Hydrochemical Characteristics and Ion Sources of River in the upstream of the Shiyang River, China

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Abstract: As the largest tributary of the Shiyang River, with the average annual inflow of total runoff accounting for 23%, the Xiying River has representative of mountain runoff of inland rivers in the Northwest of China. Using samples collected in the Xiying River basin from September 2016 to October 2017, the water chemical composition and ion source characteristics of river was studied. The results show that the river is weakly alkaline, the average values of pH is 8.01 and the TDS is 179.29 $mg \cdot L^{-1}$. With the elevation decreasing along the river, the values of TDS of main stream tend to increase firstly and then decrease, but those of TDS of each tributary decrease, and latter is lower than the former. Affected significantly by the flow, the lowest value of ion concentration in river occurs in summer, and the highest value of it occurs in autumn and winter. The hydrochemical type of river is CaMg-HCO_3. In the river, the order of cation mass concentration is $NH_4^+ < K^+ < Na^+ < Mg^{2+} < Ca^{2+}$, and that of anion mass concentration is $F^- < NO_3^- < Cl^- < SO_4^{2-} < HCO_3^-$. The sources of ions in river are mainly from the weathering of Silicates, only a little from the weathering of Evaporates and Carbonates. With the elevation decreasing along the river, the influence of Silicates on the inflowing tributaries is gradually strengthened.

Keywords: Xiying River, Hydrochemistry, Ion Sources, Silicates.

1. INTRODUCTION

Water resource is the material basis for human survival, especially in arid regions where it is scarce and the quality of it affects the ecological environment and the regional economies. As an important part of water resource research, the chemical characteristics of water can reflect the type of water and determine the source of ions, which is the prerequisite for studying water quality. The research on the surface water quality began as early as the end of the 19th century, mainly taking the Rhine River, Thames River and Seine River as observation objects to study the chemical composition of water (Ma, 2004; Shao et al., 2018; Wang et al., 2010). In 1970, Gibbs proposed the Boomerang Envelope model based on the research of anions and cations in surface water, and divided the ion sources in surface water into Rock Weathering Type, Precipitation Control Type and Evaporation Concentration Type (Gibbs, 1972). The research on hydro geochemistry has also made significant progress in China. In 1963, through monitoring 500 rivers, Le Jiaxiang found that the hydrochemical characteristics of rivers in China have zonal differences, and the types of hydrochemistry are generally bicarbonate (Le et al., 1963; Xu et al., 2016; Yu et al., 2015; Guo et al., 1987; Li et al., 2006).

The Shiyang River Basin is located in the arid region of the Northwest of China. As one of the most densely populated areas in inland river basin of China, water resource has become the core of the contradiction between people and the ecological environment. With the warming of climate and the accelerated melting of glaciers, the ecological environment of the basin has changed significantly (Zhang et al., 2021; Zhu et al., 2020; Li et al., 2009; Ding et al., 2007). Many scholars have also studied the hydrochemical characteristics of the Shiyang River Basin. In 2005, Ma Jinzhu discovered that the water chemistry of the basin exists horizontally zonal (Ding, 2010; Ma et al., 2005). In 2014, Zhu Guofeng discovered that the source of acid ions in surface water is mainly from rock weathering (Zhu et al., 2018). In 2016, through observing the water quality of six tributaries in the upper of Shiyang River, Chu Jiju found that the main reason about the water quality exceeding the standard was rural non-point source pollution and domestic sewage pollution (Chu, 2018).

The Xiying River is the largest tributary of the Shiyang River, and its average inflow accounts for 23% of the total runoff. The Xiying River with many tributaries is mainly located in the mountainous of the upstream of Shiyang River. Its hydrochemical characteristics are mainly determined by the geochemical process of rocks in the area, and are affected by climate, precipitation, soil, vegetation and human activities. By monitoring the river of main stream and each tributary of Xiying River, this study aims to understand the hydrochemical characteristics of the basin and explore its chemical composition and ion sources. Furthermore, it can provide a basis for the sustainable development, the protection of water resource and the governance of the ecological environment of Shiyang River Basin.

2. DATA AND METHOD

2.1 Study area

The Shiyang River Basin (101°22′~104°14′ E, 37°7′~39°27′ N) is located in the northern section of the Qilian Mountain, and is located in the eastern of the Hexi Corridor, and is located between Tengger Desert and Badain Jaran Desert, covering an area of about 4.16×10^4 km^2 (Figure 1). The terrain is higher in the south and lower in the north, which comprises the Qilian Mountains, the corridor plains and the low hills and the desert areas from south to north. Among of them, the Qilian Mountains are mainly composed of metamorphic sandstone, slate, clastic rock, carbonate rock, intermediate-basic volcanic rock and intermediate-acid volcanic rock in Cambrian, Ordovician and Silurian (Ding et al., 2007). The Shiyang River Basin belongs to continental arid climate of temperate, but the climate has obvious vertical zoning, which is divided into three climatic regions. The Qilian Mountains belongs to the alpine semi-arid and humid region, which has an altitude of 2000-5000 m, an annual average temperature of less than 0 ℃, an annual average precipitation of 300-600 mm and annual evaporation rate of 700-1200 mm. The central corridor belongs to the cool and arid region, which has an altitude of 1500-2000 m, an annual average temperature of less than 7.8 ℃, an annual precipitation of 150-300 mm and annual evaporation rate of 1300-2000 mm. The north of it belongs to the warm and arid region, which has an altitude of 1300-1500 m, an annual average temperature of less than 8 ℃, an annual precipitation below 150 mm and an annual evaporation rate of 2000-2600 mm. The Shiyang River includes mainly eight rivers, which are the Dajing River, the Gulang River, the Huangyang River, the Zamu River, the Jinta River, the Xiying River, the Dongda River and the Xida River from east to west. The main sources of river are atmospheric precipitation and melting snow and ice in mountains. The runoff area is 1.11×10^4 km^2, and the average annual runoff is 1.56×10^9 m^3. According to the statistics of the first glacier catalog, there are 141 glaciers in this basin, with a total area of 103.02 km^2 and ice storage volume of 3.299×10^9 m^3.

The Xiying River is the largest tributary of the Shiyang River, which originates from Lenglongling on the northern slope of the Qilian Mountains. Its source elevation is up to 4870 m, the average snow line is 4450 m, the watershed area is 1455 km^2 and the average annual runoff is 3.155×10^8 m^3 (Wang, 2018; Liu et al., 2012). The composition of rock mineral in the Xiying River Basin are mainly silicate minerals, including quartz (SiO_2), hornblende ($A_{0-1}B_2C_5[Si_4O_{11}]_2$), plagioclase (Na $[AlSi_3O_8]$-Ca $[Al_2Si_2O_8]$) and potassium feldspar ($K_2O\cdot Al_2O_3\cdot 6SiO_2$). The source of the Xiying River is the Ningchang River, which admit the Qingyang River, the Tuoluo River and the Longtan River in sequence from west to east. Then converging with the Shuiguan River at Huajian Township, it flows from southwest to northeast. After merging the Xiangshui River and the Tuta River, it flows finally into the Xiying Reservoir. The length of river channel before the reservoir is about 76 km. Although part of the river is supplied to agricultural irrigation and domestic water, it flows eventually into the Shiyang River. The climate of the Xiying River Basin belongs to the alpine and semi-arid humid type, which the elevation is 2000-5000 m, the annual average temperature is less than 0°C, the average annual precipitation is 300-600 mm and the annual evaporation is 700-1200 mm. The vertical zonality of vegetation and soil is obvious. they are alpine meadow and alpine meadow soil at altitude of 3500-3800 m, subalpine scrubland and meadow and subalpine scrubland meadow soil at altitude of 3400-3500 m, forest and mountain grey cinnamon soil at altitude of 2600~3400 m, upland meadow and mountain chestnut at altitude of 2300~2600 m, desert steppe and sierozem at altitude of 2000-2300 m (Li, 2011).

[Insert Figure 1]

Figure 1. The location of the study area and the distribution of sampling points.

