Disentangling sources and transformation mechanisms of nitrogen, sulfate, and carbon in water of a Karst Critical Zone

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**HIGHLIGHTS**

- The groundwater and surface water demonstrated frequent exchange.
- Inorganic N and S were mainly derived from the soils and sulfide oxidation.
- DIC was from the water-carbonate reaction and soil respiration.
- Sulfide oxidation could enhance CO\textsubscript{2} release in the mining area.

**GRAPHICAL ABSTRACT**

**ABSTRACT**

In the Karst Critical Zone (KCZ), mining and urbanization activities produce multiple pollutants, posing a threat to the vital groundwater and surface water resources essential for drinking and irrigation. Despite their importance, the interactions between these pollutants in the intricate hydrology and land use of the KCZ remain poorly understood. In this study, we unraveled the transformation mechanisms and sources of nitrogen, sulfate, and carbon using multiple isotopes and the MixSIAR model, following hydrology and surface analyses conducted in spatial modelling with ArcGIS. Our results revealed frequent exchange between groundwater and surface water, as evidenced by the analysis of $\delta^{18}$O-H\textsubscript{2}O and $\delta^{2}$H-H\textsubscript{2}O. Nitrification predominantly occurred in surface water, although denitrification also made a minor contribution. Inorganic nitrogen in both groundwater and surface water primarily originated from soil nitrogen (48 % and 49 %, respectively). Sewage and manure were secondary sources of inorganic nitrogen in surface water, accounting for 41 % in urban and 38 % in mining areas. Notably, inorganic sulfur oxidation displayed significant spatial disparities between urban and mining areas.

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rendering groundwater more susceptible to sulfur pollution compared to surface water. The frequent interchange between groundwater and surface water posed a higher pollution risk to groundwater. Furthermore, the primary sources of CO$_2$ and HCO$_3$ in both groundwater and surface water were water-carbonate reactions and soil respiration. Sulfide oxidation was found to enhance carbonate dissolution, leading to increased CO$_2$ release from carbonate dissolution in the KCZ. These findings enhance our understanding of the transformation mechanisms and interactions of nitrogen, sulfur, and carbon in groundwater and surface water. This knowledge is invaluable for accurately controlling and treating water pollution in the KCZ.

1. Introduction

Approximately 7–12 % of continental land globally is karst (Hartmann et al., 2014). The Karst Critical Zone (KCZ) is the thin outer veneer of a karst region ranging from the surface of the vegetation layer to the depths of drinking water aquifers (Banwart et al., 2013). Owing to its ecological vulnerability, it is at substantial risk of pollution from urbanization and mining activities (Lv et al., 2020). Karst hydrology is complex because of the multiple porosities of the regional geology, resulting in the rapid transfer of pollutants between the surface and underground streams (Ren et al., 2023; Yue et al., 2020). Groundwater in karst areas serves as both a vital water source for maintaining surface water circulation (Alley et al., 2002), and an essential resource for the formation of karst water (Romanov et al., 2003), which affects the water circulation (Alley et al., 2002), and an essential resource for purposes of drinking and irrigation in these regions. The high heterogeneity of aquifers results in significant differences between the characteristics of karst water (Romanov et al., 2003), which affects the transportation of groundwater and surface water. Understanding the interchange of groundwater and surface water, the processes of replenishment, and the mechanisms of pollutant migration and transformation are beneficial for effectively managing karst water resources. (Goldscheider et al., 2020; Kalhor et al., 2019; Moral et al., 2008).

Several pollutants and harmful substances would be outputted from mining activities, which caused a lot of environmental problems globally and threatened human healthy (Kou et al., 2023; Santana et al., 2020). During mining activities, when sulfides are exposed to oxygen (O) and water, they can undergo oxidation, resulting in the production of acid mine drainage (Sun et al., 2017). Because sulfate (SO$_4^{2-}$) is a common constituent of wastewater, different sulfur (S) turnover processes that rely on the availability of organic carbon (C) and O are prevalent in mining and urban areas (Li et al., 2019; Tuttle et al., 2009). Urban wastewater effluent and agricultural fertilizer application result in the increased dissolved inorganic nitrogen (N) (Schilling et al., 2015). Manure and sewage also have a non-negligible influence on N (Paredes et al., 2020), and S (Otero et al., 2007; Zhang et al., 2024). Understanding the transformation mechanisms and multiplex sources of typical elements can help trace pollutants and control their activities (Pug et al., 2013). Monitoring concentration features in surface water and groundwater alone is insufficient to achieve this, as it does not account for the loss of materials from the hydrological flow pathway (Huebsch et al., 2014), transformation of pollution (Jarvie et al., 2018), and source mixing in complex land uses (Ye et al., 2021). In landscape studies, isotopic methods have been applied to identify transformation mechanisms and different sources widely in past decades (Kendall, 2007).

However, a single isotopic tracer cannot distinguish between mixed sources or multiple processes. Only $\delta^{34}$S-SO$_4^{2-}$ data were obtained in early studies and the introduction of $\delta^{18}$O-SO$_4^{2-}$ measurement was a major improvement (Krouse and Mayer, 2000). The $\delta^{18}$O-SO$_4^{2-}$ as generated can provide insights into the oxidation pathways of pyrite oxidation in mining areas (Kim et al., 2019). Therefore, $\delta^{18}$O-SO$_4^{2-}$, $\delta^{18}$O-Na$_2$SO$_4$, $\delta^{18}$O-Na$_2$SO$_4$, $\delta^{18}$O-H$_2$O, $\delta^{18}$H-$\delta^{18}$O, and $\delta^{18}$C-DIC could be introduced as useful new tracers to further solve the problem of pollutant interaction. The $\delta^{18}$O-H$_2$O, and $\delta^{18}$H-$\delta^{18}$O compositions, which are part of the water molecule, have been widely used for determining the flow path and source of groundwater and surface water (Clark and Fritz, 1997; McGuire and McDonnell, 2007). Isotopes of dissolved inorganic C ($\delta^{13}$C-DIC) are useful tools for disentangling three primary sources: carbon dioxide (CO$_2$) dissolved from the atmosphere, CO$_2$ from soil respiration, and from the carbonate dissolution in groundwater and surface water systems (Qin et al., 2022; Zhang et al., 2009). Meanwhile, the water-rock reaction in the lithosphere has been underestimated because most studies on the C cycle have focused on the biologically active pedosphere in the terrestrial biosphere (Friedlingstein et al., 2019). In addition, a previous study has utilized the MixSIAR model to trace the sources and contributions of S to groundwater and surface water (Torres et al., 2020), and our study further combines it with quantitative land use divisions. These methods provide practical and precise guidance for environmental management of N and S pollution in the KCZ.

