Hydrochemical Characteristics and Water Quality Assessment of a Zn-Pb Mine Waters in Yunnan Southwest China

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Abstract. Water samples (rivers, streams, mine adits, tailings ponds) from Jinding zinc-lead polymetallic mining area and Bi River Basin were analysed for 32 indicators including major hydrochemical components and heavy metals. The correlation analysis of water chemical parameters and Gibbs diagram show that the water composition of the Bi River is influenced by human activities in addition to the rock weathering. In the streams, the main cations and anions are derived from the rock weathering of formations rich in gypsum, calcite and dolomite. Nemerow comprehensive pollution index method was performed to evaluate water quality. The water of streams and one pond is clean. Mine adits water pollution level is medium-heavy pollution. The water samples flowing through the mining area and from tailings ponds are heavy polluted.

1. Introduction

Mining activities, such as mining, mineral processing and smelting, always have an impact on the environment [1][2]. Contaminative mine drainage waters have become one of the major hydrogeological and geochemical problems in the world [3].

Jinding mine is a world-class zinc-lead polymetallic deposit in Lanping County, Yunnan Province, Southwest China. However, mining activities have a serious impact on the water environment, especially Bi River, which flows through the mining area [4][5][6]. The objective of our study is to reveal the influence of the development of Jinding Zn-Pb mine on surface water and groundwater.

2. Study area, sampling locations and methods

2.1. Brief introduction of study area

Jinding Zn-Pb mine is located in E99°25′02″, N26°24′50″, and concentrated in 6.8km² area. There are one open-pit, two underground stopes, six mineral processing plants and two smelters distributing in the valley and both sides of Bi River which flows through west part of Jinding mine. Bi River is the mother river of Lanping County and Yunlong County and the first level tributary of Mekong River. The overall length of Bi River is 169.5km, while mean annual runoff is 11.4×10⁸ m³/s. Due to historical reasons, the mining activities have resulted in serious pollution of Bi River. In addition, there are many streams and creeks in the mining area, and all of them are branches of Bi River.
The mining area has a subtropical monsoon montanic climate with 11.7°C of mean annual temperature. The wet and dry season is evident. The wet season is from June to October accounting for 80% of total precipitation, while the dry season is from November to May next year. The annual average precipitation is about 1015.5mm, and annual average evaporation is about 1577.2mm [7].

The strata in the mining area are mainly composed of meso-cenozoic continental facies. There are different lithologic assemblages of surrounding rock and intercalated rock in each ore section, but they are mainly clastic rock, clay rock, gypsum rock, and a few carbonate rocks and lapis lazuli rock. According to the mineral-bearing lithology, ores can be divided into sandstone type and calcareous breccia type. The main metallic minerals of two types are nearly same, namely galena, sphalerite, pyrite and marcasite [8]. However, non-metallic minerals differ greatly, e.g. Quartz, calcite and barite for the former type, and calcite for the later type.

According to the spatial morphology of formation lithology and aquifer, the underground water in the mining area is divided into three types, mainly consisting of fissure water, followed by karst fracture water and pore water.

2.2. Sampling and chemical analyses

In this study, 33 water samples were collected from the mining area and Bi River Basin in January 2016, composed of 2 samples from adits, 3 samples from tailings ponds, 18 samples from Bi River, 9 samples from branches of Bi River and 1 sample from a pond (figure 1).

The sampling process followed Water quality-Guidance on sampling techniques (HJ 494—2009) strictly. All samples were analyzed at the Ministry of Land and Mineral Resources Supervision and Test Center Kunming, ISO 9001 and ISO 17025 Accredited Lab in China. 32 indexes including major hydrochemical components and heavy metals were tested, namely total dissolved solids (TDS), total hardness (TH), pH, appearance, smell and taste, turbidness, chroma, Linear Alkylbenzene Sulfonates (LAS), volatile phenol, CN, HCO₃, CO₃²⁻, Mg²⁺, Ca²⁺, Cr⁶⁺, As, Se, Hg, Cl, SO₄²⁻, F, NO₃, K, Na, Ag, Cd, Cu, Fe, Mn, Ni, Pb and Zn. Quality control in the test process was performed following the specification of testing quality management for geological laboratories (DZ/T0130-2006).