2.2 Sample collection and testing

From October 2016 to October 2017, 10 sampling points for river were set along the Xiying River (Figure 1), and samples were collected once a month (some samples were not collected on few months because of weather and road impacts). Use ArcGIS 10.2 to process the Dem of the watershed and extract the river network (Set flow accumulation and extract data larger than 800), a profile of the river was drawn (Figure 2). At sampling points of SCG, SCLK (The confluence of Ningchang River and Qingyang River), GGKFQ (The confluence of Ningchang River and Tuoluo River), WMQ (The confluence of the Ningchang River and Longtan River), WGQ (The confluence of the Xiying River and the Xiangshui River), samples of the main and tributary rivers of the Xiying River are collected at the same time. When collecting river samples, use a simple sling tool to collect samples in the middle of the river, and collect samples 10 cm below the surface of the river. The polyethylene sample bottle was rinsed three times with river samples, then put the sample into the bottle and seal well, and store the sample in the refrigerator. JTL is a hydrological station for observing river flow. During the sampling period, a total of 141 samples were collected.

Table 1. Sampling location and sample quantity.

[Insert Table 1]

[Insert Figure 2]

Figure 2. Channel longitudinal profile in the Xiying River.

All samples were carried to the Ecological and Hydrological Process Laboratory of Northwest Normal University and stored in a low temperature laboratory (about -15℃). To avoid the influence of CO_2 and H_2O in the air, the samples were kept in a sealed state from sampling to the experiment. 48 hours before the test, the samples were taken out and melt naturally at room temperature (about 21°C) without opening. Thereafter pH, EC and main ion concentration were detected at the National Key Laboratory of Cryosphere Science, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences (CAREERI, CAS). TDS, EC and pH were determined by means of the Seven Excellence™ (Shanghai Lianxiang Environmental Protection Technology Co., Ltd., Shanghai, China). The measurement range of TDS is between 0.001 and 1000 $mg \cdot L^{-1}$, with an accuracy of ±0.5%, the measurement range of EC is between 0.001 and 2000$\mu s \cdot cm^{-1}$, with an accuracy of ±0.5%, and that of pH is from 0.000 to 14.000, with an accuracy of ±0.05%. Before measuring ion concentration, all samples were filtered using filter membrane of 0.45μm. The concentrations of Na^+, K^+, Mg^{2+}, Ca^{2+} and NH_4^+ were determined by means of the DIONEX DX320 ion chromatograph (DIONEX Co., Ltd., Sunnyvale, CA,USA), and those of Cl^-, F^-, NO_3^- and SO_4^{2-} were determined by means of the DIONEX ICS1500 ion chromatograph (DIONEX Co., Ltd., Sunnyvale, CA,USA). The accuracy of them can reach $ng \cdot g^{-1}$, and the error of test data does not exceed 5%. The ultrapure water used in the blank sample and the standard sample is 18.2 MΩ (Millipore Company, USA).

2.3 Data processing

After the experiment, the data of each sample was tested by the law of conservation of charge. It was found that the charge number of the cation is significantly higher than that of the anion. This may be lack of detecting important acid ion in the experiment. According to existing studies, the missing ions may be mainly HCO_3^- and CO_3^{2-}, and the contents of other acid radical ions (such as NO_2^-, etc.) are small and can be ignored (Zhao et al., 2012). Measuring the concentration of HCO_3^- requires a larger volume of samples, but fewer samples are collected in this study, so the concentration of HCO_3^- is estimated by ion balance. Because CO_2 is easily soluble in water, most natural water has CO_3^{2-} and HCO_3^-. The dissolution of CO2 in water is a reversible reaction (equation 1,2 and 3). When 6.4<pH<10.3, $c[H_2CO_3] < c[HCO_3^-] > c[CO_3^{2-}]$, the content of CO_3^{2-} is negligible when pH <8.3 (Zhao et al., 2012; Ma et al., 2019). The values of pH of river samples in study area are range from 7.05 to 8.36, so the concentrations of other acid ions except for HCO_3^- can be ignored. Using the law of conservation of charge which the total charge of cations is equal to that of anions, the concentration of HCO_3^- was estimated by the following equation 4.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \quad (1)$$

$$H_2CO_3 \rightleftharpoons CO_3^{2-} + 2H^+ \quad (2)$$

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \quad (3)$$

$$C_{Na^+} + C_{NH_4^+} + C_{K^+} + 2C_{Mg^{2+}} + 2C_{Ca^{2+}} = C_{F^-} + C_{Cl^-} + 2C_{SO_4^{2-}} + C_{NO_3^-} + C_{HCO_3^-} \quad (4)$$

2.4 Research Methods

2.4.1. Piper diagram

Piper's three-line diagram is a method for classifying water samples, which was proposed firstly by Piper in 1953 (Zhao et al., 2012). By calculating the ratio of the equivalent concentration of the main anions and cations in surface water (μeq·L^{-1}), the location of the sample in the three-line diagram is determined, and the chemical type of surface water is divided (Piper, 1944; Wang et al., 2019). This figure can be drawn by Origin 2018 software. It consists of a diamond and two equilateral triangles. The two equilateral triangles can separately discuss the proportion of the main ions in the anions and cations. The diamonds can link the anions and cations to reflect the compositional characteristics of ions and the type of water chemistry of surface water.

2.4.2 Gibbs model

The Gibbs model can show clearly the water chemistry characteristics, and can provide a basis for studying the chemical composition and formation reasons, which determine the main source of ions in surface water. This method was proposed firstly by Gibbs in 1970. In the Gibbs model, the ordinate is TDS in river, and the abscissa is mass concentration (mg·L^{-1}) ratio of $Na^+ / (Na^+ + Ca^{2+})$ or $Cl^- / (Cl^- + HCO_3^-)$.

When the surface water in study area is less affected by humans, the sources of ions in surface water can be divided into three categories. The first category is Rock Weathering Type, which the content of TDS is higher slightly, and ion ratio is lower (abscissa is less than 0.5), and the main source of ions is from the weathering of rocks in the watershed; The second category is Precipitation Type, which the content of TDS is lower very much, and ion ratio is higher (abscissa is close to 1), and the main source of ions are controlled mainly by atmospheric precipitation; The third category is Evaporation-Concentration Type, which the content of TDS is higher, and ion ratio is also higher (abscissa is close to 1), and the main source of ions are affected by strong evaporative concentration (Gao et al.,2006; Zhu et al., 2010; Lan et al., 2012; Li et al., 2007; Liu et al., 2004).

2.4.3 Ion combination and ratio method

The ion combination and ratio method are used to analyze the source of weathering products in river, which was proposed by Gaillardet in 1999 on the basis of studying 60 large rivers in the world (Gaillardet et al., 1999). Through statistical analysis, it is found that there are three main sources of weathering products in river, which are carbonates, silicates and evaporites. By calculating the ratio of molar ion concentration (mmol·L^{-1}) of Ca^{2+}/Na^{+}, Mg^{2+}/Ca^{2+} and HCO_3^{-}/Na^{+}, the type of weathering product is determined. The ion combinations and ratios used commonly are shown in Table 2.

[Insert Table 2]

Table 2. Ion combinations and ratios of three kinds of rocks (Yang, 2017)

3. RESULTS

3.1 Hydrochemical characteristics of the Xiying River

3.1.1 Annual changes of TDS and pH

According to the statistical data of the JTL Hydrological Station, the runoff changes of the Xiying River have obvious seasonal characteristics. As shown in Figure 3, as the temperature increase gradually on Mid-March, the glaciers begin to melt and the rivers begin to thaw, which cause the runoff increase gradually. The flow rate is higher from June to September. The highest daily flow rate occurs in July, which it is up to 47.9 m^3·s^{-1}. The river freezes from November to March of the following year, and the runoff is smaller.

[Insert **Figure 3**]

Figure 3. Annual variation of TDS, pH and flow in main stream of the Xiying River.

The value of TDS in the Xiying River ranges from 64.2 to 353 mg·L^{-1}, and the average value is 196.94 mg·L^{-1}. The TDS of river has a negative correlation with the flow. When the runoff is larger, the TDS is lower. In turn, when the runoff is smaller, the TDS is higher. As the river thaw on Mid-March, the spring floods appear and the flow increase gradually. At the same time, the value of TDS in the river shows a downward trend, and it reaches the lowest value in July. After September, the runoff decreases gradually, while the value of TDS in the river rises gradually, and it reaches the highest value in winter.