Understanding the transformation processes and sources of N, S, and C in groundwater and surface water within complex land-use areas in typical karst zones is crucial for effectively managing and controlling pollution in global karst watersheds. In Southern China, the total water reserves are primarily made up of karst groundwater reserves, accounting for 80 % (Lu, 2007). The region exhibits well-developed structural fissures and significant karst effects, setting it apart from other areas (Wu et al., 2009). Our hypothesis was that carbonate rocks in mining areas might partially mitigate acid pollution from inorganic S oxidation, but not N pollution. To validate this hypothesis, we employed an integrated approach to investigate the presence of N, S, and C in contaminated karst aquifers.

Our study applied a new and original hydrochemistry and multi-isotope method based on the MixSIAR model to reveal the quantitative relation between the apportionment of multi-source pollutants and complex land use. As far as we know, this study is the initial attempt to trace the different sources of S and N together using the MixSIAR model with a geographical method. The combination of the geographical approach, the land use index (LUI) (Ometto et al., 2000; Ye et al., 2021), and the spatial modelling with ArcGIS is a sophisticated classification technique that effectively differentiates study regions based on their distinct land-use attributes. We measured multiple stable isotopes, pollutant concentrations, and water quality parameters to achieve two primary objectives: (1) understand the main transformation mechanisms and source allocations of N, S, and C within distinct land-use categories and (2) explore the interactions among pollutants originating from various sources in the KCZ. The goal of this research is to establish a solid scientific foundation for unraveling the transformation processes and origins of N, S, and C. Additionally, it provides essential insights for water resource management in the KCZ and the effective control of complex pollutants.

2. Materials and methods

2.1. Study area

The research site is situated in Shuicheng Basin, Dahe Town, and Wangjiazhai Town, which is in the Zhongshan District, the center of Liupanshui City with abundant underground coal mining resources, Guizhou Province, Southwest China (104° 45′ ~ 104° 59′ E, 26° 32′ ~ 26° 44′ N; Fig. 1). It is located in the Guizhou-Yunnan Plateau, which is the heart of the Southeast Asian Karst Region and the largest contiguous karst region all over the world (Xu and Liu, 2007). It has a subtropical climate.
humid monsoon climate in the northern subtropical plateau with small overall temperature changes. The study area receives an adequate amount of surface water and groundwater, with an annual mean precipitation of 1200–1500 mm/yr and the annual mean temperature of 13.7 °C. The situation in our study area, a typical developing region of China, is that daily life, agriculture activities, and industrial activities are highly undifferentiated in spatially, and various land use types are interwoven to form complex land use types (Deng et al., 2024).

The study area is mainly used as farmland, followed by forest, grassland, urban land, surface water, coal mine land and bare land (without vegetation cover). These different spatial patterns and features are shown in the land use map which was modified from the remote sensing images of p satellite from France’s Airbus satellite company at a resolution of 1 m in 2015 (Fig. 1). The study area is defined quantitatively as two zones by analysing the LUI in different watersheds (Table S1) (Ometo et al., 2000; Ye et al., 2021). Urban area was defined as 100 < LUI < 500, and LUI > 500 was defined as a mining area. The samples of surface water and groundwater in the urban area were referred to as US and UG, and surface water and groundwater in the mining area were referred to as MS and MG, respectively (Fig. 1).

In the study area, the western and southern regions had elevated terrain, while the eastern and northern regions were characterized by lower elevation, ranging between 1700 and 1900 m. The mountain series spreads along the line of geological structure, the complex geological structure, and the terrain combinations were diverse (Fig. 2). The primary geological layers found in the study region consist of Carboniferous, Permian, Jurassic and Triassic. The strong geological tectonic movement generates complex karst fissures and karst basins, and the abundant rainfall ensures abundant groundwater resources. The samples of surface water and groundwater were mainly distributed in the Emeishan basalt, Longtan Formation, Permian (P2β and P3l), Datang Formation, Carboniferous (C4d), and Triassic (T1f, T1yn and T3g) (Fig. 2).

2.2. Sampling and pretreatment

A combined total of 23 samples from surface water and 33 samples from groundwater were gathered in September 2015 from the urban and mining areas to obtain various concentrations and isotope compositions of N, S and C (Fig. 1). Specifically, a total of 10 surface waters and 12 groundwaters were collected in the urban area, and 13 surface waters and 21 groundwaters were collected in the mining area. The samples from surface water were gathered in the main streams (Shuicheng Basin, Dahe Town, and Wangjiazhai Town). The samples from groundwater were gathered in the main-stream basin. A total of 9 surface soils were equally collected in Shuicheng Basin, Dahe Town, and Wangjiazhai Town.

The dissolved oxygen (DO), oxidation-reduction potential (ORP), electrical conductivity (EC), pH, and temperature (T) of the water samples were determined in situ using a multiple parameter controller (Multi340i, WTW, Munich, Germany). The Gran titration method was used to determine the alkalinity (HCO3-) on site (Li et al., 2019). To analyze the concentrations and isotopes of the water samples, they were filtered using syringe-tip filters with a pore size of 0.45 μm (ANPEL Laboratory Technologies Inc., Shanghai, China). Some samples for cation analysis (Ca2+, Mg2+, Na+ and K+) were immediately acidified with HNO3 (guaranteed reagent, GR) to a pH of approximately 3.0 (Li et al., 2019). For avoiding volatilization of NH3 in water samples, some of them for determining ammonium nitrogen (NH4-N) were immediately acidified with HCl (GR) to a pH value of approximately 4.0 (Li et al., 2019). Some samples for δ18O-SO42- and δ34S-SO42- were immediately acidified using HCl (GR) until the pH dropped below 2 (Ren et al., 2021). To inhibit microbial respiration, some water samples for
δ¹³C-DIC were preserved by adding 0.1 mL of HgCl₂ solution (Li et al., 2019). Some water samples for anions (Cl⁻, SO₄²⁻ and NO₃⁻), and δ¹⁸O-H₂O, δ¹⁸O-NO₃ and δ¹⁵N-NO₃ had no reagents added. All water samples were refrigerated in an ice-box and transported to the Key Laboratory of Karst Georesources and Environment (Guizhou University). Before analysis, all the water samples were refrigerated at 4 °C.

