Identification of Anthropogenic and Natural Inputs of Sulfate into River System of Carbonate Zn-Pb Mining Area in Southwest China: Evidence from Hydrochemical Composition, $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$

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Abstract: The release of pollutants from lead-zinc mining areas poses a significant threat to the environment, making pollution tracing crucial for environmental protection. However, the complexity of carbonate mining areas makes tracing these pollutants challenging. This study used $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ isotopes combined with the Stable Isotope Mixing Models in R (SIMMR) to assess anthropogenic sulfate sources in the Daliangzi mining area. The river water types were mainly $Ca^{2+}$-$Mg^{2+}$-$HCO_3^-$ and $SO_4^{2-}$, which are significantly influenced by dolomite dissolution. The $\delta^{34}S_{SO_4}$ values ranged from 6.47‰ to 17.96‰ and the $\delta^{18}O_{SO_4}$ values ranged from $-5.66‰$ to $13.98‰$. The SIMMR results showed that evaporite dissolution in tributaries, driven by gypsum, contributed 31% of sulfate, while sulfide oxidation, sewage, and atmospheric deposition contributed 19%, 18%, and 24%, respectively. The tailings pond near Xincha Creek has a higher sulfate release potential than the processing plant near Cha Creek. In the mainstream, sulfide oxidation contributed 25%, primarily from mine drainage. Anthropogenic sources, including sulfide oxidation, fertilizers, and sewage, made up about 50% of the total sulfate, with sulfide oxidation accounting for half of this input. The strong correlation between the Zn and $SO_4^{2-}$ concentrations ($R^2 = 0.82$) and between the Zn and the contribution from the sulfide oxidation ($R^2 = 0.67$) indicates their co-release during sulfide oxidation, making $SO_4^{2-}$ a proxy for tracing Zn sources. This study highlights the utility of $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ with SIMMR in tracing anthropogenic inputs and underscores the significant impact of mining on river systems and the sulfur cycle.

Keywords: sulfate; $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$; SIMMR; hydrochemical; Zn-Pb mining area; Daliangzi

1. Introduction

The mine production levels of lead and zinc in China were estimated to be 1.9 million tons and 4 million tons, respectively, in 2023, according to the United States Geological Survey [1]. These figures indicate that China is now the world’s largest producer of lead and zinc. However, this also means that a large amount of lead, zinc, and related cadmium could be released into the environment, especially water systems, through mining, smelting, and tailings disposal, posing a serious threat to human health [2–5].

The identification of sources and pathways of heavy metals is essential, and it is a prerequisite for addressing environmental health issues. Common anthropogenic source of heavy metals are the mining-related activities of coal or metal deposits in mining
areas [6,7]. The leaching of acid mine drainage (AMD) is the main pathway through which these mining activities impact the surrounding environment [8–10]. However, due to the buffer effect caused by carbonate dissolution, maintaining a steady neutral pH can reduce the concentrations of dissolved metals in carbonate mining areas [11]. This buffering effect complicates conventional tracing methods such as Pb isotopes. Additionally, if pollution sources involve multiple weak sources rather than a few strong ones, or if the Pb isotopic composition of anthropogenic and natural sources are similar, there is significant uncertainty in using Pb isotopes for source identification [12]. Some studies have already indicated that the genesis of local lead-zinc deposits is closely related to the source of ore-forming materials from the carbonate surrounding rocks [13], further complicating Pb isotope tracing in these regions.

The formation process of AMD indicates that sulfur and heavy metals are released simultaneously [14,15], which makes it possible to use sulfate to trace the sources of metals. Relying on water chemistry and traditional ion source identification methods to accurately distinguish the sources of components in water is becoming increasingly difficult. For example, relying on the concentration of sulfate (SO$_4^{2-}$) and its ratio to chloride (Cl$^-$) for determining the source of sulfate is no longer sufficient to meet requirements [16]. It is also challenging to trace the sources of sulfur in water bodies solely through $\delta^{34}$S$_{SO_4}$, primarily because sulfur sources are numerous and the $\delta^{34}$S values among different sulfur sources can be quite similar. For example, Cao et al. identified the sources of sulfate in wetlands in karst areas and found that the $\delta^{34}$S$_{SO_4}$ values for atmospheric deposition ranged from $-12$‰ to $+9.4$‰, while those for pyrite dissolution and oxidation ranged from $-40$‰ to $+5$‰, with substantial overlap between the two ranges [17]. Guan et al. studied the sources of sulfate in pine needles and found that the $\delta^{34}$S$_{SO_4}$ values in soil were approximately $-5.5$‰, and those in atmospheric dust were around $-4.9$‰, which are very similar. Thus, relying solely on $\delta^{34}$S$_{SO_4}$ is insufficient to clearly distinguish their sources, but the inclusion of $\delta^{18}$O$_{SO_4}$ can resolve this issue [18]. The method of coupling $\delta^{34}$S$_{SO_4}$ and $\delta^{18}$O$_{SO_4}$ data has been successfully applied to trace its sources in water systems [19–23].