The value of pH in the Xiying River varies from 7.05 to 8.36, and the average value is 8.01, which indicate the river belongs to alkaline water. The average value of pH in spring, summer, autumn and winter is 8.01, 8.05, 8.02, 7.97, respectively, that is winter < spring < autumn < summer. The difference is not obvious in different seasons.

3.1.2 Ionic composition of the Xiying River

The sequence of mass concentration of main cation in the Xiying River is NH_4^+ < K^+ < Na^+ < Mg^{2+} < Ca^{2+}, and their mass concentrations are 0.16, 0.65, 7.19, 11.92, 31.07 mg·L^{-1}, respectively. The sequence of mass concentration of main anion is F^- < NO_3^- < Cl^- < SO_4^{2-} < HCO_3^-, and their mass concentrations are 0.03, 1.12, 1.26, 33.52, 131.02 mg·L^{-1}, respectively. The cation concentration in the Xiying River is different from the abundance of elements in the earth's crust (Mg^{2+} < K^+ < Na^+ < Ca^{2+}). This may be due to the fact that there are many magnesium-rich salts in this basin (Liu et al., 2009; Jia et al., 2016; Lu et al., 2016; Zhou et al., 2019; Zhou et al., 2004; Zhang et al., 2006), which results from the dissolution of debris after the weathering of rocks.

The concentration compositions of anions and cations in the river at each sampling point are shown in Figure 4. The cations are mainly Ca^{2+}, Mg^{2+} and Na^+, and the first dominant cation is Ca^{2+} (accounting for 61.28% of the cation), and the second dominant cation is Mg^{2+} (accounting for 21.76% of the cation). The main anions are HCO_3^- and SO_4^{2-}, and the first dominant anion is HCO_3^- (accounting for 78.03% of the anion), and the second dominant anion is SO_4^{2-} (accounting for about 20.25% of the anion). It can be inferred that the hydrochemical type of river is CaMg-HCO_3 (Bai et al., 2007; Ding et al., 2005; Wen et al., 2004).

[Insert **Figure 4**]

Figure 4. Composition ratio of cations (a) and anions (b) in the Xiying River.

3.1.3 Hydrochemical types of the Xiying River

The ratio of ionic components determines the chemical properties and Hydrochemical types of water. According to the three - line diagram proposed by Piper, and using the data of the Xiying River samples, Figure 5 was obtained. As shown in Figure 5, in the cation diagram, the data points are mostly located in the middle - left area, and Ca^{2+} is the dominant cation. In the anion diagram, the data points are mostly located in the lower left corner, and HCO_3^- is the dominant anion because its content is higher than 60%. The samples of the Xiying River fall mainly in the left area of the diamond where the equivalent concentration of alkaline earth metal exceeds that of the alkali metal (Ca^{2+} + Mg^{2+} > 50%). About 98% of the samples fall in the area of ①, so the Hydrochemical type is mainly bicarbonate type, that is CaMg-HCO_3.

[Insert **Figure 5**]

Figure 5. Piper three-line diagram of samples in the Xiying River.

3.2 Hydrochemical characteristics of the Xiying River

3.2.1 Analysis of ion source based on Gibbs model

The data of river collected in the Xiying River was substituted into the model proposed by Gibbs, the Figure 6 can be obtained. As shown in Figure 6, most of the samples fall within the model, and some of the samples fall outside the dotted line, which indicates that the Xiying river are mainly controlled by natural factors in study area. The values of TDS of river range mainly from 100 to 300 mg·L^{-1}, and Na^+/ (Na^+ + Ca^{2+}) is basically below 0.5, and the Cl^-/ (Cl^- + HCO_3^-) is basically below 0.1, which shows that the ion sources of them belong to Rock Weathering Type. Some samples at the end of glacier are close to the Precipitation Control Type. This may be due to the fact that the samples have less dissolved substances in the process of transforming from precipitation into river, so the chemical compositions of them are similar to those of the precipitation. From the results of existing research (Ding, 2010; Yang, 2017), the ion source of river in the downstream reaches of the Shiyang River belongs to the Evaporation Concentration Type. The Xiying River is the upper reaches of the Shiyang River, which is located in the Qilian Mountains where the altitude is relatively higher and the temperature is lower. The annual evaporation of it is about 800 mm, which is only 35% of the downstream reaches of the Shiyang River, so there is not obvious evaporation effect.

[Insert **Figure 6**]

Figure 6. Gibbs model of the Xiying River: (a) cations (b) anions.

3.2.2 Analysis of ion source based on ion combination and ratio method

According to Gibbs model, the sources of ions in river mainly come from rock weathering. In order to explore the main types and chemical composition of weathered rocks, the method of molar ion concentration ($mmol \cdot L^{-1}$) ratio method proposed by Gaillardet was used (Khadka et al., 2013; Yang et al., 2014; Zhu et al., 2008; Ma et al., 2019; Nie et al., 2005). In conjunction with Table 2, Figure 7 is obtained by Origin 2018 software and the data of all samples. From the distribution of data point in Figure 7, it can be seen that the samples of river fall mainly near the silicates. The ratio of Ca^{2+}/Na^{+} varies between 0.52 to 12.43, and HCO_3^{-}/Na^{+} varies between 2.15 to 25.04, and Mg^{2+}/Na^{+} varies between 0.12 to 4, which indicate that the samples of them fall mainly between silicates type and carbonates type. The ion sources of river mainly come from the weathering products of silicates, but there are some weathering products of carbonates that calcium carbonates dissolve in water.

[Insert **Figure 7**]

Figure 7. Diagram of ion combination ratio of the Xiying River.

3.2.3 Analysis of ion source based on the correlation of various ions

The Correlation Matrix is a statistical tool, which is widely used to establish the relationship between two hydrogeochemical variables to predict the dependent degree of one variable on another. The correlation between various ions in water can indicate the material source and chemical reaction process of ions to a certain extent. Generally speaking, ions with a high degree of positive correlation may have the same material source and chemical reaction process. In SPSS23, the Correlation Matrix is used to analyze the correlation of main ions in river, and the results are shown in Table 3. Because the contents of NH_4^{+} (0.16 $mg \cdot L^{-1}$) and F^{-} (0.03 $mg \cdot L^{-1}$) are lower in all samples, and some samples are below the minimum detection limit of the experiment, so NH_4^{+} and F^{-} are not considered in the correlation analysis.

It can be seen from Table 3 that the correlations between TDS and Na^{+}, Mg^{2+}, Ca^{2+}, SO_4^{2-} and HCO_3^{-} are significant. According to Figure 4, it can be seen that the mass concentrations of Na^{+}, Mg^{2+} and Ca^{2+} account for about 95% of the cations, and those of SO_4^{2-} and HCO_3^{-} account for 97% of the anions. TDS is highly correlated with SO_4^{2-}, and Ca^{2+} and Mg^{2+} are also correlated significantly with SO_4^{2-}, which shows that the dissolution of $CaSO_4$ and $MgSO_4$ has a greater contribution to TDS. Na^{+} is highly related to Cl^{-}, that their source may mainly be the inputs of the sea salt brought by the atmospheric circulation and the salt particles of the air in the middle and lower reaches of the Shiyang River. Mg^+, Ca^{2+}, K^+ and HCO_3^- are highly correlated, which is mainly due to the dissolution of these ions that is mainly contributed by the weathering of silicate and carbonate rocks. NO_3^- has a certain correlation with Na^+ and Cl^-, and the concentration of NO_3^- is basically consistent with the natural background concentration, which may be related to the dissolution of a small amount of evaporite rocks (Cao et al., 2020).

Table 3. Correlation of various ions in the Xiying river.