2.3. Laboratory analysis

Anions (NO₃⁻, SO₄²⁻ and Cl⁻) and cations (Mg²⁺, Ca²⁺, K⁺ and Na⁺) were determined by an ion chromatography (ICS-1100, Dionex, Sunnyvale, CA, USA) and a flame atomic absorption spectrophotometry (ICP2000, Thermo Fisher Scientific, Waltham, MA, USA) to obtain an ionic mass balance error of less than ±5 % (Ye et al., 2019; Ye et al., 2017). The concentration of NO₃ was converted into a concentration of NO₃-N. The concentration of NH₄-N was determined utilizing the method of indophenol blue with a UV-VIS spectrophotometer (Shimadzu UV-2600, Kyoto, Japan). δ¹³C-DIC was acidified using phosphoric acid to produce CO₂ which was determined using GasBench-IRMS (DELTA-V Advantage, Thermo Fisher Scientific, Waltham, MA, USA). Calibration was used as an internal standard (NaHCO₃, −15.5 % δ¹³C) and an international standard (IAEA-CO-8, −5.8 % δ¹³C) with an analytical precision of ±0.1 %, δ¹⁸O-H₂O and δ¹³C-H₂O were determined using a laser isotope analyzer with high-precision (Picarro, Santa Clara, USA). The analytical precision rates of δ¹⁸O-H₂O and δ¹³C-H₂O were 0.02 ‰ and 0.10 ‰, respectively. δ¹³C-DIC, δ¹⁸O-H₂O, and δ¹³C-H₂O were determined in a laboratory at the School of Environmental Science and Engineering, Sun Yat-Sen University. The bacteria denitrifier method were used to determine the values of δ¹⁸O-NO₃ and δ¹⁵N-NO₃ (Casciotti et al., 2002; Sigman, 2001), and then analyzed with an isotope ratio mass spectrometer (DELTA-plus, Thermo Fisher Scientific, Waltham, MA, USA). The values of δ¹⁸O-NO₃ and δ¹⁵N-NO₃ were determined in batches containing blanks according to international standards such as USGS-35, IAEA-N3, and USGS-34. The analytical precision rates of δ¹⁸O-NO₃ and δ¹⁵N-NO₃ were ±0.5 ‰ and ±0.3 ‰, respectively. BaSO₄ was formed by introducing a saturated solution of BaCl₂ which had been heated in an electric furnace, resulting in the production of SO₄²⁻. In addition, the BaCO₃ solids were removed by adding HCl to avoid the effect of BaCO₃ on δ¹⁸O, and Cl⁻ was flushed with pure water and tested using an AgNO₃ solution. The solid was combusted at a temperature of 850 °C for 4 h in a muffle furnace, which was converted into SO₂ with an elemental analyzer (Euro EA 3000, Euro Vector S.P.A., Italy) and then determined using CF-IRMS for δ⁵³S-SO₄²⁻ and δ³⁴S-SO₄²⁻ with precision rates of ±0.2 ‰ and ±0.5 ‰, respectively (GV Instrument Corp., Manchester, UK). δ¹³C-O-NO₃, δ¹⁸O-SO₄²⁻, δ¹⁵N-NO₃ and δ³⁴S-SO₄²⁻ were determined in a laboratory at the Institute of Geochemistry, Chinese Academy of Sciences. There were three repeated times of the measurements and provided as the results of arithmetic mean and standard deviation.

Isotopic values are expressed by using delta (δ):

$$\delta(\%) = \left( \frac{R_{sample}}{R_{standard}} \right) - 1 \times 1000$$

where $R = \left( ^{15}N/^{14}N, ^{34}S/^{32}S, ^{18}O/^{16}O \right)$ or D/H. ¹⁵N/¹⁴N reference was N₂ in air (Air-N₂), ³⁴S/³²S reference was Vienna Canyon Diablo Troilite (V-CDT), ¹³C/¹²C reference was Vienna PeeDee Belemnite (V-PDB), ¹⁸O/¹⁶O and D/H references were Vienna Standard Mean Ocean Water (V-SMOW).
2.4. Statistical analysis and MixSIAR model

Pearson correlation analysis and two-way ANOVA were conducted using SPSS 20.0, for Windows (IBM, Armonk, NY, USA). Different areas and water types were the two independent fixed factors. The concentrations of \( \text{SO}_4^{2-}, \text{NH}_4^{+}, \text{NO}_2^-, \text{NO}_3^-, \text{and} \text{HCO}_3^- \) and compositions of \( ^{15}\text{N}-\text{NO}_3, ^{34}\text{S}-\text{SO}_4^{2-}, ^{13}\text{C}-\text{DIC}, ^{34}\text{O}-\text{H}_2\text{O}, ^{18}\text{O}-\text{NO}_3, ^{18}\text{O}-\text{SO}_4^{2-} \) and \( ^{18}\text{O}-\text{H}_2\text{O} \) were the dependent analyzed variables. The hydrology and surface analyses in spatial modelling, remote sensing interpretation for land use map, and hydrogeological mapping were conducted with ArcGIS 10.2 (ESRI Inc., Redlands, CA, USA). The figures were drafted using the Origin 2021 software (OriginLab Inc., Northampton, MA, USA). The ORP was converted to Eh using Excel 2019 (Microsoft Office, Redmond, WA, USA).