The Daliangzi lead-zinc mining area has a long history of mining development and has evolved into a human settlement centered around the lead-zinc industry. The region features small-scale crop farming and has extensive outcrops of carbonate rocks. Consequently, the river system receives inputs from both anthropogenic and natural sources, resulting in a complex mixture of input sources. Anthropogenic activities such as mining, agriculture, and sewage significantly impact riverine sulfate concentrations. To address these challenges, this study was designed to accurately determine the contributions of various sulfate sources using $\delta^{34}$S$_{SO_4}$ and $\delta^{18}$O$_{SO_4}$ isotopes combined with the Stable Isotope Mixing Models in R (SIMMR). The isotope mass balance mixing model can be used to determine sulfur-source contributions [18,24]. However, SIMMR based on a Bayesian statistical framework is a more precise method to identify source contributions, especially when there are more than three potential sources [25–27]. Samples from local sulfate sources and river water were collected in the Daliangzi mining area. The analysis revealed significant contributions from evaporite dissolution, sulfide oxidation, sewage, and atmospheric deposition. The results highlight the substantial impact of anthropogenic activities, particularly mining, on water quality. This research provides a comprehensive understanding of the interactions between natural processes and human activities in mining-impacted watersheds, which are essential for effective environmental protection and pollution management. By elucidating the sources and pathways of sulfate pollution, this study contributes to the development of targeted strategies for mitigating the adverse effects of mining and other human activities on river systems. Understanding these interactions is crucial for the implementation of effective environmental policies and the sustainable management of water resources in mining regions.
2. Materials and Methods

2.1. Study Area

The Daliangzi Pb-Zn Mining area is located in Daqiao town, Huidong county, Sichuan Province, southwestern China (Figure 1a). The climate is monsoonal and subtropical high-prototype. The average annual temperature is 16.17 °C. The average annual precipitation in Huidong county is 1063 mm, of which 80% occurs between June and September. The Daqiao River, which features the largest surface runoff in the study area, flows from northwest to southeast and merges into the Jinsha River. Xincha Creek and Cha Creek are tributaries of the Daqiao River. The mine area includes a tailing dump, concentrating mill, and minery. The tailing dump is located in the Xincha Creek Basin, with a leachate circulation tank and a connecting ditch. The concentrating mill is situated in the Cha Creek Basin, releasing treated wastewater into Cha Creek. The mine is located near the Daqiao River, with mine drainage flowing directly into the river.

Figure 1. Geological map and sampling points. (a) The location of Daliangzi Zn-Pb mining area; (b) Stratigraphy and structure of the study area; (c) The locations of the mainstream, tributaries, and water samples collected in the Daqiao River Basin. Note: The red points represent mine water, the gray points represent tailings leachate, the orange points represent main stream water samples, and the white points represent tributary water samples.
The stratigraphy of the area includes pre-Sinian metamorphic rocks, Sinian and Palaeozoic carbonates, Mesozoic terrestrial red clastic rocks, and Quaternary deposits in valleys and basins. The major ore minerals are sphalerite and galena (Figure 1b). Mining activities started in the 1950s and continue, in the present [13].

2.2. Sample Collection and Analysis

A total of 18 surface water samples were collected in the study area in June 2019, including 10 mainstream samples and 8 tributary samples. Meanwhile, 2 mining drainage samples and 2 tailings leachate samples were collected, as well as 1 spring sample. Figure 1c illustrates the distribution of the sampling points.

The water samples that were collected in PE bottles were then filtered through a 0.45-micrometer-pore-size membrane and filled into precleaned 50-milliliter polypropylene tubes. Samples for the analysis of cations were preserved by adding a few drops of concentrated HNO$_3$ to maintain pH < 2. Sample bottles for the analysis of cations, anions, $\delta^{34}$SO$_4$ and $\delta^{18}$O SO$_4$ were completely filled and capped with elastic laboratory film to avoid air contact and stored in an ice box or refrigerator at 4°C until analysis.

The concentrations of major ions, including calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), chloride (Cl), sulfate (SO$_4$), and total dissolved solids (TDS), were analyzed using a combination of ICP-AES (Perkin Elmer OPTIMA 3000 XL, Beijing, China) and IC (Dionex 120, Beijing, China). Minor and trace elements such as zinc (Zn) and lead (Pb) were analyzed using ICP-MS (Perkin Elmer ELAN 3000, Beijing, China). These analyses were conducted by Sichuan Tianshengyuan Environmental Services Co., Ltd. (Chengdu, China). The pH of the water samples was tested on-site using a WTW Multi 340i/SET multi-parameter instrument (Weilheim, Germany). The detection of $\delta^{34}$SO$_4$ and $\delta^{18}$O SO$_4$ was conducted using BaSO$_4$ precipitation. The testing and analysis were performed by Beijing Createch Testing Technology Co., Ltd. (Beijing, China), using a 253 Plus + Flash EA (Thermo Fisher Scientific, Waltham, MA, USA) instrument. The detailed testing procedures and methods are described in relevant studies [16,28,29].

2.3. Data Analysis

The Stable Isotope Mixing Models in R (SIMMR) is an R package (4.1) used to analyze stable isotope compositions within a Bayesian framework. It employs the Markov chain Monte Carlo (MCMC) algorithm to estimate the contributions of different sources to a mixture. The model is described by the following equations:

\[
X_{ij} = \sum_{k=1}^{K} P_k \left( s_{jk} + c_{jk} \right) + \varepsilon_{ij} \tag{1}
\]

\[
s_{jk} \sim N \left( \mu_{jk}, \omega_{jk}^2 \right) \tag{2}
\]

\[
c_{jk} \sim N \left( \lambda_{jk}, \tau_{jk}^2 \right) \tag{3}
\]

\[
\varepsilon_{ij} \sim N \left( 0, \sigma_j^2 \right) \tag{4}
\]

where the following apply:

- $X_{ij}$ is the isotope value $j$ of the mixture $i$ (in this study $j = \delta^{34}$SO$_4$ and $\delta^{18}$O SO$_4$).
- $s_{jk}$ is the source value $k$ of isotope $j$, normally distributed with mean $\mu_{jk}$ and standard deviation $\omega_{jk}$.
- $P_k$ is the contribution of source $P_k$, estimated by the SIMMR model. Five sulfate sources were included in this study ($k = 5$).
- $c_{jk}$ is the fractionation factor for isotope $j$ of source $k$, normally distributed with a mean value $\lambda_{jk}$ and standard deviation $\tau_{jk}$. Fractionation factors were neglected due to the slow exchange of $\delta^{34}$SO$_4$ and $\delta^{18}$O SO$_4$ after sulfate enters water [30].
• \( \varepsilon_{ij} \) is the residual error, representing additional unquantified variation between individual mixtures, normally distributed with mean 0 and standard deviation \( \sigma_j \). In this study, the residual error was not considered.