[Insert **Table 3**]

4. DISCUSSION

4.1 Differences of TDS and pH in the main stream and tributaries of the Xiying River

The values of TDS and pH of each sampling point in the main stream of the Xiying River are shown in Figure 8. With the altitude decreases, the value of TDS rises firstly from the BCMD to the SCLK reach, while it decreases gradually from the SCLK to the XYSK reach. From the BCMD to the SCLK reach, the river has a larger drop with the slope ratio of 0.034, so the flow rate is faster and the physical erosion is stronger. After continuously washing the river bed and bank, the minerals of natural environment are dissolved by the river, which cause the dissolved substances to increase. At this reach, the water vapor circulation is stronger, and the precipitation is more. The aerosol dissolved in precipitation also contributes to the value of TDS in river. Furthermore, after the precipitation reaches the ground, part of it dissolves surface materials and then merges into the river by the form of surface runoff. Therefore, the value of TDS from the BCMD to the SCLK reach is higher (Liu et al., 2013). From the SCLK to the XYSK reach, the slope ratio is about 0.014, and the river bed tends to be flat. As the tributaries continue to converge, the runoff increases, which dilute the TDS and cause the value of it to decrease. However, the value of TDS of the river in the sampling point of HJX is higher than that of the adjacent reach. From Figure 4, we can know that, the proportion of SO_4^{2-} and NO_3^- near the sampling point in HJX has a tendency to increase. This may be affected by human activities, because the villages distribute on both sides of the river, which may be related to the use of coal resources and the discharge of domestic sewage. The domestic sewage is discharged directly into the river by residents, which leads to a higher value of TDS in this reach of the river (from the SCLK to the XYSK) (Man et al., 2016; Jia et al., 2005; Zhao et al., 2017; Zhou et al., 2014).

[Insert **Figure 8**]

Figure 8. Spatial variation of TDS and pH in the Xiying River.

As shown in Figure 9, the variation range of TDS in the main stream of the Xiying River is 64.2~353 mg·L^{-1}, with an average value of 196.94 mg·L^{-1}, but that of tributaries is 61.5~288 mg·L^{-1}. The value of TDS of the river at the BCMD is only 28.05 mg·L^{-1}, which is significantly lower than that of the remaining rivers. This is because the newly melted river has little dissolved substances, which cause that the value of TDS is lower. The value of TDS of the XYSK is slightly lower than that of the Xiying River, which may be due to the fact that the ion concentrations of the tributaries are lower than the main stream of the Xiying River, and the inflow of the tributary dilutes the ion concentration of the main stream.

The order of the average TDS of each tributary is Qingyang River > Tuoluo River > Longtan River > Xiangshui River > Shangchigou. It shows that the value of TDS of the tributaries also gradually decreases as the altitude decreases. This is due to the fact that the slope ratios of these tributaries decrease gradually with altitude, and the river channels tend to be gentle. So, the scouring ability of the river is weakening relatively, and the dissolved substances in the river are decreasing correspondingly. Except for the tributary of Qingyang River, the average values of TDS of the other tributaries are lower than that of main stream of the Xiying River. Compared to other tributaries, the Qingyang River is longer and the drop ratio is larger, so the dissolved substances are more and the value of TDS in river is higher. Because the runoff of the tributary of Shangchigou is smaller and its river course is relatively shorter, so the value of TDS of it is relatively lower.

[Insert **Figure 9**]

Figure 9. TDS distribution interval of some tributaries and main stream in the Xiying River.

4.2 Differences of ion concentration between main stream and tributaries of the Xiying River

The temporal change of the mass concentration of main ion in the Xiying River is shown in Figure 10. The lowest value of each ion concentration occurs generally in January, which is mainly affected by runoff and climate. Because the temperature is the lowest at this time, the river is frozen and the rocks are weakly weathered, so the ion concentration in river is the lowest. The highest values of Ca^{2+} and HCO_3^- appears in April, and the remaining ions also show an upward trend at the same time. This is mainly due to the spring flooding that increase the scouring capacity of the river, which accelerate the dissolution of the weathering products of rocks. Except for Ca^{2+} and HCO_3^-, the highest values of other anions occur in November, and the concentrations of other cations are also higher at the same time, which is affected by climate factors. After September, the melting speed of glaciers slows down as the temperature decrease gradually (Chen, 1958; Bao, 2019; Zhang et al., 2011; Wang et al., 2018; Xiao et al., 2016; Zhao et al., 2014), and the amount of precipitation and the runoff of the river also decrease gradually, so the concentration of various ions increase correspondingly. On the middle and late November, the river enters the freezing period and the weathering products of the rock weakens, so the concentrations of most ions in the river appear the lowest values (Yan et al., 2009; Yao, 2003; Kou et al., 2018). Beginning in late of March, spring floods are coming as ice and snow melt. River erosion is strengthened during this period, and the solubility of inorganic salts increase by the rise of river temperature. At the same time, the sand and dust weather occur more frequently, which causes that the value of TDS in the river also increase. So, the ion concentration increases gradually, and the higher values of it often appears in spring. From May to August, as the temperature rises and the precipitation increases, the runoff of the river increases gradually and the ion concentration decreases correspondingly.

[Insert **Figure 10**]

Figure 10. Annual variation of main ion concentration in the Xiying River ($mg \cdot L^{-1}$).

The seasonal changes of ion concentration of each tributary are shown in Table 4. In the tributary of Shangchigou, samples were not collected because of road icing in winter. The ion concentrations are higher in spring and lower in summer. This is mainly affected by the flood in spring that causes the value of TDS increase and affected by more precipitation in summer that dilute the ion concentration in the river. The ion concentrations of the Qingyang River, Tuoluo River and Xiangshui River are higher in summer, and the HCO_3^- in all seasons is higher than that of the Xiying River. This is due to their larger river drop, stronger weathering of rocks and the larger and faster flow in summer, which leads to strong erosion. The tributary of the Longtan River has higher ion concentration in summer and autumn but lower in winter and spring. This is because the river course of it is shorter and the precipitation is heavy. In summer and autumn, the precipitation is heavier and the river flow is larger, which cause the erosion of the river is stronger and the ion concentration of the river is higher. It is opposite in winter and spring.

[Insert **Table 4**]

Table 4. Seasonal variation of main ion concentrations in tributaries of the Xiying River ($mg \cdot L^{-1}$).

4.3 Differences of ion sources between the main stream and tributaries of the Xiying River

By exploring the source of ions in the section of results, it can know that the ion composition of the Xiying River is controlled mainly by rock weathering, and the type of rock in study area is mainly silicates. It can be seen from Figure 11 that the ion sources of the five tributaries of the Xiying River is basically the same as that of the main stream, and they distribute mainly between the silicates and the carbonates (closer to the silicates). It shows that the ion source of river in study area is controlled mainly by the weathering of silicates, and it may also be affected weakly by the weathering of evaporative and carbonates.

In Figure 10a, the data points are on a straight line basically, and the ordinate changes greatly, which indicate that the sources of Ca^{2+} and HCO_3^- have a certain correlation. In the Figure 10b, the change ratio of Mg^{2+}/Na^+ is small and stable, which is related mainly to the composition of the rock.The rock types in the Xiying River Basin are intrusive rocks basically, that are granite and diorite mainly. Therefore, the ion source of river is controlled by the weathering of silicates and carbonates. The rock types of the Shangchigou and Qingyang River are monzonite, which is composed of plagioclase, potash feldspar and quartz. The rock types of the Tuoluo River and Longtan River are diorite and granodiorite, which are composed of plagioclase, quartz, potash feldspar and hornblende. Affected by the types of rocks, the data of samples of the Shangchigou, Qingyang River and Longtan River fall into the middle of the silicates and carbonate. The samples data of the Tuoluo River is more scattered, which may be related to the changes of dissolved substances which are affected by seasonal glacial meltwater and temperature changes. The rock types of the Xiangshui River are plagioclase and monzonite, which are composed of plagioclase and quartz. The ion ratio of it is closest to silicates.

As the altitude decreases, the slope ratio of the tributaries of the Xiying River decreases, and the erosion ability of the river decreases correspondingly. At the same time, the ion composition of them approaches the silicates, which can be seen from the tributaries of Qingyang River, Tuoluo River and Xiangshui River. Although the overall rock environment of the Xiying River Basin is similar, the dissolution capacity of the river is different. Affected by rock weathering, temperature, precipitaiton, river drop and runoff, the ion composition ratios of the tributaries and the main stream of the Xiying River are different.

[Insert **Figure 11**]

Figure 11. Ion ratio diagram of the Xiying river and its tributaries.