The proportions of different potential sources of \( \text{NO}_3^- \) and \( \text{SO}_4^{2-} \) were calculated in the MixSIAR model. Four major sources of \( \text{NO}_3^- \) and five major sources of \( \text{SO}_4^{2-} \) were considered based on field investigations in the study area and laboratory data analysis. Soil N, manure and sewage, chemical fertilizers (KNO_3), and atmospheric N deposition were the main sources of \( \text{NO}_3^- \). The main sources of \( \text{SO}_4^{2-} \) included oxidation of reduced inorganic S, soil S, pyrite oxidation, atmospheric deposition, manure, and sewage. The isotopic values of different potential sources were shown in Tables S2 and S3.

The values of \( ^{15}\text{N}-\text{NO}_3, ^{34}\text{S}-\text{SO}_4^{2-}, ^{13}\text{C}-\text{DIC} \) and \( ^{18}\text{O}-\text{SO}_4^{2-} \) in different endmembers and samples, and the isotope fractionation coefficient (setting as zero) were input in the R which runs with Bayesian mixing models to calculate the proportions of different potential nitrogen and sulfate sources in the samples (Torres et al., 2020; Xuan et al., 2020; Xue et al., 2009). The MixSIAR model can calculate the n isotopes that have more than n – 1 sources, taking into account uncertainties in all the calculated parameters (Stock et al., 2018). The proportions calculated by the MixSIAR model in R (4.2.1) are provided as mean values (Tables 1 and 2). The MixSIAR model for mixture measurements of \( \text{NO}_3^- \) and \( \text{SO}_4^{2-} \) with k sources and j isotopes is cited from the prior study (Parnell et al., 2010). The equations can be found in the part of MixSIAR model in the Supplementary Material.

3. Results

3.1. Spatial patterns of nitrogen, sulfur, carbon and water features

3.1.1. Nitrogen, sulfur, carbon and concentrations

The spatial changes of \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), \( \text{HCO}_3^- \) and \( \text{NH}_4^+ \) concentrations are shown in Fig. 3a, b and Table S4. The two-way ANOVA of N concentrations revealed a significant difference in \( \text{NO}_3^- \) between groundwater and surface water (p < 0.05). However, there was no significant difference in spatial distribution between the urban and mining areas (p > 0.05). Specifically, the mean concentration of \( \text{NO}_3^- \) in surface water was lower than that in groundwater. There were significant spatial and water type differences in the \( \text{NH}_4^+ \) concentration between groundwater and surface water (p < 0.01), urban areas, and mining areas (p < 0.05). Specifically, the mean concentration of \( \text{NH}_4^+ \) in the surface water was four times higher than that in the groundwater in the urban and mining areas. The concentration of \( \text{SO}_4^{2-} \) between surface water and groundwater was significantly different (p < 0.05), but not significant in spatial difference of both types of water (p > 0.05). In surface water, the amount of \( \text{SO}_4^{2-} \) was twice as high as in groundwater. There were no significant water type and spatial differences in the concentration of \( \text{HCO}_3^- \) (p > 0.05).

3.1.2. Physicochemical parameters and water chemical features

The pH varied between 3.82 and 8.72 with a mean value of 7.73 ± 0.64 (Table S4). In the mining area, the surface water exhibited the lowest pH value. The ORP varied between −3.00 mV and 460.00 mV with a mean value of 207.91 ± 62.78 mV. The TDS varied between 67.06 mg/L and 1865.60 mg/L. The mean TDS was 432.39 ± 103.53 mg/L in the urban area, which was lower than that in the mining area (515.37 ± 363.27 mg/L) (p > 0.05). The chemical features of the urban area’s surface water and groundwater were \( \text{HCO}_3^-\text{Ca} \) and \( \text{HCO}_3^-\text{Ca-Mg} \), respectively, which differed from those in the mining area. The groundwater and surface water primarily consisted of \( \text{HCO}_3^-\text{Ca} \) (Fig. S1).

3.2. Isotope compositions

The compositions of \( ^{15}\text{N}-\text{NO}_3, ^{34}\text{S}-\text{SO}_4^{2-}, ^{13}\text{C}-\text{DIC}, ^{34}\text{O}-\text{H}_2\text{O}, ^{18}\text{O}-\text{NO}_3, ^{18}\text{O}-\text{SO}_4^{2-} \) and \( ^{18}\text{O}-\text{H}_2\text{O} \) are shown in Fig. 3c-d and Table S4. The isotopic values of \( ^{18}\text{O}-\text{H}_2\text{O} \) and \( ^{34}\text{O}-\text{H}_2\text{O} \) did not show significant differences in water types (groundwater and surface water), and spatial areas (mining area and urban area) (p > 0.05). However, the mean isotopic values of \( ^{18}\text{O}-\text{H}_2\text{O} \) and \( ^{34}\text{O}-\text{H}_2\text{O} \) in the groundwater exhibited a slight elevation compared to surface water in the both mining and urban areas. There were no significant differences of water type and spatial variation in \( ^{18}\text{O}-\text{NO}_3 \) and \( ^{15}\text{N}-\text{NO}_3 \) (p > 0.05). In the mining and urban areas, the groundwater exhibited lower mean isotopic values of \( ^{18}\text{O}-\text{NO}_3 \) and higher mean isotopic values of \( ^{15}\text{N}-\text{NO}_3 \) compared to the surface water. There were the significant spatial differences in \( ^{34}\text{S}-\text{SO}_4^{2-} \) (p < 0.05) and water type differences in \( ^{18}\text{O}-\text{SO}_4^{2-} \) (p < 0.05). The mean isotopic values of \( ^{34}\text{S}-\text{SO}_4^{2-} \) of both groundwater and surface water in the mining area was higher than those in the urban area. The mean isotopic values of \( ^{18}\text{O}-\text{SO}_4^{2-} \) in the groundwater were higher than those in surface water from the mining and urban areas. There were no significant differences in the water type or spatial changes in \( ^{13}\text{C}-\text{DIC} \) (p > 0.05). The mean isotopic values of \( ^{15}\text{C}-\text{DIC} \) in both the surface water and groundwater in the urban area were slightly lower than those in the mining area.