A detailed explanation of the model can be found in relevant studies [28,31].

A normality test was conducted, and the results indicated that \( p > 0.05 \). Differences were assessed using a one-way analysis of variance (ANOVA), with significance set at \( p < 0.05 \). All statistical analyses were carried out using OriginPro 2021 software (OriginLab Corporation, Northampton, MA, USA).

3. Results

3.1. Hydrochemical Characteristics

The hydrochemical analysis of the Daliangzi mining area reveals significant variations among different sample types (Table 1), including tailings leachate (L1, L2), mining drainage (MD1, MD2), tributaries (T1–T8), springs (S01), and the mainstream river (M01–M10).

### Table 1. Water sample and source temple parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>HCO(_3)</th>
<th>SO(_4^{2-})</th>
<th>Cl(^-)</th>
<th>Pb</th>
<th>Zn</th>
<th>TDS</th>
<th>( \delta^{34})SO(_4)</th>
<th>( \delta^{18})O(_{SO4})</th>
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<td>53</td>
<td>55</td>
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<td>4.41</td>
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<td>31.1</td>
<td>35.4</td>
<td>123</td>
<td>1155.41</td>
<td>53.5</td>
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<td>183</td>
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<td>2.26</td>
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<td>0.06</td>
<td>334.63</td>
<td>12.63</td>
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Note: PH is dimensionless, \( \delta^{34}\)SO\(_4\) and \( \delta^{18}\)O\(_{SO4}\) values are in ‰, and the rest are in mg/L.

The tailings leachate samples exhibited extremely high pH values (10.5–10.9) and very high calcium concentrations (501 mg/L). The magnesium ranged from 7.29 to 10.9 mg/L, while the sodium and potassium concentrations were 33.5–34.4 mg/L and 53–68.8 mg/L, respectively. The sulfate concentrations were notably high, averaging 1145.68 mg/L, and the TDS values were exceptionally high, ranging from 1281 to 1296 mg/L. In contrast, the mining drainage samples had neutral pH values (7.94–8.1). The calcium concentrations were significantly lower (44.1–79.2 mg/L), and the magnesium levels were higher (41.3–57.7 mg/L) compared to the tailings leachate. The sodium and potassium levels were
relatively low (1–5.2 mg/L and 1.1–2.4 mg/L). The sulfate concentrations were considerably lower, averaging 184.36 mg/L, and the TDS values were also lower, averaging 357.5 mg/L. The differences between the tailings leachate and the mining drainage can be attributed to the flotation process used in lead-zinc mining. This process typically involves both gravity flotation and the addition of reagents to enhance the separation of lead and zinc. Xanthate (ROCSSNa, where R is an alkyl group) is a commonly used flotation agent. Additionally, lime (CaO) is often added during post-treatment to neutralize the flotation reagents [32]. This results in the extremely high pH and altered chemical composition observed in the tailings leachate.

The spring water sample exhibited an alkaline pH of 9.06 and a remarkably low TDS content of 55 mg/L, indicating that it was low-salinity water. The primary cations, ranked by concentration, were sodium (23.5 mg/L), calcium (10 mg/L), potassium (8.6 mg/L), and magnesium (7.29 mg/L). Notably, the Pb concentration was below the detection limit (0.01 mg/L), and Zn was detected at a concentration of 0.037 mg/L. Among the anions, sulfate was the most prevalent (31.76 mg/L), followed by bicarbonate (4.9 mg/L), nitrate (3.57 mg/L), and chloride (0.52 mg/L). The composition characteristics of the spring sample, in comparison to the other samples, suggested minimal anthropogenic influence.

The tributaries exhibited pH values ranging from 7.33 to 8.41. The calcium concentrations showed a wide range (28.1–463.9 mg/L), with the magnesium levels varying from 17.6 to 28.6 mg/L. The sodium and potassium concentrations were generally low. The sulfate concentrations also varied widely (18.21–1155.41 mg/L), with an average of 178.38 mg/L. The chloride and nitrate levels varied significantly, and the TDS values averaged 334.63 mg/L. The mainstream samples displayed pH values from 7.74 to 8.39, which were slightly lower than those of the tributaries. The calcium concentrations ranged from 24 to 52.1 mg/L, which were generally lower than those in the tributaries, while the magnesium levels varied from 12.2 to 26.7 mg/L. The sodium and potassium levels were also low. The sulfate concentrations were relatively stable, averaging 25.124 mg/L. The chloride and nitrate levels were low, and the TDS values averaged 180.7 mg/L, indicating lower mineral content compared to the tributaries. The tributaries exhibited higher variability in terms of ion concentrations compared to the more stable conditions of the mainstream. These variations were influenced by both natural processes and anthropogenic activities, with the mining activities significantly impacting the tributaries more frequently than the mainstream. Slightly alkaline pH is very common in carbonate rock areas due to the release of HCO_3^- ions from the dissolution of carbonate rocks [11,33,34].

### 3.2. Sulfur and Oxygen Isotope Values of Sulfate

The δ³⁴S_SO₄ and δ¹⁸O_SO₄ values for the tailings leachate were comparatively low and moderate, respectively. The δ³⁴S_SO₄ values ranged from +6.47 to +6.48‰, with an average of +6.475‰, while the δ¹⁸O_SO₄ values ranged from +5.56 to +7.46‰, averaging +6.51‰. The mine drainage samples showed moderate δ³⁴S_SO₄ values, ranging from +6.93 to +9.55‰, and notably negative δ¹⁸O_SO₄ values, ranging from −5.66 to −3.70‰. This difference reflects the distinct geochemical processes involved in mine water drainage compared to tailings leachate. The addition of flotation agents during ore processing could be one contributing factor. Additionally, the recycling of tailings leachate and evaporation may amplify the influence of atmospheric precipitation on the isotopes [24].