5. CONCLUSIONS

In the Xiying River Basin, the Rivers are weakly alkaline ($\overline{pH}$ is about 8.01), and the seasonal changes are not obvious. $\overline{TDS}$ of the Xiying River is 179.29 mg·L^{-1}. The seasonal difference of ion concentration is obvious, that is lowest in summer and highest in spring. The cation concentration in river is $NH_4^+ < K^+ < Na^+ < Mg^{2+} < Ca^{2+}$, and the anion concentration is $F^- < NO_3^- < Cl^- < SO_4^{2-} < HCO_3^-$. The type of water chemistry in study area is CaMg-HCO_3.

The sources of ions in the Xiying River and its tributaries are controlled significantly by the weathering of rocks, which is mainly weathering products of silicates, but they are less affected relatively by human activities. From the BCMD to the SCLK reach, the value of TDS of the main stream increases gradually. From the SCLK to the XYSK reach, the value of TDS of the main stream decreases gradually. As the altitude decreases, the incoming tributaries are affected more significantly by the silicates. But there may be a small amount of dissolution from evaporites and carbonates.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

AUTHOR CONTRIBUTIONS

Zhiyuan Zhang and Wenxiong Jia conceived the idea of the study; Guofeng Zhu provided sampling plan and funding; Hui Xiong and Le Yang participated in the experiment; Zhiyuan Zhang and Yang Shi were responsible for field sampling; Zhiyuan Zhang wrote the paper; Miaomiao Zhang and Fuhua Zhang checked and edited the Language. All authors discussed the results and revised the manuscript.

DATA AVAILABILITY

The data used in this article is collected from the field, the author chooses not to share the data.

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TABLES

Table 1. Sampling location and sample quantity.

Sampling point	Sample quantity	Longitude (E)	Latitude (N)	Elevation (m)	Sample type	Note
BCMD	4	101.85°	37.55°	3577	River	Bingchuanmoduan
SD	7	101.84°	37.58°	3364	River	Suidao
SCG	14	101.85°	37.64°	3029	River	Shangchigou
SCLK	22	101.93°	37.72°	2592	River	Sanchalukou
GGKFQ	24	101.98°	37.77°	2451	River	Gaigekaifang Bridge
WMQ	24	102.00°	37.81°	2380	River	Weiming Bridge
HJX	12	102.01°	37.83°	2338	River	Huajian Township
WGQ	22	102.12°	37.89°	2167	River	Wenge Bridge
XYSK	12	102.22°	37.92°	2025	River	Xiying Reservoir
JTL		102.07°	37.88°	2235	Hydrological Station	Jiutiaoling

Table 2. Ion combinations and ratios of three kinds of rocks [27]

Ion Type	Carbonates	Silicates	Evaporites
Ca^{2+}/Na^{+}	50	0.35 ± 0.15	< 0.2
Mg^{2+}/Ca^{2+}	10	0.24 ± 0.12	< 0.12
HCO_3^{-}/Na^{+}	120	2 ± 1	< 1

Table 3. Correlation of various ions in the Xiying river.

Type	TDS	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	Cl^{-}	SO_4^{2-}	NO_3^{-}	HCO_3^{-}
TDS	1								
Na^{+}	0.641**	1							
K^{+}	0.373**	0.304**	1						
Mg^{2+}	0.549**	0.271**	0.797**	1					
Ca^{2+}	0.577**	0.174*	0.712**	0.840**	1				
Cl^{-}	0.435**	0.828**	0.236**	0.110	0.100	1			

SO_4^{2-}	0.819**	0.531**	0.345**	0.630**	0.646**	0.343**	1		
NO_3^-	0.410**	0.729**	0.244**	0.090	0.100	0.807**	0.266**	1	
HCO_3^-	0.546**	0.251**	0.827**	0.938**	0.956**	0.140	0.573**	0.130	1

Note: **means p<0.01 (two-tailed); *means p<0.05 (two-tailed).

Table 4. Seasonal variation of main ion concentrations in tributaries of the Xiying River ($mg \cdot L^{-1}$).

Tributary	Season	Na^+	K^+	Mg^{2+}	Ca^{2+}	CL^-	SO_4^{2-}	NO_3^-	HCO_3^-
Shangchigou	Spring	6.81	0.98	22.86	79.01	1.14	62.93	1.31	293.58
	Summer	6.43	1.02	17.67	62.05	1.36	50.17	1.39	230.23
	Autumn	7.24	1.10	22.00	74.56	1.35	53.60	1.39	288.31
	Average	6.82	1.03	20.84	71.87	1.28	55.57	1.36	270.71
Qingyang River	Spring	6.93	0.90	15.03	47.55	1.31	35.95	0.92	192.39
	Summer	8.71	1.20	22.91	57.66	1.59	51.60	1.48	247.52
	Autumn	6.10	1.06	15.68	50.01	1.28	36.25	1.85	199.97
	Winter	4.04	0.78	14.35	63.27	0.62	45.75	0.98	217.68
	Average	6.52	1.00	17.76	58.07	1.21	45.02	1.32	225.65
Tuoluo River	Spring	7.45	1.25	13.78	39.72	2.38	23.33	1.69	177.56
	Summer	11.86	1.00	24.05	66.39	3.11	47.12	1.56	291.00
	Autumn	5.35	0.83	11.00	36.88	1.77	23.05	1.21	150.35
	Winter	4.65	0.75	14.15	55.73	0.85	36.85	1.06	206.07
	Average	7.33	0.96	15.75	49.68	2.03	32.59	1.38	206.24
Longtan River	Spring	5.28	0.75	8.27	32.99	1.23	19.68	1.31	129.43
	Summer	7.59	0.22	7.19	22.07	1.18	34.55	1.00	77.44
	Autumn	7.98	0.49	8.25	26.20	1.67	29.57	0.95	102.38
	Winter	1.80	0.34	3.30	23.98	0.42	7.33	0.37	84.84
	Average	5.66	0.45	6.76	26.31	1.12	22.78	0.91	98.53
Xiangshui River	Spring	9.23	0.32	4.27	13.96	2.25	15.34	1.98	63.97
	Summer	14.66	0.39	5.12	17.65	4.65	24.25	2.44	78.12
	Autumn	8.02	0.31	5.20	16.61	2.07	22.52	1.63	65.06
	Winter	4.74	0.24	4.40	13.94	0.81	16.64	1.06	54.23
	Average	9.16	0.32	4.75	15.54	2.44	19.69	1.78	65.35
Xiying River	Spring	7.56	0.71	12.62	34.64	1.20	31.40	1.40	147.59
	Summer	8.42	0.72	9.96	27.36	1.50	31.26	1.39	114.02

	Autumn	8.63	0.56	11.60	31.00	1.70	34.17	1.84	129.23
	Winter	6.95	0.62	12.55	27.90	1.24	31.68	1.17	124.76
	Average	8.07	0.64	11.62	30.58	1.47	32.49	1.53	129.50

