low population density; MPD = medium population density; HPD = high population density; EC = electrical conductivity.
be impacted by various degree of human activities (Ustaoğlu and Tepe, 2019; Yin et al., 2021). Concentrations of Cd, Co, Sn, Ni, As, Li, Fe, and Sr in LPD, MPD, and HPD sites were observed significant differences, meaning that human activities may affect their distributions. Notably, the one-way ANOVA cannot show that the content of trace elements follows population density increasing or decreasing. The Content of Co, Sn, Ni, Li, Fe, and Sr decreased by the sequence MPD > LPD > HPD, while As was on the contrary. In addition, Cd concentrations decreased by the sequence MPD > HPD > LPD. In a developed city, the tertiary industry agglomerate in HPD, and the second industry were dominant in MPD, while the agriculture mainly distributed in LPD (W. Wang et al., 2017). Therefore, the highest concentrations of the 8 elements were observed in MPD rather than HPD (except As, the highest concentration is observed in HPD), implying that Co, Sn, Ni, Li, Fe, Sr, and Cd might be mainly derived from industrial sources.

3.2.3. Correlation and cluster analysis

The Spearman correlation matrix was employed to distinguish associations between the 15 trace elements and Gd in the study area (Figure 3). In general, elements with significant positive correlation may have similar sources, migration, and conversion behaviors (J. Wang et al., 2017). The significant positive correlation were observed among Cd, Gd, Li, Sr, Co, Fe, Ni, and Sn ($P < .01$, except Gd and Cd, Gd and Sn), meaning that these elements might origin from the same sources. V, Mo, Gd, Li, Sr, and Sn were also observed a significant positive correlation ($P < .01$, except Gd and Sn), but V and Mo were weakly correlated with other elements, suggesting that the origins of V and Mo were distinct from other elements.

The hierarchical cluster analysis was carried out to differentiate the possible origins of each element in Suzhou surface water. The black rectangles represent 3 clusters of hierarchical cluster analysis by Ward method in Figure 3. The Cluster 1 contains 9 elements, including Pb, Cd, Gd, Li, Sr, Co, Fe, Ni, and Sn; the Cluster 2 contains Zn, Cu, and Al; the Cluster 3 contains V, Mo, As, and Sb. Most of the elements in cluster are observed positive correlations among each other in Cluster 1 except Pb (Figure 3). Combined with the ANOVA results (concentration of Cd, Co, Sn, Ni, Li, Fe, Sr and Cd in different population density are significantly distinct) and the presence of anthropogenic Gd, here we infer that the Cluster 1 is dominantly influenced by urban sewage and industrial activities in Suzhou surface water. The Cluster 2 contains Zn, Cu, and Al, with relative weakly correlated among them. Al is the most abundant metal of continental crust and thus anthropogenic input on its content do little effect (Taylor and McLennan, 1995). Although industrial wastes may discharge Zn and Cu into the aquatic environment, the relative low concentration of Zn and Cu comparing to other rivers (Table S2) indicate that the 2 elements may be little affected by human activities (Li and Zhang, 2010). Therefore, the Cluster 2 can be attributed to geologic sources, such as rock weathering (Zeng and Han, 2020). In addition, the Cluster 3 includes V, Mo, As, and Sb, while As contents is related to population density and decreased by the sequence HPD > LPD > MPD. Combined
with the positive correlation is observed among V and Mo with elements in Cluster 1 (Cd, Gd, Li, Sr, Co, Fe, Ni, and Sn), the origins of the elements in Cluster 3 may origin from the combined action of agricultural and urban activities.