The δ³⁴S_SO₄ and δ¹⁸O_SO₄ values for the tailings leachate tributary samples displayed a broad range, from +8.17‰ to +14.92‰ for the δ³⁴S_SO₄ and from +1.37‰ to +13.52‰ for the δ¹⁸O_SO₄. In contrast, the mainstream river samples exhibited higher and more consistent values: the δ³⁴S_SO₄ ranged from +11.50‰ to +17.86‰ and the δ¹⁸O_SO₄ ranged from +1.91‰ to +11.95‰. This suggests that the stable isotope values in the mainstream indicated a more consistent source of sulfate or, alternatively, that the variation in source contributions was less pronounced compared to the tributaries.

The δ³⁴S_SO₄ and δ¹⁸O_SO₄ values for the tailing for the spring sample were +17.96‰ and +13.98‰, respectively. These values indicate a heavier isotope composition, suggesting
that the sulfate in the spring water was influenced by the dissolution of evaporite minerals, particularly gypsum.

4. Discussion

4.1. Impact of Water–Rock Interaction Processes on the Hydrochemical Compositions

According to the Piper diagram (Figure 2), most of the samples plot extremely near the Ca$^{2+}$ and Mg$^{2+}$ line, indicating that the water chemistry is strongly influenced by the weathering or dissolution of carbonate rocks, such as dolomite ($\text{CaMg(CO}_3\text{)}_2$). The higher proportion of bicarbonate ions ($\text{HCO}_3^-$) in the tributary and mainstream water samples further supports this process. Additionally, many water samples plot close to the SO$_4^{2-}$ end, suggesting an association with the dissolution of evaporite rocks and the oxidation of sulfide minerals. The water samples are mainly dominated by Ca$^{2+}$-Mg$^{2+}$-HCO$_3^-$ and SO$_4^{2-}$, indicating that the hydrochemical evolution involves these processes. The distinct positions of the tailing leachate and mine drainage points on the diagram suggest different evolutionary processes from those of the other water samples.

![Figure 2. Piper diagram of different types of water sample in Daliangzi mining area.](image)

The sulfate concentration is crucial for distinguishing the chemical processes in water. Therefore, correlations between sulfate concentrations and other major anions or cations can be employed to determine the end sources affecting types of water [35]. To better understand these sources, a correlation was established between the sulfate and several major anions or cations in the water. According to the scatter plots (Figure 3), there was a good positive linear correlation between SO$_4^{2-}$ and Ca$^{2+}$, SO$_4^{2-}$ and Na$^+$ + K$^+$, SO$_4^{2-}$ and Cl$^-$, and SO$_4^{2-}$ and TDS in most of the samples. Conversely, there was a negative correlation between SO$_4^{2-}$ and HCO$_3^-$, while there was no obvious correlation between SO$_4^{2-}$ and Mg$^{2+}$. 


water samples in the study area is neutral to slightly alkaline, a buffering effect occurs with bicarbonate (HCO$_3^-$). Dissolution processes can be expressed by the following reactions [40]:

\begin{equation}
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-
\end{equation}

\begin{equation}
\text{CaMg(CO}_3\text{)}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^-
\end{equation}

\begin{equation}
\text{CaCO}_3 + \text{CaMg(CO}_3\text{)}_2 + 3\text{CO}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{Ca}^{2+} + \text{Mg}^{2+} + 6\text{HCO}_3^-
\end{equation}

\begin{equation}
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O} + \text{SO}_4^{2-}
\end{equation}

These findings indicate that the sulfate in the study area may primarily originate from the dissolution of evaporite rocks, especially gypsum (CaSO$_4 \cdot 2$H$_2$O) [36]. The relationship between sulfate and carbonate dissolution is mainly reflected in the dissolution of calcite (CaCO$_3$), with a weaker relationship to the dissolution of dolomite (CaMg(CO$_3$)$_2$). This is evidenced by the weak correlation with magnesium (Mg$^{2+}$) and the negative correlation with bicarbonate (HCO$_3^-$). The strong positive correlation between sulfate and TDS suggests that the presence of sulfate significantly contributes to the total dissolved solids in the water. Areas with high sulfate concentrations are likely to have higher TDS values, reflecting the overall mineral content of the water [37,38]. The negative correlation between sulfate and bicarbonate may be due to the formation of precipitates between cations released simultaneously with sulfate and bicarbonate. Additionally, since the pH of the water samples in the study area is neutral to slightly alkaline, a buffering effect occurs between the two [39]. The positions of the tailing leachate and the mine drainage points are significantly distant from the fitted line, indicating that their evolutionary processes differ from those of other water samples.

According to the findings detailed above, the hydrochemistry characteristics of water in the study area are controlled by several geochemical processes, including the dissolution of calcite, dolomite, and gypsum, as well as the oxidation of sulfide minerals. These dissolution processes can be expressed by the following reactions [40]:

\begin{equation}
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-
\end{equation}

\begin{equation}
\text{CaMg(CO}_3\text{)}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^-
\end{equation}

\begin{equation}
\text{CaCO}_3 + \text{CaMg(CO}_3\text{)}_2 + 3\text{CO}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{Ca}^{2+} + \text{Mg}^{2+} + 6\text{HCO}_3^-
\end{equation}

\begin{equation}
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O} + \text{SO}_4^{2-}
\end{equation}