2.3. Data processing

The minimum, maximum and average values of all test indexes of surface water and groundwater in dry season were calculated. Piper diagram was drawn by AquaChem 3.70, and Gibbs diagram was drawn by Origin 8.5. Pearson correlation coefficient between main hydrochemical parameters was performed by SPSS 19 (IBM Corp., New York, USA).

2.4. Water quality assessment

Single factor index and Nemerow multi-factor index method was used to evaluate waters quality. The formula of Nemerow multi-factor index method was calculated as follows:

\[
I_i = \frac{\rho_i}{S_i}; \quad I_{ave} = \frac{1}{n} \sum_{i=1}^{n} I_i; \quad NI = \sqrt{\frac{I_{max}^2+I_{ave}^2}{2}}
\]

where \(I_i\) is single factor pollution index and \(NI\) is Nemerow comprehensive index; \(\rho_i\) and \(S_i\) represent measured mass concentration of water samples and reference standard values respectively. Reference standard values of surface water and underground water were ascertained due to limits of IV type in Environmental quality standards for surface water (GB3838—2002) and Quality standard for ground water (GB/T 14848-93) (table 1). Pollution degree was shown in table 5.
3. Results and discussion

3.1. Basic hydrochemical characteristics

(1) Main ion composition and mass concentration

Statistical results of main hydrochemical indexes of water samples were shown in table 1.

pH of water samples from branches of Bi River, the tailings pond and the pond ranges from 7.3 to 8.12, both of which are weakly alkaline. pH of Bi River ranges from 7.6 to 8.29 except that when it flows through the mining area (S26) with the value of 6.72. pH of water samples from adits ranges from 7.65 to 7.72.
Mean concentration of total dissolved solids (TDS) in streams (branches of Bi River) and the pond is 274.7mg/L and 247.2mg/L, respectively, which can be considered as background value. TDS in waters from tailings pond and adits is on the high side obviously, and mean concentration is 3139mg/L and 2396.5mg/L, respectively. TDS ranges from 253 to 4268 mg/L in Bi River, and the average is 618.8mg/L. The value becomes very high rapidly when Bi River flows through Jinding mining area, showing that TDS was influenced by mining activities distinctly. The change of total hardness (TH) is similar as TDS (figure 2).

Figure 2. Content variation diagram of total dissolved solids and total hardness in Bi River

Mean concentration of positive ions in all water samples are Ca^{2+}>Na^{+}>Mg^{2+}>K^{+} successively. The change of mean concentration of anions is complex. The order is \(\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^-\) in streams and the pond. The order is \(\text{SO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{F}^-\) in Bi River. The order is \(\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^- > \text{NO}_3^- > \text{F}^-\) in the tailings pond. The order is \(\text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^- > \text{Cl}^- > \text{F}^-\) in waters from adits.