3.3. Source apportionments of nitrogen and sulfur

3.3.1. Nitrogen

Tables S2, 1 and S5 display the isotopic values from various sources and the outcomes of source apportionments for \( \text{NO}_3^- \) with uncertainties. According to the MixSIAR model, the different source contributions to \( \text{NO}_3^- \) in the urban area ranked in descending order: soil N (44 %), manure and sewage (44 %), chemical fertilizer (11 %), and atmospheric N (1 %) in the groundwater; soil N (49 %), manure and sewage (37 %), chemical fertilizer (13 %) and atmospheric N (1 %) in the surface water. The different source contributions to \( \text{NO}_3^- \) in the mining area ranked in descending order: soil N (51 %), manure and sewage (40 %), chemical fertilizer (8 %) and atmospheric N (1 %) in the groundwater; and soil N (49 %), manure and sewage (36 %), chemical fertilizer (14 %) and atmospheric N (1 %) in the surface water.

Table 1
The sources proportion of \( \text{NO}_3^- \) in the MixSIAR model.

<table>
<thead>
<tr>
<th>Area</th>
<th>Water type</th>
<th>Abbreviation</th>
<th>Soil nitrogen (%)</th>
<th>Manure and sewage (%)</th>
<th>Chemical fertilizer (%)</th>
<th>Atmospheric deposition (%)</th>
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</thead>
<tbody>
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<td>Urban area</td>
<td>Groundwater</td>
<td>UG</td>
<td>44</td>
<td>44</td>
<td>11</td>
<td>1</td>
</tr>
<tr>
<td>Urban area</td>
<td>Surface water</td>
<td>US</td>
<td>49</td>
<td>37</td>
<td>13</td>
<td>1</td>
</tr>
<tr>
<td>Mining area</td>
<td>Groundwater</td>
<td>MG</td>
<td>51</td>
<td>40</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>Mining area</td>
<td>Surface water</td>
<td>MS</td>
<td>49</td>
<td>36</td>
<td>14</td>
<td>1</td>
</tr>
</tbody>
</table>
3.3.2. Sulfate

Table 2 displays the isotopic values of various sources and the outcomes of source apportionments for $\text{SO}_4^{2-}$ with uncertainties. In the urban area, the MixSIAR model revealed that oxidation products of reduced inorganic S (51 % and 65 %) contributed the most to $\text{SO}_4^{2-}$ in groundwater and surface water. It was then followed by soil S (22 %), atmospheric deposition (16 %), manure and sewage (11 %) in the groundwater from the urban area. The different source contributions to $\text{SO}_4^{2-}$ in the surface water from the urban area ranked in descending order: soil S (16 %), manure and sewage (11 %), and atmospheric deposition (8 %).

In the mining area, oxidation products of reduced inorganic S contributed the most to $\text{SO}_4^{2-}$ in the groundwater (36 %) and surface water (68 %). It was then followed by $\text{SO}_4^{2-}$ coming from soil S (34 %), manure and sewage (16 %), atmospheric deposition (13 %) in the groundwater. With a same trend in the groundwater, the sources of $\text{SO}_4^{2-}$ in the surface water was followed by soil S (14 %), manure and sewage (11 %), and atmospheric deposition (7 %).

4. Discussion

4.1. Transformation mechanisms of nitrogen, sulfate, and carbon

4.1.1. Exchange and redox analysis of karst water

The 6D$_2$O and $\delta^{18}$O-H$_2$O of groundwaters were distributed between the global meteoric water line (Craig, 1961) and the local meteoric water line (Lao et al., 2013), showing that the origin of the groundwaters were from precipitation (Fig. 4). The isotopic values of deuterium and oxygen in H$_2$O (δD-H$_2$O and $\delta^{18}$O-H$_2$O) in the surface water were similar in the groundwater, indicating that they exchanged frequently in the KCZ. The physicochemical compositions of surface water and groundwater, such as the DO, ORP, and pollutants, vary. Surface water systems are usually characterized by turbulent flow; therefore, they exhibit typical oxidation conditions. DO is usually reduced according to the biological and chemical demands in the subsurface environment (Valett and Reinhold, 2002). Due to the frequent exchanges of surface water and groundwater, the redox conditions of the groundwater are mostly oxidant. The redox conditions of surface water and groundwater play a key role in controlling elemental species, such as N, S, and C (Li et al., 2019; Shaw et al., 1994). Overall, both the surface water and groundwater exhibited an oxidized condition, thus the dominant species of N was NO$_3^-$ and the oxygen isotope values was negative indicating almost no denitrification process in the surface water (Widory et al., 2005). The mean concentrations of NH$_4^-$N in the groundwater were only 0.55 mg/L in the urban area and 0.28 mg/L in the mining area (Fig. 5a and Table S4). Therefore, the high NO$_3^-$ concentrations in groundwater can be explained mostly due to the NO$_3^-$ formation by nitrification from NH$_4^-$N in the surface waters, which entered thereafter in the groundwater increasing the concentrations of NO$_3^-$ in the groundwaters (Fig. 5a).

There is little denitrification process contribution to the N transformations under oxidant status of surface water (Ye et al., 2021), which is different from the mechanism of denitrification for groundwater. The oxidizing conditions of groundwater from mining areas inhibited the denitrification process and the isotopic values of δ$^{15}$N-NO$_3^-$ and δ$^{18}$N-NO$_3^-$ also proved that the denitrification process was nonexistent. Specifically, the surface water and groundwater were scattered, which were not located along the denitrification lines of 1:1 or 2:1 (Fig. 5b) (Kendall, 2007). In addition, ln (NO$_3^-$N) and δ$^{13}$N-NO$_3^-$ had a weak positive correlation (Fig. 5c), indicating that the results of denitrification of the groundwater in the mining area was negligible (Fukada et al., 2004; Kendall et al., 2007). In the groundwater of urban areas, the denitrification process was also absent. Despite the fact that the groundwater samples in the urban area showed a scattered distribution along the denitrification line of 1:1 or 2:1 (Fig. 5b), the correlation between ln (NO$_3^-$N) and δ$^{15}$N-NO$_3^-$ was not significant negative in these surface water and groundwater samples ($p > 0.05$) (Fig. 5c). Therefore, there was a weak denitrification process in both the surface water and groundwater from the mining and urban areas.