3.3. A new indicator of urban-impacted sources

Conventional WWTP are designed to deal with traditional contaminants, so that a series of emerging contaminants can even enter the environment via sewage systems (Reoyo-Prats et al., 2018). For instance, Gd and Li cannot be efficiently removed during conventional wastewater process and then are released into aquatic ecosystem along with the effluent of WWTP (Bau and Dulski, 1996; Birka et al., 2016; Choi et al., 2019). Considering that Gd and Li are both in the Cluster 1 with a significant positive correlation ($P < .01$; Figure 3), the Gd versus Li plot (Figure 4) implies the similar urban geochemistry behavior between the 2 elements. As shown in Figure 4, the obvious abnormal distribution of the downstream samples of WWTP is primarily caused by the high Gd concentrations, in which the Li concentrations were relatively high as well. The rest of surface water samples are linear distributed with Gd versus Li contents with positive correlation. Therefore, Gd versus Li can be used as a new indicator to trace the anthropogenic impact on urban waters, while the contents of Gd and Li indicate the degree of urban impact.

3.4. Trace elements of emerging concern in urban waters

The man-made products help to increase human’s standard of living, and the changing demands continue to fuel research and development for products (Schirmer and Schirmer, 2008). Therefore, applications and demands of various elements are constantly changing, and many elements have transferred to the aquatic environment, especially in urban area. Anthropogenic Gd has used as a contrasting agent in MRI since 1980s, then its worldwide use increased almost 10-fold between 1998 and 2008 (Rogowska et al., 2018). The growing industrial demands for Li are as the key materials of the secondary Li-ion battery. Compared to the traditional heavy metal pollutants (e.g., Fe and Cu), Gd and Li are widely used in recent years, especially in high-tech industrial and medical applications rather than conventional industrial (Negrel et al., 2020; Kaegi et al., 2021). Meanwhile, due to the ecotoxicity, adverse ecological and human health effects of Gd and Li remain unclear, these high-tech elements have not been monitored in policy or reduced in sewage system. In this study, the significantly anthropogenic input of Gd and

![Figure 3. Spearman correlation and hierarchical cluster analysis for the trace element. * Represents correlation is significant at the .05 level (2-tailed), and ** represents correlation is significant at the .01 level (2-tailed). The black rectangles represent the 3 clusters of hierarchical cluster analysis by Ward method. DOI: https://doi.org/10.1525/elementa.2020.00151.f3](http://online.ucpress.edu/elementa/article-pdf/9/1/00151/485375/elementa.2020.00151.pdf)
Li were observed in Suzhou surface water. It is therefore urgent to control the aqueous Gd and Li and any other emerging pollutants in urban area.

4. Conclusions
This study was performed to investigate the urban geochemistry and anthropogenic impact on 15 trace elements (Cd, Pb, Co, Sn, Cu, Ni, V, As, Mo, Sb, Al, Li, Fe, Zn, and Sr) and REEs in Suzhou surface water. The multiple statistics result show that conventional and unconventional element contaminations are under the influence of human activities in a high-tech industrial city, Suzhou. Urban sewage and industrial activities were the primary origin of Pb, Cd, Gd, Li, Sr, Co, Fe, Ni, and Sn, while Zn, Cu, and Al were controlled by natural processes. Moreover, V, Mo, As, and Sb were dominated by combined action of agricultural and urban activities. The distribution of Cd, Co, Sn, Ni, As, Li, Fe, and Sr were correlated with population density. In addition, the relation of Gd and Li can be a new indicator to trace and indicate the degree of anthropogenic impact in urban area. Overall, this study provides clear evidence of human impact on Gd and Li and the vital to control the aqueous Gd and Li and any other emerging pollutants in urban areas.

Data accessibility statement
Data used in this study can be found in online Supplemental Tables S1–S3.

Supplemental files
The supplemental files for this article can be found as follows:
Table S1. Concentrations of dissolved trace elements, pH, and electric conductivity in Suzhou surface water. xlsx
Table S2. Dissolved trace element concentrations (μg/L) in other rivers. xlsx
Table S3. Dissolved rare earth element concentrations (ng/L) in Suzhou surface water. xlsx

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Competing interests
The authors declare no conflict of interest.

Author contributions
Contributed to conception and design: SG, QW, ZW.
Contributed to acquisition of data: SG, CP, YW.
Contributed to analysis and interpretation of data: SG, QW, ZW.
Drafted and/or revised the article: ZW, JZ.
Approved the submitted version for publication: SG, QW, ZW, CP.

References