**Figure 3.** Correlations between sulfate and (a) Ca$^{2+}$, (b) Na$^+$ + K$^+$, (c) Cl$^-$, (d) HCO$_3^-$, (e) Mg$^{2+}$, and (f) TDS.
Assuming that all the SO\(_4^{2-}\) is from gypsum dissolution, non-gypsum-source calcium can be calculated by \([\text{Ca}^{2+}] - \text{SO}_4^{2-}\) (in mmol/L), and non-carbonate-source calcium can be calculated by \([\text{Ca}^{2+}] - 0.33[\text{HCO}_3^-]\) (in mmol/L) [41]. As shown in Figure 4a, the ratios of \([\text{Ca}^{2+}] - 0.33[\text{HCO}_3^-] : \text{SO}_4^{2-}\) for most of the water sample plot near the 1:1 line, indicating that gypsum dissolution might be a significant source of the Ca\(^{2+}\) and SO\(_4^{2-}\) in the water. However, some plots of \([\text{Ca}^{2+}] : \text{SO}_4^{2-}\) : HCO\(_3^-\) fall in the negative area (Figure 4b), indicating that there are sources of SO\(_4^{2-}\) other than gypsum. The ratios of \([\text{Ca}^{2+}] : \text{SO}_4^{2-} : \text{HCO}_3^-\) for most of the samples fall beneath the 1:2 line and near the 1:4 line, suggesting that carbonate dissolution might dominate the main water–rock interaction processes (except for gypsum). The plots for the Mg\(^{2+}\) : HCO\(_3^-\) (Figure 4c), show that most of the samples are scattered near the 1:4 line, indicating that dolomite dissolution, rather than calcite, plays a dominant role in the carbonate rock dissolution process. This inference explains the weak correlation between the Mg\(^{2+}\) and SO\(_4^{2-}\) concentrations mentioned earlier. Additionally, previous studies have shown that the dolomite content in the carbonate rocks in the study area is much higher than that of calcite [42], which is consistent with our observations. The plots of the tailings leachate and mine drainage scattered away from the line suggest that their sulfate source might be the oxidation of metal sulfides, rather than the previously mentioned water–rock interactions.

![Figure 4. Graphs of (a) non-gypsum-source Ca\(^{2+}\) vs. HCO\(_3^-\) and (b) Mg\(^{2+}\) vs. HCO\(_3^-\); (c) non-carbonate source of Ca\(^{2+}\) vs. SO\(_4^{2-}\).](image-url)
4.2. Sulfate Sources and Mixing in the Daqiao River

4.2.1. Potential Sulfate Sources and Their Isotope Compositions

The sources of sulfur in water bodies can be broadly divided into anthropogenic and natural sources. Natural sources include the dissolution of evaporite rocks, primarily composed of gypsum, the oxidation of sulfur-containing minerals and biological sulfur, and atmospheric acid deposition. Anthropogenic sources mainly include the discharge of industrial and domestic wastewater, the use of agricultural fertilizers, and various mining activities [43]. Based on the aforementioned analysis, it is indicated that the primary sources of sulfate in the Daqiao River are the confirmed dissolution and oxidation of sulfur-bearing minerals (mining drainage or tailings leachate) and the dissolution of evaporite rocks (gypsum). Additionally, there are potential contributions from atmospheric precipitation, as well as chemical fertilizers and sewage, since the study area includes a residential town. See Table 2.

Table 2. Characteristics of isotope values of potential sulfate sources.

<table>
<thead>
<tr>
<th>ID</th>
<th>Sulfate Sources</th>
<th>(\delta^{34}\text{S}_{\text{SO}_4}) (%)</th>
<th>(\delta^{18}\text{O}_{\text{SO}_4}) (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average Value</td>
<td>Standard Deviation</td>
<td>Average Value</td>
</tr>
<tr>
<td>1</td>
<td>Oxidation of sulfide</td>
<td>8.24</td>
<td>1.85</td>
<td>−4.68</td>
</tr>
<tr>
<td>2</td>
<td>Evaporite</td>
<td>17.96</td>
<td>0</td>
<td>13.98</td>
</tr>
<tr>
<td>3</td>
<td>Chemical fertilizer</td>
<td>5.8</td>
<td>5.5</td>
<td>10.7</td>
</tr>
<tr>
<td>4</td>
<td>Domestic sewage</td>
<td>5.98</td>
<td>1.98</td>
<td>6.86</td>
</tr>
<tr>
<td>5</td>
<td>Atmospheric deposition</td>
<td>3.9</td>
<td>0</td>
<td>11.65</td>
</tr>
</tbody>
</table>