FIGURE LEGENDS

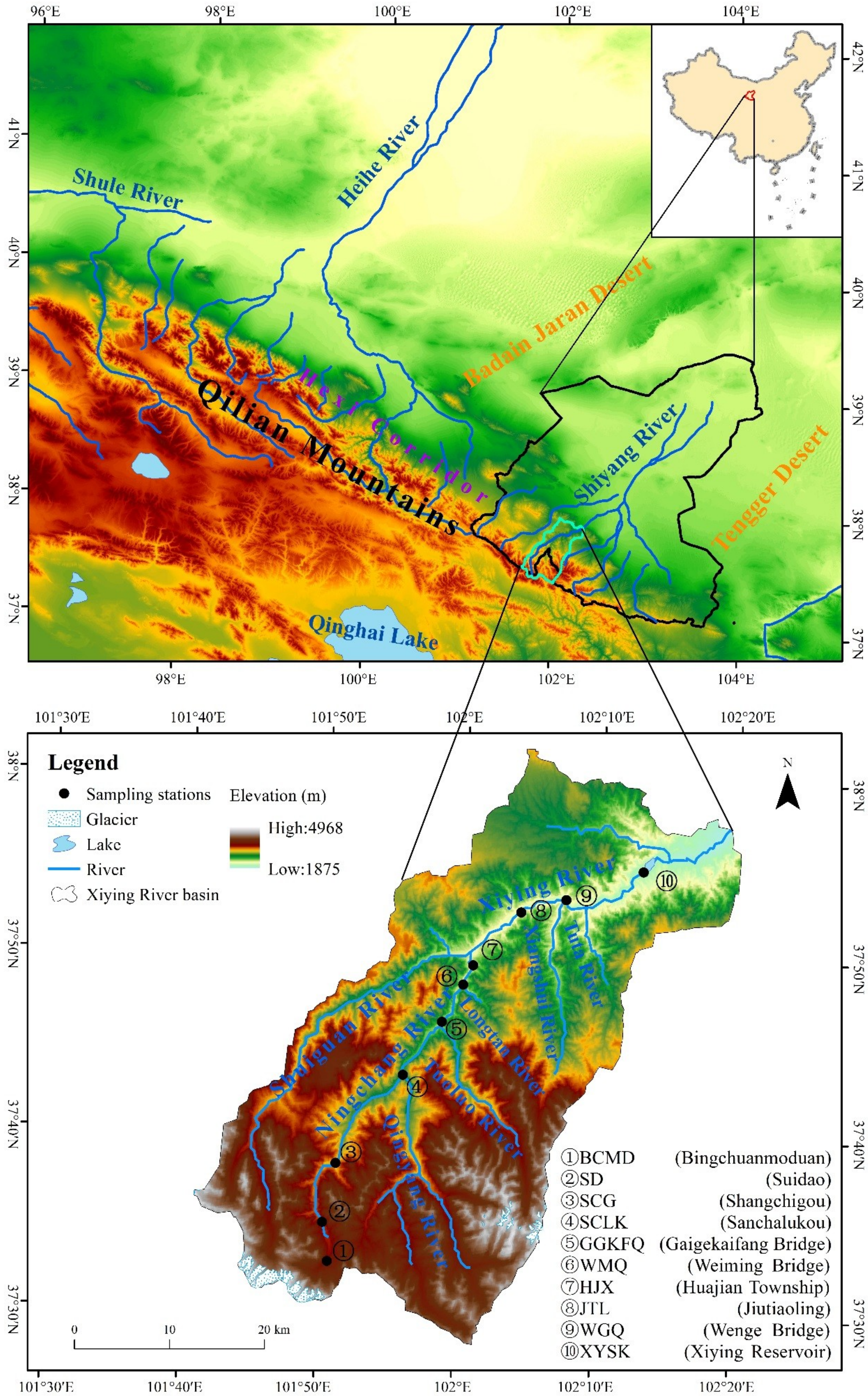
Shule River
Heihe River
Badain Jaran Desert
Hexi Corridor
Qilian Mountains
Shiyang River
Tengger Desert
Qinghai Lake
Legend
Sampling stations
Glacier
Lake
River
Xiying River basin
Elevation (m)
High:4968
Low:1875
Xiying River
Xiangshui River
Tuta River
Longtan River
Shuiguan River
Ningchang River
Tuolmo River
Qingyang River
0 10 20 km
①BCMD (Bingchuanmoduan)
②SD (Suidao)
③SCG (Shangchigou)
④SCLK (Sanchalukou)
⑤GGKFQ (Gaigekaifang Bridge)
⑥WMQ (Weiming Bridge)
⑦HJX (Huajian Township)
⑧JTL (Jiutiaoling)
⑨WGQ (Wenge Bridge)
⑩XYSK (Xiying Reservoir)

Figure 1. The location of the study area and the distribution of sampling points.

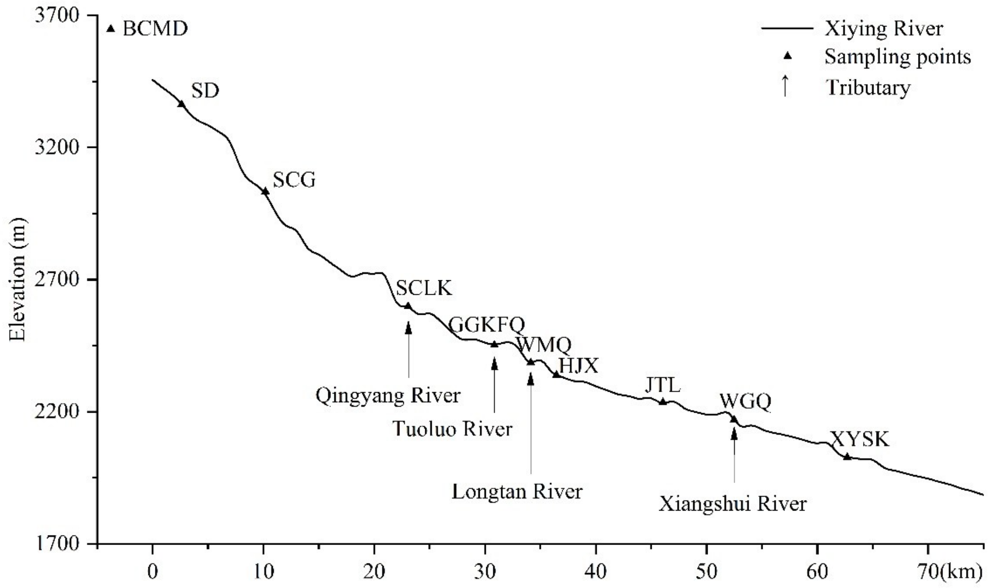

Figure 2. Channel longitudinal profile in the Xiying River.

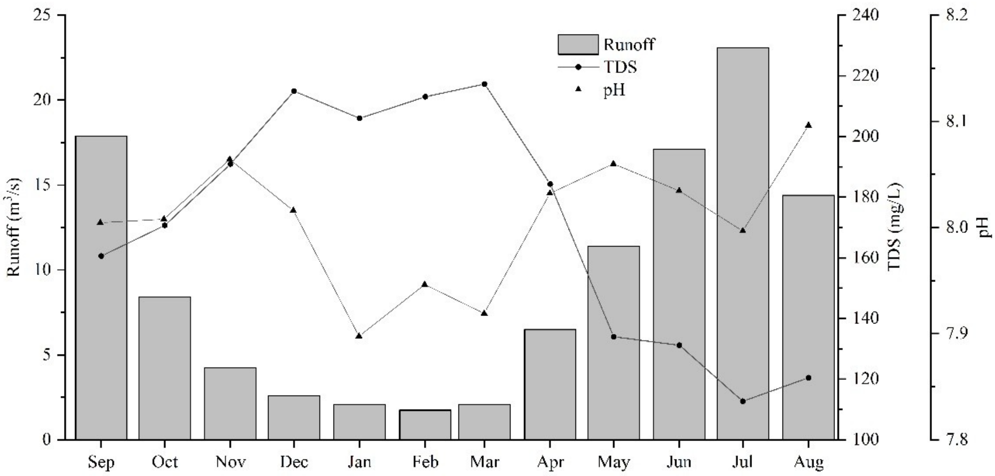

Figure 3. Annual variation of TDS, pH and flow in main stream of the Xiying River.