4.1.3. Water-rock reaction

The relationship between the ionic components of surface water and groundwater reflects the different source of water element composition and the characteristics of the water-rock reaction (Kacem et al., 2016), which provides strong evidence for revealing the effect of natural processes. The lithology of the recharge area and development of karst conduits typically play a crucial role in shaping the chemical properties of karst groundwater (Hartmann et al., 2014; Kalhor et al., 2019). Surface water and groundwater were mainly sampled from the Emeishan hills O-O in the nitrification oxidation process (Eq. 2) (Kendall et al., 2007; Ye et al., 2021). Due to O exchanges, less than one-sixth of the oxygen in the new NO$_3^-$N is from Oair (Kool et al., 2011; Sigman et al., 2009). Assuming that one-sixth of the oxygen in NO$_3^-$N is from Oair in the ammonia oxidation process and the remaining five-sixth of the oxygen is from H$_2$O-O in the nitrification oxidation process, the theoretical values of δ$^{18}$O-NO$_3^-$ will be lower than those in the Eq. 3 (Ye et al., 2021).

\[
\delta^{18}O-\text{NO}_3^- = 2/3 \delta^{18}O-H_2O + 1/3 \delta^{18}O_{air} \tag{2}
\]

\[
\delta^{18}O-\text{NO}_3^- = 5/6 \delta^{18}O-H_2O + 1/6 \delta^{18}O_{air} \tag{3}
\]
Fig. 3. Boxplots for NH$_4^+$-N, NO$_3^-$-N, SO$_4^{2-}$ and HCO$_3^-$ concentrations, and δD-H$_2$O, δ$^{18}$O-H$_2$O, δ$^{15}$N-NH$_4^+$, δ$^{15}$N-NO$_3^-$, δ$^{18}$O-NO$_3^-$, δ$^{34}$S-SO$_4^{2-}$, δ$^{18}$O- SO$_4^{2-}$ and δ$^{13}$C- HCO$_3^-$ of groundwater (a, c and d) and surface water (b, e and f) in the urban and the mining areas.
basalt, Longtan Formation, Permian (Pdj and Psj), Datang Formation, Carboniferous (Cjd), and Triassic (Tjd, Tjyn and Tdg) which mainly contained detrital rock, dolomite, and limestone (Fig. 2 and Table S7). The water-rock interaction among calcite, dolomite, and aquifer bedrock leads to significant variations of HCO$_3^-$, Mg$^{2+}$ and Ca$^{2+}$ concentrations in water samples (Fig. S1 and S3). According to the previous studies, carbonic acid could weather carbonate and silicate (Galy and France-Lanord, 1999; Spence and Telmer, 2005) (Eqs. 4 and 5). Lime- stone and dolomite were the dominant minerals of the site rocks, and the water quality was mainly HCO$_3^-$Ca and HCO$_3^-$Ca-Mg type (Fig. 2 and Fig. S1).

$$\text{CaMg(CO}_3\text{)}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + \text{Ca}^{2+} + 4\text{HCO}_3^-$$  \hspace{1cm} (4)

$$\text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$$  \hspace{1cm} (5)

The contributions of rock weathering for the compositions of main elements in the water have been described by the mixing of three major end-members from the products of weathering: carbonates, silicates, and evaporites (Mia et al., 2022; Olivier et al., 2010). Consequently, the dissolution of carbonate appeared to be the primary contributor to the composition of major ions in the groundwater, whereas the dissolution between carbonate and silicate was the main contributor in the surface water as expected in a karst area (Han and Liu, 2004). From the urban and mining areas, the samples of groundwater and surface water are displayed in plots of the Na-normalized molar ratios (Fig. 6). The groundwater and surface water with low ratios of HCO$_3^-$/Na$^+$, Mg$^{2+}$/Na$^+$, and Ca$^{2+}$/Na$^+$ were likely influenced by the dissolutions between silicates and evaporites. The contributions from the dissolution of evaporite responded to the end-member of low-Mg$^{2+}$/Na$^+$, Ca$^{2+}$/Na$^+$ and low-Na$^+$ which was close to the left lower corner. The contributions from the dissolution of carbonate in the groundwater responded to the end-members of high-Ca$^{2+}$ and high-HCO$_3^-$ which were close to the right upper corner (Li et al., 2018). The water samples with the highest molar ratios of Mg$^{2+}$/Na$^+$, HCO$_3^-$/Na$^+$ and Ca$^{2+}$/Na$^+$ were weathered from the zones of high carbonate ratios, and the samples located towards the end-member of carbonate in the Fig. 6.

4.2. Source apportionment and interaction in the KCZ

Under complex land use in a typical karst mining area, urbanization (Barron et al., 2013; Graniel et al., 1999), agricultural and mining activities (Sun et al., 2017; Yue et al., 2020; Zeng et al., 2020) change the various components of groundwater and surface water. The maximum concentrations of NO$_3^-$N were 13.81 mg/L, 4.75 mg/L, 31.91 mg/L, and 6.22 mg/L in the UG, US, MG, and MS, respectively (Table S4 and Fig. S4), which were not suitable for drinking (EPA., 2002). The maximum concentrations of SO$_4^{2-}$ were 179.61 mg/L and 204.35 mg/L in the UG and MG, respectively (Table S4 and Fig. S5), which were classified as III level for industrial and agricultural use (QSA., 2017). Besides these assessments of NO$_3^-$N and SO$_4^{2-}$ concentrations, disentangling the sources of them is the most important foundation for controlling pollutions.