The typical \(\delta^{34}\text{S}_{\text{SO}_4}\) and \(\delta^{18}\text{O}_{\text{SO}_4}\) ranges for sulfide oxidation are −5‰ to 10‰ and −5‰ to 4‰ [23,48], respectively. The average \(\delta^{18}\text{O}_{\text{SO}_4}\) and \(\delta^{34}\text{S}_{\text{SO}_4}\) values for mining drainage are −4.68‰ and +8.24‰, respectively, while the average \(\delta^{18}\text{O}_{\text{SO}_4}\) and \(\delta^{34}\text{S}_{\text{SO}_4}\) values for tailings leachate are 6.51‰ and 6.48‰, respectively. The \(\delta^{34}\text{S}_{\text{SO}_4}\) values for galena, sphalerite, and pyrite in the study area range from −8.5‰ to 20.6‰ [13]. After the oxidation of sulfide minerals, sulfur isotopes in sulfate do not undergo significant fractionation, with a fractionation between precipitated and soluble sulfate of less than 2‰. Edraki et al. [49] found that the \(\delta^{34}\text{S}_{\text{SO}_4}\) range in mine drainage from the Mt. Morgan mine in Australia is very narrow (1.8‰ to 3.7‰) and closely matches the sulfur isotopic composition of sulfide ores. Other studies also show that sulfur isotopes in sulfate closely match those in sulfide minerals [50,51]. Therefore, the sulfur isotopic composition of metal sulfides in the study area can represent the \(\delta^{34}\text{S}_{\text{SO}_4}\) characteristics of sulfate produced by sulfide oxidation. Moreover, the typical \(\delta^{34}\text{S}_{\text{SO}_4}\) range for AMD is −13.6‰ to 8.0‰. This indicates that the \(\delta^{34}\text{S}_{\text{SO}_4}\) values of mining drainage and tailings leachate in this study could represent the \(\delta^{34}\text{S}_{\text{SO}_4}\) values from sulfide mineral oxidation in the study area. However, there is a significant difference in their \(\delta^{18}\text{O}_{\text{SO}_4}\) values. The \(\delta^{18}\text{O}_{\text{SO}_4}\) values in the mining drainage show noticeable depletion. During sulfide oxidation, oxygen is required, and rapid fractionation of oxygen isotopes occurs. Typically, more than 80% of the oxygen needed for sulfide oxidation is provided by local water. Experimental evidence shows that under neutral conditions, dissolved oxygen does not participate in pyrite oxidation [52]. Consequently, the oxygen isotopic composition of sulfate reflects that of local water [53]. Atmospheric \(\text{O}_2\) is strongly enriched in \(^{18}\text{O}\), whereas the \(^{18}\text{O}\) in environmental waters is depleted to varying degrees [54]. The \(^{18}\text{O}\) depletion in sulfate in mining water indicates that the oxygen for sulfide oxidation is provided by \(^{18}\text{O}\)-depleted water. The \(\delta^{18}\text{O}_{\text{SO}_4}\) values in the tailings leachate, which are close to those of atmospheric precipitation (+7‰ to +17‰ [55]), suggest an influence from atmospheric precipitation. Therefore, the \(\delta^{18}\text{O}_{\text{SO}_4}\) values in mining drainage more accurately represent the \(\delta^{18}\text{O}_{\text{SO}_4}\) values from sulfide mineral oxidation in the study area.

The sulfate produced by the dissolution of evaporite rocks (primarily gypsum: \(2\text{CaSO}_4\cdot\text{H}_2\text{O}\)) is characterized by enriched heavy S and O isotopes, with \(\delta^{34}\text{S}_{\text{SO}_4}\) values ranging from
12% to 35%, reaching up to 40%, and $\delta^{18}O_{SO_4}$ values ranging from 6% to 20% [24,38]. Gypsum is present in the Cretaceous strata of the Daliangzi mining area [56], with $^{34}S_{SO_4}$ values ranging from 18.1% to 19.0% ($\pm 0.5\%$) and $\delta^{18}O_{SO_4}$ values ranging from 11.0% to 15.2% ($\pm 0.5\%$), which are typical isotopic values recorded in marine evaporites of this age [57]. Based on these results, in this study, we collected a spring sample from the Cretaceous strata in the study area, with $^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values of 17.96% and 13.98%, respectively. It can be assumed that this sample represents the $^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values of the sulfate derived from gypsum in this area.

The typical sulfate isotope variation ranges for atmospheric deposition are $^{34}S_{SO_4}$ values ranging from 0% to +6‰ and $\delta^{18}O_{SO_4}$ values ranging from +7% to +18% [35]. The $^{34}S_{SO_4}$ values of rainwater in the Sichuan Basin range from 1.7% to 5.6% (average 3.9%) [46]. The mean $\delta^{18}O_{SO_4}$ values for atmospheric deposition plumes in temperate regions range from +7% to +17% [48]. In the downstream reach of the Yangtze River, the atmospheric deposition in Wuhan collected in 2011 had $^{34}S_{SO_4}$ values ranging from 2.1% to 6.9% (average 4.5%) and $\delta^{18}O_{SO_4}$ values ranging from 8.8% to 14.1% (average 11.5%) [47]. Based on these results, $^{34}S_{SO_4}$ of 3.9% and $\delta^{18}O_{SO_4}$ of 11.5% can be assumed to represent the $^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values of precipitation in the study area.

The $^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values of chemical fertilizer were obtained from 22 samples collected in the adjacent Henan Province, with values of 5.8 ± 5.5% and 10.7 ± 2.7‰, respectively [44]. The typical $^{34}S_{SO_4}$ values of domestic sewage are 2–12.5% and 8.2–12.5‰, with an average of 7.4% and 10.05‰, respectively [45].

### 4.2.2. Sulfate Mixing in the Daqiao River

Identifying the bacterial sulfate reduction (BSR) process is crucial for accurately determining sources of SO$_4^{2-}$ pollution using isotope methods. This importance arises because BSR leads to significant fractionation of sulfur isotopes [27].

Previous studies have shown that BSR causes the simultaneous enrichment of $^{18}$O and $^{34}$S isotopes and reductions in SO$_4^{2-}$ concentrations. During the reduction of sulfate to sulfide, the ratio of $^{18}$O enrichment to $^{34}$S enrichment in the remaining sulfate is approximately 1:4 [27,58,59]. When BSR occurs, scatter plots of $^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ typically exhibit strong linear relationships and correlations, accompanied by high slopes. Furthermore, $^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ often show a significant negative correlation and a good linear relationship with SO$_4^{2-}$ concentration. To illustrate the potential effects of BSR, we plotted the relationships between the $^{34}S_{SO_4}$, $\delta^{18}O_{SO_4}$, and SO$_4^{2-}$ concentrations in Figure 5. In this study, we observed a poor linear fit ($R^2 = 0.39$), a low slope (0.45), and a low correlation coefficient ($p = 0.57$) between $^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ (Figure 5a). Furthermore, there was no correlation between the $^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values and the SO$_4^{2-}$ concentration (Figure 5b). The samples we collected were all surface water, which typically exists in oxidizing environments. Redox conditions are unsuitable for BSR. Therefore, BSR is unlikely to occur in this study area. These findings suggest that the impact of BSR in this study can be considered negligible.