(2) Hydrochemical type

Piper diagram shows that, the concentration of alkaline earth metals is more than that of alkali metals in all water samples, and cations are dominated by Ca^{2+}; the concentration of strong acid radical ions is basically equal to that of weak acid radical ions, and anions are dominated by \(\text{SO}_4^{2-}\) and \(\text{HCO}_3^-\) (figure 3). Hydrochemical type is \(\text{Ca}^{2+} \cdot \text{SO}_4^{2-}\) in both adits and tailings ponds. The hydrochemical types of streams water are complex and variable, which is dominated by \(\text{Ca}^{2+} \cdot \text{HCO}_3^-\), followed by \(\text{Ca}^{2+} \cdot \text{Mg}^{2+} \cdot \text{HCO}_3^-\), \(\text{Ca}^{2+} \cdot \text{Mg}^{2+} \cdot \text{SO}_4^{2-} \cdot \text{HCO}_3^-\), \(\text{Ca}^{2+} \cdot \text{HCO}_3^- \cdot \text{SO}_4^{2-}\), \(\text{Na}^+ \cdot \text{Ca}^{2+} \cdot \text{SO}_4^{2-} \cdot \text{HCO}_3^-\), and so on. The hydrochemical types of Bi River are mainly \(\text{Ca}^{2+} \cdot \text{Na}^+ \cdot \text{HCO}_3^- \cdot \text{SO}_4^{2-}\) and \(\text{Ca}^{2+} \cdot \text{Na}^+ \cdot \text{SO}_4^{2-} \cdot \text{HCO}_3^-\), and the general trend downstream is as follows: \(\text{Ca}^{2+} \cdot \text{Na}^+ \cdot \text{HCO}_3^- \cdot \text{Cl}^-\) (Lanping upstream) \(\rightarrow\) \(\text{Ca}^{2+} \cdot \text{HCO}_3^- \cdot \text{SO}_4^{2-}\), \(\text{Ca}^{2+} \cdot \text{Na}^+ \cdot \text{SO}_4^{2-}\) (mining area) \(\rightarrow\) \(\text{Ca}^{2+} \cdot \text{Na}^+ \cdot \text{SO}_4^{2-} \cdot \text{HCO}_3^-\) (middle reaches) \(\rightarrow\) \(\text{Ca}^{2+} \cdot \text{Na}^+ \cdot \text{HCO}_3^- \cdot \text{SO}_4^{2-}\) (lower reaches), showing that mining activities are main reason for large releases of \(\text{SO}_4^{2-}\).
### Table 1: Statistics of main hydrochemical indexes of water samples in Jinding mining area and Bi River basin

| Water samples | data range   | pH  | TDS | TH  | Na⁺ | K⁺ | Mg²⁺ | Ca²⁺ | HCO₃⁻ | CO₃²⁻ | Cl⁻ | SO₄²⁻ | F⁻ | NO₃⁻ |
|---------------|--------------|-----|-----|-----|-----|----|------|------|-------|-------|-----|-------|----|------|
| **Limit of IV type for surface water** | | | | | | | | | | | | | | |
| Min           | 6.72         | 253 | 141.8| 6.61| 1.62| 6.4 | 43.81| 112.5 | n.d.  | 4.56  | 33.03| 0.06 | 1.62|
| Max           | 8.29         | 4268| 2654 |116.5| 10.21|302.5| 563.8| 337.4 |11.34  |45.57  |2879 |0.31  |9.16 |
| AVG           | 7.82         | 618.8|319.64 |44.47| 3.26| 26.43| 84.41|159.89 | 1.42  |24.09  |268.75|0.10  |3.66 |
| SD            | 0.40         | 922.3|585.1 | 25.4 |1.9  | 69.0 | 121.0|47.7  | 3.4   |10.6  |659.5 |0.1  |1.8  |
| CV            | 4.50         | 149.0|183.0 | 57.0 | 58.4 |261.0| 143.3|29.8  |240.1  |44.0  |245.4 |58.2 |50.3 |
| over-limit ratio (%) | | | | | | | | | | | | | | |
| Min           | 7.30         | 144.7|60.77 | 3.32 | 0.66 | 1.48| 17.04| 54.79 | n.d.  |0.91  |2.76 |0.05 |0.34 |
| Max           | 8.12         | 536 | 281.6| 26.12| 2.03 |16.23| 92.48| 222   | n.d.  |4.47  |191.7 |0.1  |4.96 |
| AVG           | 7.80         | 274.7|149.5 | 9.3  |1.53 | 7.6 | 47.3 | 126.6 | n.d.  |2.0   |70.7 |0.07 |1.27 |
| SD            | 0.30         | 146.5|90.3  | 8.1  | 0.5  | 5.0 | 28.7 | 47.0  |-      |1.2   |78.9 |0.02 |1.4  |
| CV            | 3.70         | 53.3 |60.4  | 87.1 | 34.4 |65.8 | 60.7 | 37.1  | -     |58.2  |111.7|28.5 |112.5|
| over-limit ratio (%) | | | | | | | | | | | | | | |
| Min           | 7.37         | 3062| 1712 | 62.59| 27.63|34.44| 600.3|40.37  | n.d.  |49.93 |2144 |0.17 |13.98|
| Max           | 7.54         | 3259| 1752 | 68.15| 33.05|54.11| 628.7|49.02  | n.d.  |62.39 |2371 |0.18 |23.16|
| AVG           | 7.45         | 3139| 1729 | 65.81| 29.73|45.09| 617.9|44.22  | n.d.  |55.04 |2238 |0.18 |18.0 |
| SD            | 0.40         | 146.5|90.3  | 8.1  | 0.5  | 5.0 | 28.7 | 47.0  |-      |1.2   |78.9 |0.02 |1.4  |
| CV            | 3.70         | 53.3 |60.4  | 87.1 | 34.4 |65.8 | 60.7 | 37.1  | -     |58.2  |111.7|28.5 |112.5|
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| CV            | 3.70         | 53.3 |60.4  | 87.1 | 34.4 |65.8 | 60.7 | 37.1  | -     |58.2  |111.7|28.5 |112.5|
| over-limit ratio (%) | | | | | | | | | | | | | | |
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| Max           | 7.54         | 3259| 1752 | 68.15| 33.05|54.11| 628.7|49.02  | n.d.  |62.39 |2371 |0.18 |23.16|
| AVG           | 7.45         | 3139| 1729 | 65.81| 29.73|45.09| 617.9|44.22  | n.d.  |55.04 |2238 |0.18 |18.0 |
| SD            | 0.40         | 146.5|90.3  | 8.1  | 0.5  | 5.0 | 28.7 | 47.0  |-      |1.2   |78.9 |0.02 |1.4  |
| CV            | 3.70         | 53.3 |60.4  | 87.1 | 34.4 |65.8 | 60.7 | 37.1  | -     |58.2  |111.7|28.5 |112.5|
| over-limit ratio (%) | | | | | | | | | | | | | | |
| Min           | 7.37         | 3062| 1712 | 62.59| 27.63|34.44| 600.3|40.37  | n.d.  |49.93 |2144 |0.17 |13.98|
| Max           | 7.54         | 3259| 1752 | 68.15| 33.05|54.11| 628.7|49.02  | n.d.  |62.39 |2371 |0.18 |23.16|
| AVG           | 7.45         | 3139| 1729 | 65.81| 29.73|45.09| 617.9|44.22  | n.d.  |55.04 |2238 |0.18 |18.0 |
| SD            | 0.40         | 146.5|90.3  | 8.1  | 0.5  | 5.0 | 28.7 | 47.0  |-      |1.2   |78.9 |0.02 |1.4  |
| CV            | 3.70         | 53.3 |60.4  | 87.1 | 34.4 |65.8 | 60.7 | 37.1  | -     |58.2  |111.7|28.5 |112.5|
| over-limit ratio (%) | | | | | | | | | | | | | | |