4.2.1. Nitrogen

In urban areas, the contributions of soil N, manure and sewage to the groundwater, soil N and chemical fertilizer to the surface water were the dominant sources of NO$_3^-$N (Table 1), which showed different pollution types in the groundwater and surface water. The quality of groundwater showed a trend of manure and sewage input (Fig. 5d) because of its frequent exchange with surface water, as discussed in Section 4.1.1, or leaked from the sewer. The soil N in the groundwater was mainly leached from the farmland, forest, and grassland in the sample locations of urban areas (Fig. 1). The N runoff by soil erosion would also be the critical source of soil N in the surface water (Chen et al., 2021; Melese et al., 2021). Therefore, except for the different sources, the key drivers of N pollution between surface water and groundwater were transformation and migration. Differences in migration paths would lead to changes in these different proportions between surface water and groundwater of chemical fertilizer, manure and sewage, which are directly related to the level of domestic sewage discharge (Dong and Xu, 2020), mineralization, nitrification and denitrification in soils (Coskun et al., 2017; Geiseler et al., 2010). The mean concentration of NO$_3^-$N in the groundwater was significantly higher than that in the surface water. The maximum concentration of NO$_3^-$N in groundwater of mining area was 31.91 mg/L (MG8), which was affected by untreated domestic sewage discharged from the living area of coal miners and farmers, and leached from application of manure in the farmland (Torres et al., 2020; Ye et al., 2021).

Farmland and coal mining industrial areas account for 85 % and 14 % of the land in total mining area, respectively (Fig. 1 and Table S1). The pollutants were mainly inorganic N from farmland, high sulfide and low pH from the two coal mine industrial areas, because pollution from non-point sources was the major source of inorganic N in the mining area (Sikhosana et al., 2020; Zhang et al., 2021). Surface water and groundwater in the mining area showed a trend of agricultural input from N runoff (Fig. 5d) (Wang and Li, 2019). Specifically, N runoff caused by leaching and soil erosion is the major pathway in farmland watersheds and is one of the critical factors which would influence N transformation (Park et al., 2011; Rong et al., 2020). Atmospheric N in the mining area was relatively higher compared to that in the urban area, because there is a local coal power plant in the mining area with an installed capacity of 3 × 200,000 kW (https://ymzfld.dizbbox.com/). Therefore, atmospheric deposition of N in the mining area was also a source of NO$_3^-$N (Pan et al., 2012; Yau et al., 2020).

4.2.2. Sulfate

There were mainly four sources of SO$_4^{2-}$ in our study area, including oxidation of reduced inorganic S, such as pyrite associated with coal (Hong et al., 1993; Ren et al., 2019) and other reduced inorganic S compounds in detrital rock (Krouse and Mayer, 2000), soil S (Torres et al., 2020; Zhang et al., 2015), manure and sewage (Otero et al., 2007; Zhang et al., 2024), and atmospheric deposition (Krouse and Mayer, 2000) (Fig. 7a). In a previous study, SO$_4^{2-}$ with an acid mining discharge was mainly from the oxidation of pyrite in coal mining areas, which offered enough chemical reacting H$_2$SO$_4$ and was involved in the geochemical reaction actively due to the mechanisms of the following reactions (Eqs. 6, 7, and 8) (van Everdingen and Krouse, 1985). From the

Fig. 4. Scatter plots for δD-H$_2$O and δ$^{18}$O-H$_2$O of groundwater and surface water in the urban and the mining areas.
The proportion of SO$_4^{2-}$ in the groundwater (36%) was lower than that in the surface water (68%), showing that the surface water was polluted more seriously by the mine discharge than that in the groundwater. In addition, the coal resources were abundant and mining industries were very active (Ye et al., 2019). Hence the most severely polluted source of SO$_4^{2-}$ was from pyrite oxidation in the surface water in the mining area (Eqs. 6, 7 and 8):

$$2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{3+} + 4\text{SO}_4^{2-} + 4\text{H}^+ \quad (6)$$

$$4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \quad (7)$$

$$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad (8)$$

In the surface water and groundwater, lithospheric S compounds were the largest contributor to SO$_4^{2-}$ from the urban area, indicating the reaction of water-rock in the pathway of flow (Krouse and Mayer, 2000). In general, gypsum dissolution might be a primary water-rock reaction for the increase in concentration of SO$_4^{2-}$. However, there was almost no gypsum formation in the geologic map of our study area (Table S7). In addition, the saturation index of gypsum calculated using PHREEQC for groundwater from urban and mining areas was unsaturated (Ye et al., 2019; Ye et al., 2017). Therefore, SO$_4^{2-}$ can be contributed from the oxidation products of reduced inorganic S in the urban area (Krouse and Mayer, 2000), which accounted 51% in the groundwater and 65% in the surface water. Soil S was the second largest contributor to the source of SO$_4^{2-}$ in surface water (15%) and groundwater (28%) (Table 2), which need to be considered in a conclusive interpretation of the sources of SO$_4^{2-}$. Soil S exists in inorganic and organic binding forms (Sanchez, 2019). Inorganic S may directly occur in soil solution, which is easy to migrate with the movement of groundwater. Organically bound S, such as carbon-bonded S, would mineralize and result in SO$_4^{2-}$ formation (Krouse and Mayer, 2000).

Manure and sewage were the third largest contributors of SO$_4^{2-}$ to groundwater in the mining area. Thus, more than the urban area, waters in the mining area were also affected by the same source of manure and sewage as N pollution (Torres et al., 2020). The groundwater was more susceptible to SO$_4^{2-}$ pollution than surface water, for there were more pollutants from manure and sewage introduced into groundwater (16%) than surface water (11%) (Table 2). Acid rain has frequently occurred in Southwest China since the late 1970s and the early 1980s.
Based on data from the monitoring stations, the pH isolines showed that the pH of rain was lower than 4.4 in Guizhou Province, China from 1993 to 2001 (Wu et al., 2013). The contribution of atmospheric S sources could not be ignored (Ren et al., 2021), due to the high emission of sulfur dioxide, 152,700 tons in 2015 (https://ymzfd.dlzbxx.com/). Deposition of atmospheric S contributed 7% in the mining area and 8% in the urban area to SO$_4^{2-}$ of the surface water, respectively (Table 2). Due to exchange of SO$_4^{2-}$ between groundwater and surface water, SO$_4^{2-}$ was preserved and accumulated in groundwater (16% and 13% from the urban and mining areas, respectively) and had not been reduced under the redox conditions (Fig. 7b and S2b).