The results showed that most of the $^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ tended to be located in the mixing region of potential sources, and a correlation between them was absent (Figure 5a). In addition, there was no linear relationship between the $^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values and the SO$_4^{2-}$ concentrations ($R^2 = 0.44$ and 0.09, respectively, Figure 5b), which indicated that the SO$_4^{2-}$ may originate from multiple sources, and that there is no obvious dominant sources.

Sample M1 represents the initial characteristics of the mainstream. Sample M2 was collected at the junction of the mainstream and a tributary (Xincha Creek), representing a mixed sample. While the concentrations of SO$_4^{2-}$, Cl$^-$, and $^{34}$S in M2 were slightly different from those in M1 (with values of 23.82 mg/L and 23.49 mg/L for sulfates, 3.85 mg/L and 3.46 mg/L for chlorides, and 17.86% and 17.31% for $^{34}$S, respectively), these differences were not particularly significant. However, a noticeable change was observed in the $^{18}$O values (11.95% in M1 and 6.77% in M2). Similarly, M4, which was collected at
the junction of the mainstream and Cha Creek, also showed slight differences from the mainstream, particularly in the $\delta^{18}O$ values. These two tributaries flow through tailings and processing areas, respectively. This variation, particularly in $\delta^{18}O$, indicates their impact on the water chemistry and sulfur isotopes, suggesting that sulfide oxidation contributes to the introduction of $SO_4^{2-}$. Furthermore, when mine water is discharged into the mainstream, as seen in the comparison between M08 and M07, there are noticeable changes in $SO_4^{2-}$, $Cl^-$, $\delta^{34}S$, and $\delta^{18}O$ (Figure 6). These observations indicate that sulfide oxidation was a significant potential source of the sulfate in the water samples from the study area.

![Figure 5](image1.png)

**Figure 5.** The relations between (a) $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ and (b) $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}-1/[SO_4^{2-}]$.

![Figure 6](image2.png)

**Figure 6.** The spatial variation of (a) $SO_4^{2-}$, (b) $Cl^-$, (c) $\delta^{34}S$, and (d) $\delta^{18}O$ characteristics.

4.3. Contributions of Potential Sources to Riverine Sulfate

4.3.1. Sulfate Contributions to the Tributary Water

We evaluated the sulfate contributions of sources by using the Stable Isotope Mixing Models in R (SIMMR), and the results show the contributions of the potential sulfate source variations along the tributaries (Xincha Creek and Cha Creek) and the mainstream. The dissolution of evaporites in the tributaries, driven by the presence of gypsum in the Cretaceous strata, contributed significantly (31%) and played a dominant role. This finding aligns with previous research highlighting the role of evaporite dissolution in sulfate levels in mining regions [45]. In contrast, the fertilizer-derived sulfate contribution (8%) had the lowest impact, which aligns with field observations showing that only a small amount of
agricultural land is distributed in river valley areas. The contributions from the oxidation of sulfide (19%), domestic sewage (18%), and atmospheric deposition (24%) showed a moderate impact (Figure 7a). Notably, the contributions from the oxidation of sulfide in Xincha Creek (7~54%) were significantly higher than in Cha Creek (2~12%). As mentioned earlier, the tailings pond is located near Xincha Creek, while the processing plant is near Cha Creek. This indicates that the potential threat of sulfite influx from the tailings pond to the tributary is greater than that from the processing plant, necessitating greater attention.

![Figure 7. (a) Sulfate contributions at tributaries and (b) their correlations with each other.](image)

The sulfate contributions from sulfide oxidation showed a negative correlation with the residual sulfate contributions (Figure 7b), implying that these processes occur separately. This observation aligns with studies demonstrating independent processes in sulfate sources in mining areas [60,61]. The atmospheric deposition and fertilizers showed a moderate positive correlation, indicating that these sources jointly contribute to the riverine sulfate in the tributaries. This can be attributed to surface runoff from precipitation through agricultural soil, carrying sulfite from fertilizers and releasing both sources into the river simultaneously [45]. Other sources showed weak negative correlations, indicating that their releases are relatively independent processes.

4.3.2. Sulfate Contributions to the Mainstream Water

Figure 8a shows that the contribution from sulfide oxidation in the mainstream (25%) remains relatively stable along the flow direction, indicating a more significant role compared to the tributaries. This suggests a greater impact from direct mine drainage discharge. The contribution from evaporites decreased to 24%, which was consistent with the widespread presence of carbonate rocks and relatively small amount of evaporite minerals in the basin. Atmospheric deposition also contributed significantly (24%), while fertilizer (11%) and sewage (15%) had the least impact. The atmospheric deposition did not show significant correlations with other sources, but it exhibited a strong negative correlation with evaporite dissolution in contributing sulfate to the river (−0.72, Figure 8b). This may be because high-intensity precipitation rapidly carries atmospheric sulfates into rivers through surface runoff, increasing river flow volume and speed. This dilutes the sulfate concentration from evaporite dissolution. Additionally, the high flow rate reduces the time taken for water to interact with evaporite minerals, further decreasing their contributions.
Figure 8. (a) Sulfate contributions at mainstream and (b) their correlations with each other.

Other potential sources showed weak negative correlations with each other, implying that their impacts on riverine sulfate occurred independently. This observation is supported by recent studies on mining-water environments, which highlight the independent behavior of sulfate sources. For instance, Cheng et al. [62] discussed the use of stable isotopes to trace sulfate sources in mining areas, indicating the distinct contributions of various sulfate sources in river systems. Similarly, research by Taylor et al. [63] and Krouse [48] emphasized the role of multiple sulfur sources and their independent pathways in water-quality assessments in mining regions.