**Notes:** *from GB3838-2002; **from GBT14848-93*
(3) Ion correlation analysis

The correlation matrix of hydrochemical parameters in Bi River shows that, \( \text{SO}_4^{2-} \) has significant positive correlation with \( \text{Ca}^{2+}, \text{Mg}^{2+}, \text{K}^+, \text{F}^-, \text{HCO}_3^- \), and correlation coefficients are 0.999, 0.992, 0.951, 0.918 and 0.912, respectively (table 2). \( \text{HCO}_3^- \) has significant positive correlation with \( \text{Mg}^{2+}, \text{Ca}^{2+}, \text{F}^-, \text{K}^+ \), and correlation coefficients are 0.929, 0.923, 0.905 and 0.829, respectively. \( \text{Ca}^{2+} \) has significant positive correlation with \( \text{Mg}^{2+} \) and \( \text{K}^+ \), and correlation coefficients are 0.992 and 0.946, respectively. Complexity of hydrochemical parameters in Bi River reflects that besides the water composition derived from rock weathering, it is also affected by human activities.

The correlation matrix of hydrochemical parameters in branches of Bi River shows that, \( \text{SO}_4^{2-} \) has significant positive correlation with \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \), and correlation coefficients are 0.927 and 0.905, respectively (table 3). \( \text{HCO}_3^- \) has significant positive correlation with \( \text{Ca}^{2+} \), and correlation coefficient is 0.804. \( \text{Ca}^{2+} \) has significant positive correlation with \( \text{Mg}^{2+} \), and correlation coefficient is 0.873. In combination with the geological background of Lanping, the main anion in streams maybe derived from the dissolution of gypsum, calcite and dolomite in the strata.