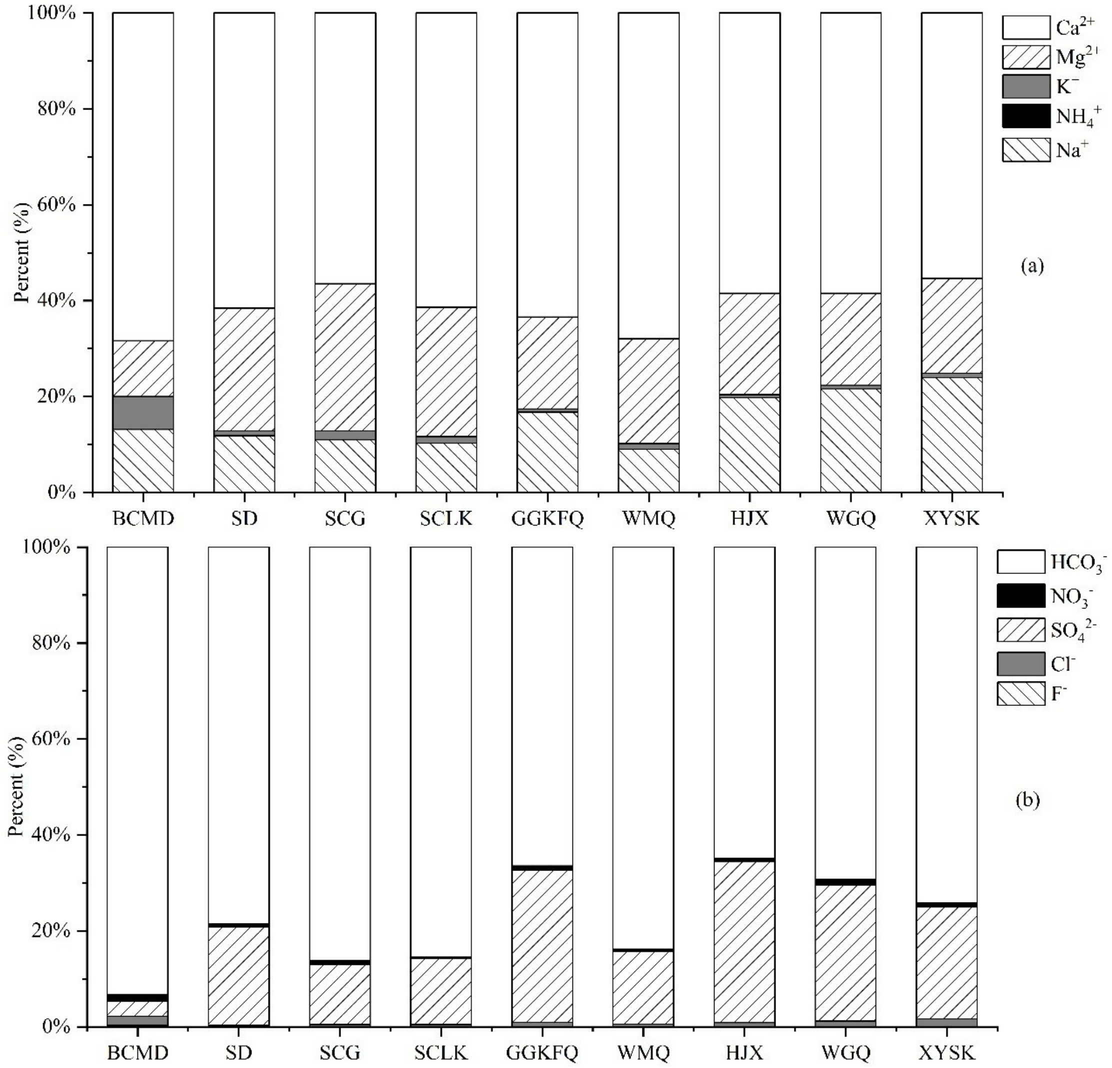

Figure 4. Composition ratio of cations (a) and anions (b) in the Xiying River.

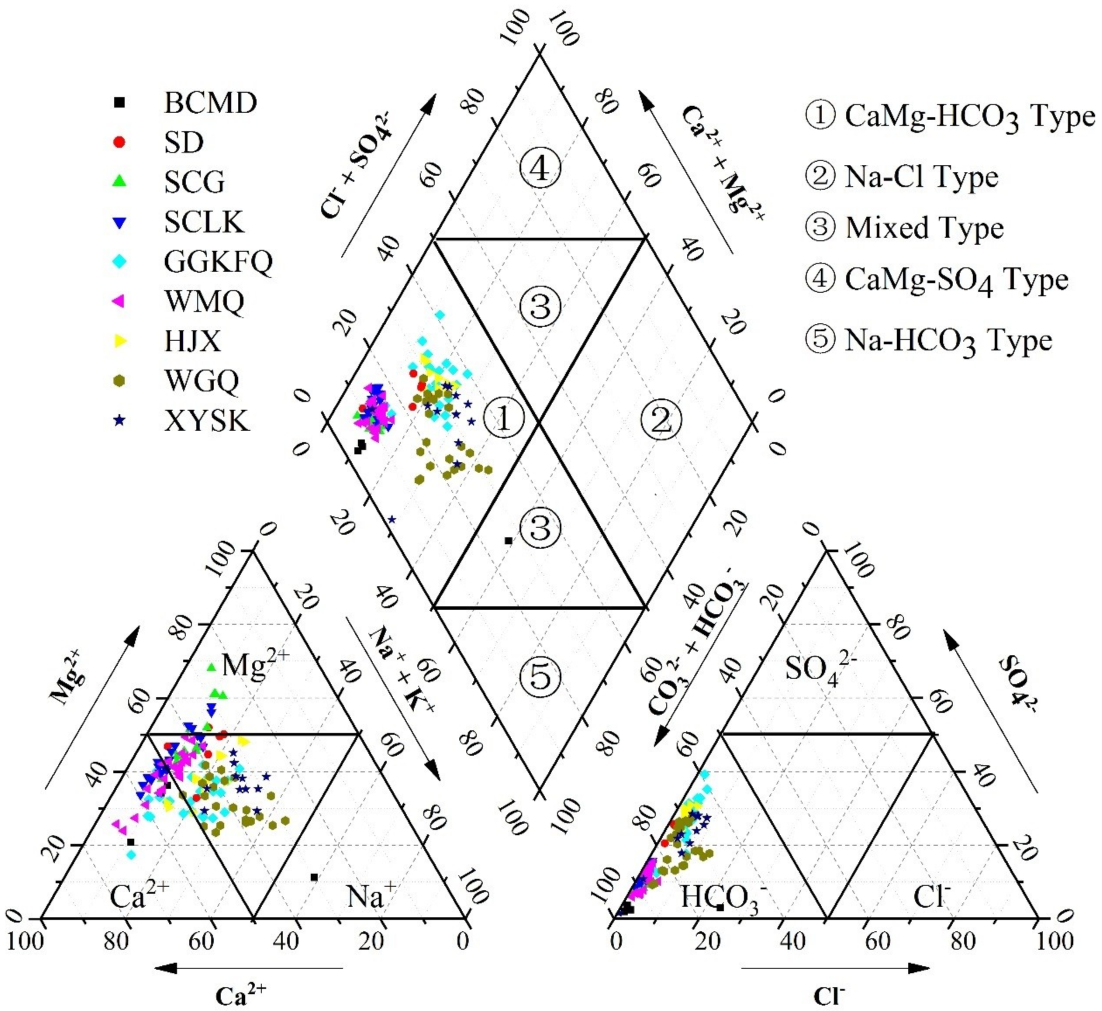

Figure 5. Piper three-line diagram of samples in the Xiying River.

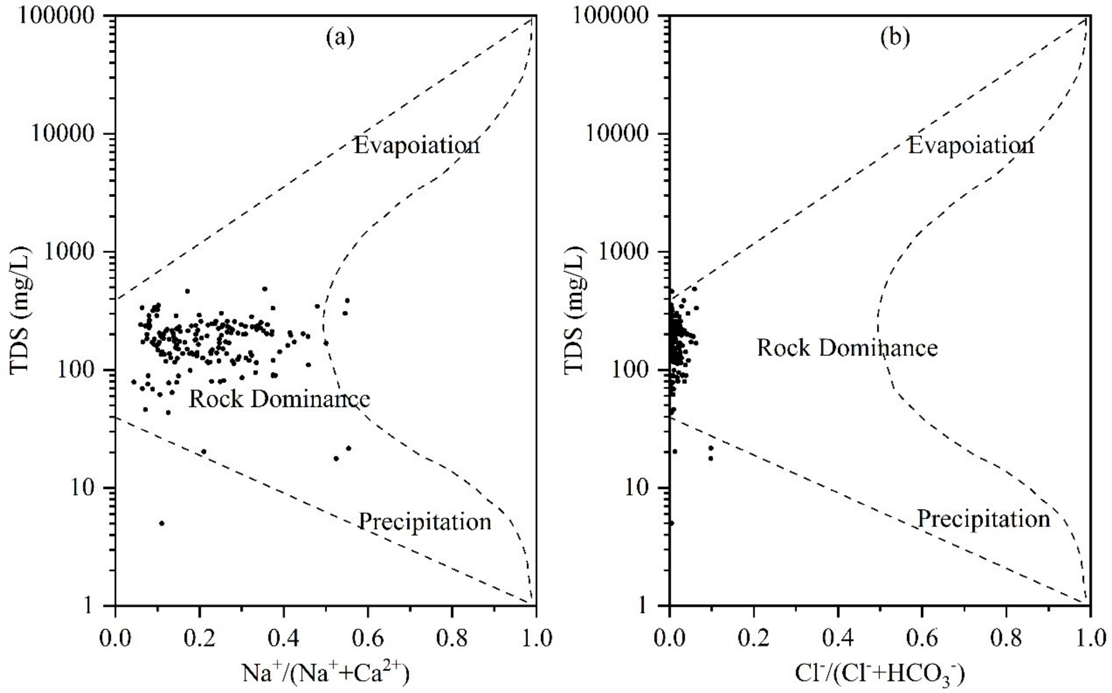

Figure 6. Gibbs model of the Xiying River: (a) cations (b) anions.