Sulfide oxidation in mining areas is primarily driven by mining activities [23,24]. The exposure of sulfide minerals to atmospheric oxygen and water during mining operations accelerates the oxidation process, leading to increased concentrations of SO$_4^{2-}$ in both tributaries and the mainstream. This anthropogenic input includes not only sulfide oxidation, but also contributions from fertilizers and domestic sewage. Collectively, these sources contribute approximately 50% of the total sulfate input in the study area.

4.4. Sulfate Sources to Trace Zinc

In the study area, the concentrations of Pb and Zn in surface water are relatively low. Previous research shows that Pb and Zn are more likely to desorb and be released at low pH, while they tend to adsorb at high pH. In the Daliangzi lead-zinc mining area, the dissolution of carbonate minerals (such as dolomite) raises the surface water pH to between 7.33 and 10.90. In this pH range, Pb and Zn tend to precipitate and adsorb more, leading to their lower concentrations in the water.

The oxidation of ZnS in water can be expressed by the following reaction:

$$\text{ZnS} + 2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-} + 4\text{H}^+ \quad (9)$$

During this process, equal amounts of Zn ions and sulfate ions (SO$_4^{2-}$) are released, suggesting a positive correlation between these two ions in the water. To explore the relationship between Zn and its sources, a plot of the Zn concentration versus the SO$_4^{2-}$ concentration and contributions from sulfide oxidation was created (Figure 9). Samples with Zn concentrations below the detection limit were excluded from the analysis. Additionally, most of the Pb concentrations were below the detection limit and thus not used. The results show that the Zn concentration increases with increasing SO$_4^{2-}$ concentrations and contributions from sulfide oxidation, demonstrating a strong linear relationship. The linear fit indices ($R^2$) are 0.82 and 0.67, respectively. This indicates that Zn and SO$_4^{2-}$ are
released together during the oxidation of sulfide and share a common source. The findings highlight the significant impact of mining activities on the geochemistry of the study area. The release of Zn and SO$_4^{2−}$ through sulfide oxidation not only affects water quality, but also poses risks to aquatic ecosystems and human health [64]. High concentrations of zinc can be toxic to aquatic life, while elevated sulfate levels can lead to the formation of AMD, further exacerbating environmental degradation.

![Figure 9. Correlations between Zn and (a) SO$_4^{2−}$ and (b) contribution of sulfide oxidation.](image)

The strong linear relationship between Zn and SO$_4^{2−}$ suggests that tracing SO$_4^{2−}$ can indirectly trace Zn. The oxidative weathering of sulfide minerals, often associated with mining activities, significantly contributes to the concentrations of these ions in water. Therefore, SO$_4^{2−}$ can serve as a proxy for identifying Zn sources and their geochemical pathways in aquatic environments. The relationship between Zn and SO$_4^{2−}$ in mining environments has been well documented in previous studies. Studies by Blowes et al. [65] and Seal and Hammarstrom [66] have documented the co-release of metals and sulfates during sulfide oxidation. Their research highlights the geochemical processes involved in AMD formation and the implications of this for metal mobility in mining areas.

5. Conclusions

To investigate the impacts of anthropogenic activities on riverine sulfate concentrations and $δ^{34}$SO$_4$ and $δ^{18}$O$_{SO_4}$ values, water samples were collected from the Daliangzi mining area. The SIMMR model was utilized to quantify the impact of anthropogenic sulfate sources on riverine sulfate in both tributaries and the mainstream.

The river water types in the Daliangzi mining area are predominantly Ca$^{2+}$-Mg$^{2+}$-HCO$_3$$^−$ and SO$_4^{2−}$. The weathering and dissolution of carbonate rocks significantly influence water chemistry, with dolomite playing a more significant role compared to calcite. Additionally, significant contributions arise from the dissolution of evaporite rocks and the oxidation of sulfide minerals.

The SIMMR model results revealed that the dissolution of evaporites in the tributaries, driven by gypsum in the Cretaceous strata, contributed significantly (31%) and played a dominant role. Sulfide oxidation (19%), domestic sewage (18%), and atmospheric deposition (24%) showed moderate contributions. Notably, the tailings pond near Xincha Creek has greater potential for sulfate release compared to the processing plant near Cha Creek. In the mainstream, sulfate oxidation contributed 25%, mainly due to the direct release from the mine drainage.

Anthropogenic sulfate input, including sulfide oxidation, fertilizers, and domestic sewage, collectively contributed approximately 50% of the total sulfate input in both
tributaries and the mainstream of the Daqiao River, with sulfide oxidation accounting for half of the anthropogenic input. The strong correlation between the Zn and $\text{SO}_4^{2-}$ concentrations and the contributions from sulfide oxidation indicates that they are released together during sulfide oxidation. Tracing $\text{SO}_4^{2-}$ can serve as a proxy for identifying Zn sources and their geochemical pathways.

This study effectively demonstrates the utility of using $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values in combination with the Stable Isotope Mixing Models in R (SIMMR). By integrating hydrochemical and isotopic data, we obtain a comprehensive understanding of how natural processes and human activities interact to influence water quality. Notably, the significant contribution of sulfide oxidation to sulfate levels suggests that controlling mine drainage and treating tailings ponds could greatly reduce sulfate and associated metal pollution. These findings provide valuable insights for policymakers, enabling them to develop and enforce regulations that limit sulfate emissions from mining activities, thereby ensuring better protection of water resources.

However, this study indicates that the overall chemical composition of the mainstream shows minimal variation, which is likely influenced by the water flow volume. Future research should investigate the temporal variations in sulfate and metal concentrations to understand the seasonal impacts and long-term trends in watersheds affected by mining activities. Additionally, the low levels of toxic metals in the water suggest that river sediments may serve as a significant “sink”. Future studies should focus on sediments to trace the complete migration pathways of heavy metals in this region.

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