(4) Causes of formation of hydrochemical characteristics

Gibbs boomerang diagram, a semilog plot identified by Gibbs in 1970, has been one of the important tools to investigate geochemical processes [9]. Figure 4 shows that most of 33 water samples lie in the region of \( \text{Na}^+/ (\text{Na}^+ + \text{Ca}^{2+}) \) or \( \text{Cl}^-/ (\text{Cl}^- + \text{HCO}_3^-) \) value less than 0.5, and TDS values are moderate. This indicates that the ionic composition is mainly derived from the rock weathering process. The value of \( \text{Cl}^-/ (\text{Cl}^- + \text{HCO}_3^-) \) in tailings ponds water is inclined to be evaporation-crystallization type, which is consistent with evaporation more than precipitation in dry season in Lanping.
Table 2. The correlation matrix of hydrochemical parameters in Bi River

|       | pH    | TDS   | TH    | HCO₃⁻  | SO₄²⁻  | Cl⁻   | NO₃⁻  | F⁻     | Ca²⁺   | Mg²⁺   | Na⁺    | K⁺     |
|-------|-------|-------|-------|--------|--------|-------|--------|--------|--------|--------|--------|--------|
| pH    | 1     | -0.314| -0.178| -0.095 | -0.360 | 0.328 | 0.058  | 0.253  | -0.195 | -0.099 | -0.876 | 0.141  |
| TDS   | 1     | 0.981 | 0.829 | 0.922  | -0.105 | 0.399 | 0.406  | 0.787  | 0.149  | 0.234  |        |        |
| TH    | 1     | 0.769 | 0.943 | 0.062  | -0.062 | 0.492 | 0.536  | 0.994  | 0.248  | 0.183  |        |        |
| HCO₃⁻ | 1     | 0.554 | 0.034 | 0.177  | 0.077  | 0.804 | 0.572  | 0.359  | 0.554  |        |        |        |
| SO₄²⁻ | 1     | -0.162| 0.484 | 0.541  | 0.927  | 0.905 | 0.335  | -0.050 |        |        |        |        |
| Cl⁻   | 1     | -0.001| 0.006 | -0.045 | -0.117 | -0.246| 0.386  |        |        |        |        |        |
| NO₃⁻  | 1     | 0.651 | 0.431 | 0.657  | -0.314 | 0.150 |        |        |        |        |        |        |
| F⁻    | 1     | 0.466 | 0.728 | -0.389 | -0.142 |        |        |        |        |        |        |        |
| Ca²⁺  | 1     | 0.873 | 0.279 | 0.251  |        |        |        |        |        |        |        |        |
| Mg²⁺  | 1     | 0.118 | -0.073|        |        |        |        |        |        |        |        |        |
| Na⁺   | 1     | -0.109|        |        |        |        |        |        |        |        |        |        |
| K⁺    | 1     |        |        |        |        |        |        |        |        |        |        |        |

**. Correlation is significant at the 0.01 level. *. Correlation is significant at the 0.05 level.

Table 3. The correlation matrix of hydrochemical parameters in branches of Bi River

|       | pH    | TDS   | TH    | HCO₃⁻  | SO₄²⁻  | Cl⁻   | NO₃⁻  | F⁻     | Ca²⁺   | Mg²⁺   | Na⁺    | K⁺     |
|-------|-------|-------|-------|--------|--------|-------|--------|--------|--------|--------|--------|--------|
| pH    | 1     | -0.793| -0.789| -0.883 | 0.786  | -0.328| 0.250  | 0.814  | 0.793  | 0.782  | -0.586 | 0.711  |
| TDS   | 1     | 0.997 | 0.921 | 0.999  | 0.375  | -0.123| 0.924  | 0.999  | 0.992  | 0.796  | 0.950  |        |
| TH    | 1     | 0.927 | 0.997 | 0.363  | -0.176 | 0.918  | 0.998  | 0.998  | 0.755  | 0.935  |        |        |
| HCO₃⁻ | 1     | 0.912 | 0.484 | -0.306 | 0.905  | 0.923  | 0.929  | 0.642  | 0.829  |        |        |        |
| SO₄²⁻ | 1     | 0.348 | 0.121 | 0.918  | 0.999  | 0.992  | 0.790  | 0.951  |        |        |        |        |
| Cl⁻   | 1     | -0.103| 0.396 | 0.355  | 0.370  | 0.470  | 0.310  |        |        |        |        |        |
| NO₃⁻  | 1     | -0.101| -0.128| -0.227 | 0.272  | 0.131  |        |        |        |        |        |        |
| F⁻    | 1     | 0.922 | 0.910 | 0.750  | 0.886  |        |        |        |        |        |        |        |
| Ca²⁺  | 1     | 0.992 | 0.773 | 0.946  |        |        |        |        |        |        |        |        |
| Mg²⁺  | 1     | 0.733 | 0.922 |        |        |        |        |        |        |        |        |        |
| Na⁺   | 1     | 0.850 |        |        |        |        |        |        |        |        |        |        |
| K⁺    | 1     |        |        |        |        |        |        |        |        |        |        |        |