4.2.3. Carbon

There were three major sources in the end-member mixing diagrams, and most of the samples originated from natural sources (Fig. 8a). When CO$_2$(g) from atmosphere was dissolved in waters, the value of $\delta^{13}$C was approximately $-7\%$ and $-8\%$. The CO$_2$ in soils is derived from decarbonization, and the respiration of plant roots and soil microorganisms (Li et al., 2019). The diffusion rate of CO$_2$ and the composition ratio of C$_3$ plants to C$_4$ plants would control values of $\delta^{13}$C-CO$_2$ (Yao et al., 2007). Guizhou Province was primarily populated with C$_3$ plants and the $\delta^{13}$C-DIC of soil was approximately $24\%$ (Lang et al., 2006). Specifically, the $\delta^{13}$C-DIC ranged from $17.94\%$ to $12.74\%$ in the urban area and $-33.25\%$ to $-11.55\%$ in the mining area, which was consistent with the two results from soil CO$_2$ and carbonate dissolution (Fig. 8b).

According to a previous study, the signature of $\delta^{13}$C-POC (particulate organic C) was $-25\%$ in Southwest China, the $\delta^{13}$C of soil CO$_2$ was $-21\%$, and the proportion of the fractionation value of $\delta^{13}$C caused by the diffusion of $^{13}$CO$_2$(g) was approximately $4.4\%$ (Li et al., 2008). The $\delta^{13}$C value of the carbonate minerals was $0\%$. There were rich dolomite and limestone formations in the study area (Table S7). Consequently, the $\delta^{13}$C-DIC which resulted from soil CO$_2$ and carbonate dissolution would be $11\% \pm 2\%$, because HCO$_3^-$ was from CO$_2$(aq) ($\delta^{13}$C = $-22\%$ in CO$_2$(aq)) and the CaCO$_3$ ($\delta^{13}$C = $0\%$) with approximately equal proportions (Li et al., 2010). In addition, the water-carbonate reaction was a major inorganic carbon source in the urban area because of the
significant positive Pearson correlation between Ca$^{2+}$ and HCO$_3^-$ ($p < 0.01$).

Sulfide oxidation could enhance carbonate dissolved and increase CO$_2$ release from dissolution of carbonate to surface water and groundwater, especially in the coal mining area of a karst region. According to a previous study of carbonate weathering by sulfuric acid (Eqs. 9 and 10) (Torres et al., 2014), there was a strong relationship between sulfide oxidation and C erosion (Calmels et al., 2007). The results showed that sulfide oxidation could enhance carbonate dissolution and increase CO$_2$ release from dissolution of carbonate (Torres et al., 2014). The dissolution of carbonate rocks would cause irreversible damage to the dolomite, and limestone of critical karst surface zones. In addition, the C release from the lithosphere to hydrosphere and thereafter to the atmosphere was underappreciated.

$$2\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow 2\text{Ca}^{2+} + 2\text{HCO}_3^- + \text{SO}_4^{2-}$$

$$\text{HCO}_3^- + \text{H}_2\text{SO}_4 \rightarrow \text{SO}_4^{2-} + \text{CO}_2(g) + \text{H}_2\text{O}$$

As the dilution process has not an effect on the isotopic composition of S, the analysis of $\delta^{34}$S-SO$_4^{2-}$ in water samples provided an excellent discrimination tool for quantifying the influence of mining activities on both the surface water and groundwater in the mining area (Otero and Soler, 2002). In the whole urban and mining areas, the combined percentage of inorganic S oxidation as the source of SO$_4^{2-}$ was 20 % in both surface and groundwater, contributing to the overall average value. Therefore, sulfuric acid which was produced by the oxidation of pyrite could react with carbonate rock in karst regions, which could increase CO$_2$ production and decrease HCO$_3^-$ in groundwater and surface water (Eqs. 9 and 10). This irreversible reaction erodes carbonates and releases generally unrecognized C into the Earth’s atmosphere, which should be considered a potentially important factor in the long-term C cycle. Therefore, carbonate dissolution coupled with sulfide oxidation is an important C source, and C is carried from the lithosphere to the hydrosphere in this reaction.

5. Conclusions

We demonstrated the effectiveness of multiple isotope methods (N, S, C, hydrogen, and O) and the MixSIAR model in unraveling the complexities of pollutant sources and transformation mechanisms in a karst critical zone (KCZ) under intricate land use patterns. Nitrification was the prevalent process in the N cycle within surface water in both urban and mining areas. Conversely, nitrification was relatively weak in groundwater. Denitrification’s contribution to the N cycle in groundwater and surface water was minimal. Soil was the predominant contributor to inorganic N in groundwater (48 %) and surface water (49 %). In urban and mining areas, sewage and manure emerged as secondary contributors to inorganic N in surface water, accounting for 46 % ~ 47 %. The oxidation of reduced inorganic S constituted the major source of SO$_4^{2-}$. The mining area’s groundwater was vulnerable to SO$_4^{2-}$ pollution from pyrite oxidation due to frequent exchanges with surface water. Isotope values indicated that interactions among water, carbonates, and soil respiration were major sources of CO$_2$ and HCO$_3^-$ in groundwater and surface water. Additionally, sulfide oxidation could enhance carbonate dissolution, increasing CO$_2$ release when H$^+$ and SO$_4^{2-}$ produced. These findings provide valuable insights into the coupling of sulfide oxidation and carbonate dissolution from various quantitative sources. Understanding these processes is instrumental for effective karst water management and comprehending anthropogenic impacts on the biogeochemical coupling of N, S, and C in KCZs.

CRediT authorship contribution statement

Huijun Ye: Conceptualization, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing. Zhiwei Han: Conceptualization, Methodology, Writing – original draft, Writing – review & editing. Pan Wu: Conceptualization, Supervision, Writing – review & editing. Xuefang Zha: Conceptualization, Investigation. Xuexian Li: Investigation. Enqing Hou: Writing – review & editing. Yingjie Cao: Writing – review & editing. Changyuan Tang: Writing – review & editing. Ruixue Zhang: Conceptualization, Methodology, Supervision, Writing – original draft, Writing – review & editing. Jordi Sardans: Methodology, Writing – review & editing. Josep Peñuelas: Methodology, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing interests that could influence the work reported in this paper.

Data availability

Data will be made available on request.


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