**. Correlation is significant at the 0.01 level. *. Correlation is significant at the 0.05 level.

3.2 Concentrations of heavy metals and Single index assessment of water quality

Concentrations of Linear Alkylbenzene Sulfonates, volatile phenol, CN⁻, Se, Hg, Ag, Cr⁶⁺ in any water samples are not detected or trace. Concentrations of Fe, Mn and some heavy metals are listed in table 4.

According to Function Division of Water Environment for Surface Water in Yunnan Province (2010-2020), the function of Bi River (headwater to entrance to Mekong River) is industrial and agricultural water, and IV type is operative standard, which can be used as drinking water by proper treatment besides industrial and agricultural purpose.
Figure 4. The Gibbs boomerang envelope of water samples in Jinding mining area

Table 4. Concentrations of Fe, Mn and heavy metals in waters in Jinding mining area and Bi River Basin

| Water samples | data range | Pb | Zn | Cd | As | Cu | Ni | Fe | Mn |
|---------------|------------|----|----|----|----|----|----|----|----|
| Limit of IV type for surface water * | | | | | | | | | |
| Min | 0.007 0.007 0.007 0.007 0.007 0.007 0.007 0.007 |
| Max | 0.007 0.007 0.007 0.007 0.007 0.007 0.007 0.007 |
| AVG | 0.007 0.007 0.007 0.007 0.007 0.007 0.007 0.007 |
| SD | 0.007 0.007 0.007 0.007 0.007 0.007 0.007 0.007 |
| CV | 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 |
| Over-limit ratio (%) | 0 0 0 0 0 0 0 0 |
| Bi River (n=18) | Min | 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 |
| Max | 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 |
| AVG | 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 |
| SD | 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 |
| CV | 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 |
| Over-limit ratio (%) | 0 0 0 0 0 0 0 0 |
| Branches of Bi River (n=9) | Min | 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 |
| Max | 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 |
| AVG | 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 |
| SD | 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 |
| CV | 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 |
| Over-limit ratio (%) | 0 0 0 0 0 0 0 0 |
| Tailings pond (n=3) | Min | 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 |
| Max | 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 |
| AVG | 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 |
| Over-limit ratio (%) | 0 0 0 0 0 0 0 0 |
| A pond (n=1) | Test value | 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 |
| Limit of IV type for underground water ** | Min | 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 |
| adits (n=2) | Max | 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 |
| AVG | 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 |
| Over-limit ratio (%) | 0 0 0 0 0 0 0 0 |
The statistical results show that any test index of streams and the pond is not out of limits. Concentrations of SO$_4^{2-}$, NO$_3^-$, Zn, Cd and Mn in tailings ponds water are out of limits with over-limit ratio of 100%, and maximum excess multiples are 8.5, 1.3, 4.8, 21 and 109, respectively. Concentrations of SO$_4^{2-}$, Zn, Cd and Mn in Bi River are out of limits with over-limit ratios of 11.1%, 11.1%, 44.4% and 61.1%, and maximum excess multiples are 10.5, 36.7, 35 and 416, respectively.

Compared with surface waters, concentrations of Fe, Mn and heavy metals are not out of limits. However, SO$_4^{2-}$, TH and TDS are out of limits with over-limit ratios of 100%, 100% and 50%, and maximum excess multiples are 4.5, 1.6 and 0.4, respectively.

3.3 Nemerow comprehensive index assessment

11 indexes were selected to perform comprehensive assessment, namely SO$_4^{2-}$, F$^-$, NO$_3^-$, Cl$^-$, Pb, Zn, As, Cd, Cu, Fe and Mn. The results of assessment were shown in table 5. It is shown that all samples from streams and the pond are clean. More than half of samples from Bi River are also clean, mainly distributing upstream and downstream far from Jinding mine (figure 5). 3 samples from Bi River are on the warning line and mild pollution, which distribute in the midstream. There are 2 samples from Bi River flowing through the mining area are polluted seriously, especially Nemerow pollution index (NI) of S26 reaches up to 30.24. Nemerow pollution index of tailings ponds water is 13.84~15.82, indicating heavy pollution. Nemerow pollution index of adits water is 2.64 and 3.92, and pollution degree is moderate pollution and heavy pollution, respectively.

![Graph](image)

**Figure 5.** The variation diagram of Nemerow Pollution Index (NI) in Bi River
Table 5: Classification Criteria of Nemerow pollution index and evaluation result

| Evaluation level | Nemerow pollution index | pollution degree | level of pollution | samples distribution                      |
|------------------|-------------------------|------------------|--------------------|------------------------------------------|
| I                | NI≤0.7                  | safe             | clean              | All samples from streams and the pond    |
|                  |                         |                  |                    | Bi River: S18, S16, S17, S08, S14, S25, S06, S21, S20, S19 |
| II               | 0.7<NI≤1.0             | warning line     | still clean        | Bi River: S29, S15, S30                  |
| III              | 1.0<NI≤2.0             | mild pollution   | start to be polluted | Bi River: S33, S31, S32                 |
| IV               | 2.0<NI≤3.0             | moderate pollution | moderately polluted | adits: S01                                   |
| V                | NI>3.0                 | heavy pollution  | polluted seriously | Bi River: S26, S28                        |
|                  |                         |                  |                    | adits: S02, tailings ponds: S04, S03, S05 |

4. Conclusions
- According to the Piper trilinear chart, the content of alkaline earth metals in all water bodies is more than that of the alkali metal, and the cation is the absolute advantage of Ca$^{2+}$. The strong acid group anion is in accordance with weak acid ion, and the anion is dominated by SO$_4^{2-}$ and HCO$_3^-$. The change trend of the water chemical type in the Bi river basin reflects that the mining activity is the main reason for the large release of SO$_4^{2-}$. The correlation analysis of water chemical parameters and Gibbs diagram show that the water composition of the Bi River is influenced by human activities in addition to the rock weathering. In the stream, the main cation and anion are derived from the rock weathering of formations rich in gypsum, calcite and dolomite.

- Concentrations of Linear Alkylbenzene Sulfonates, volatile phenol, CN$^-$, Se, Hg, Ag, Cr$^{6+}$ in any water samples are not detected or trace. Compared with water environment quality standard of the grade IV, none of test index of water samples from streams and one pond exceeded the standard. The content of SO$_4^{2-}$, NO$_3^-$, Zn, Cd and Mn in the water of the tailings pond exceeded the standard, while the content of SO$_4^{2-}$, Zn, Cd and Mn in the water of the Bi River exceeded the standard. The mining activities have a direct impact on the pollution of the Bi River, which has a sudden pollution from the mining area, and the downstream pollution is rapidly decreasing. None of the heavy metals and Fe, Mn in the mine water exceeded the standard, but the total hardness, the total dissolved solids and SO$_4^{2-}$ exceeded the standard.

- Nemerow comprehensive pollution index method was performed to evaluate water quality. The water of streams and one pond is clean. More than half of the water samples from the Bi River are also clean, which mainly distributed in the upper reaches of the mining area and downstream from the mine. The water with warning line and light pollution distributed in the middle reaches. The water samples flowing through the mining area are heavy polluted. All the tailings pond water samples pollution level is heavy polluted. Mine adits water pollution level is medium-heavy pollution.

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