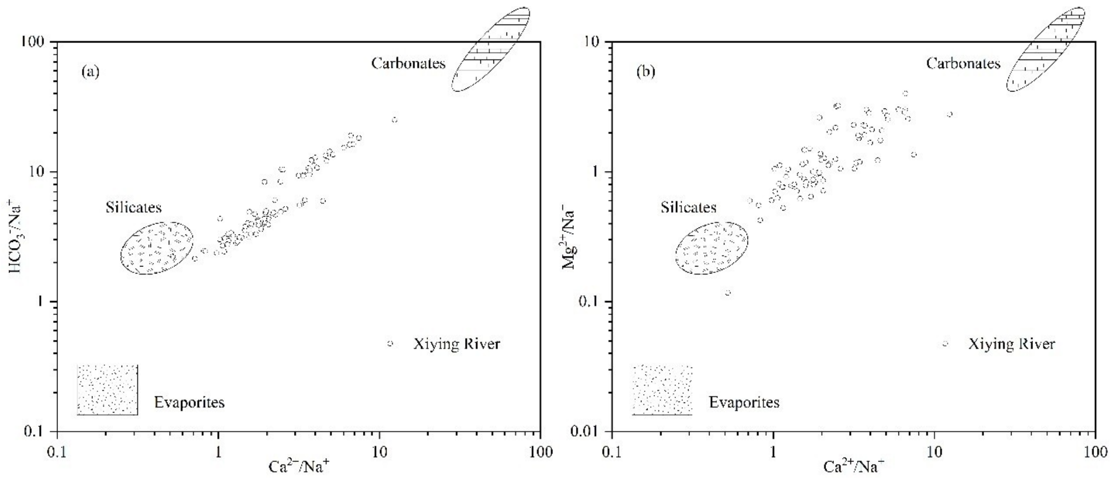

Figure 7. Diagram of ion combination ratio of the Xiying River.

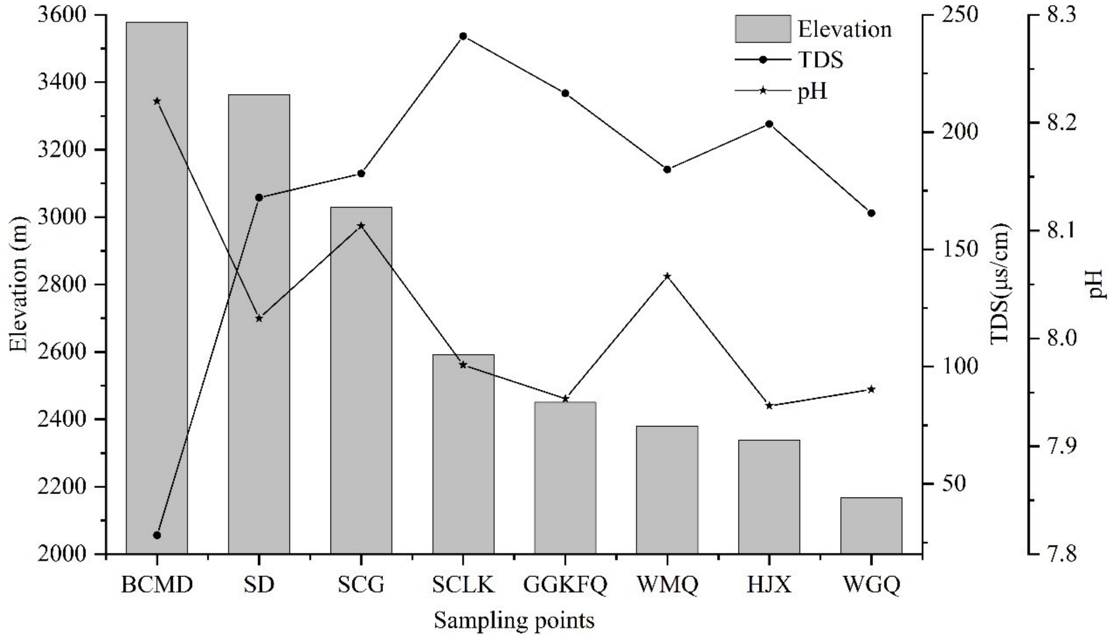

Figure 8. Spatial variation of TDS and pH in the Xiying River.

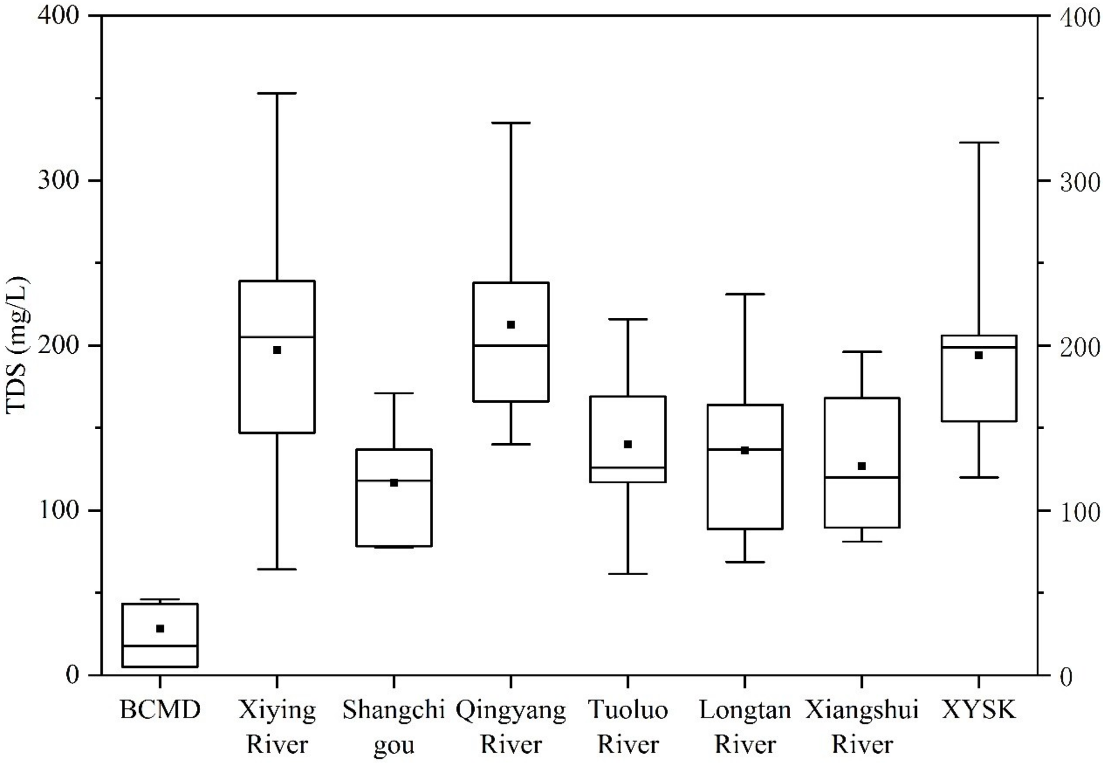

Figure 9. TDS distribution interval of some tributaries and main stream in the Xiying River.

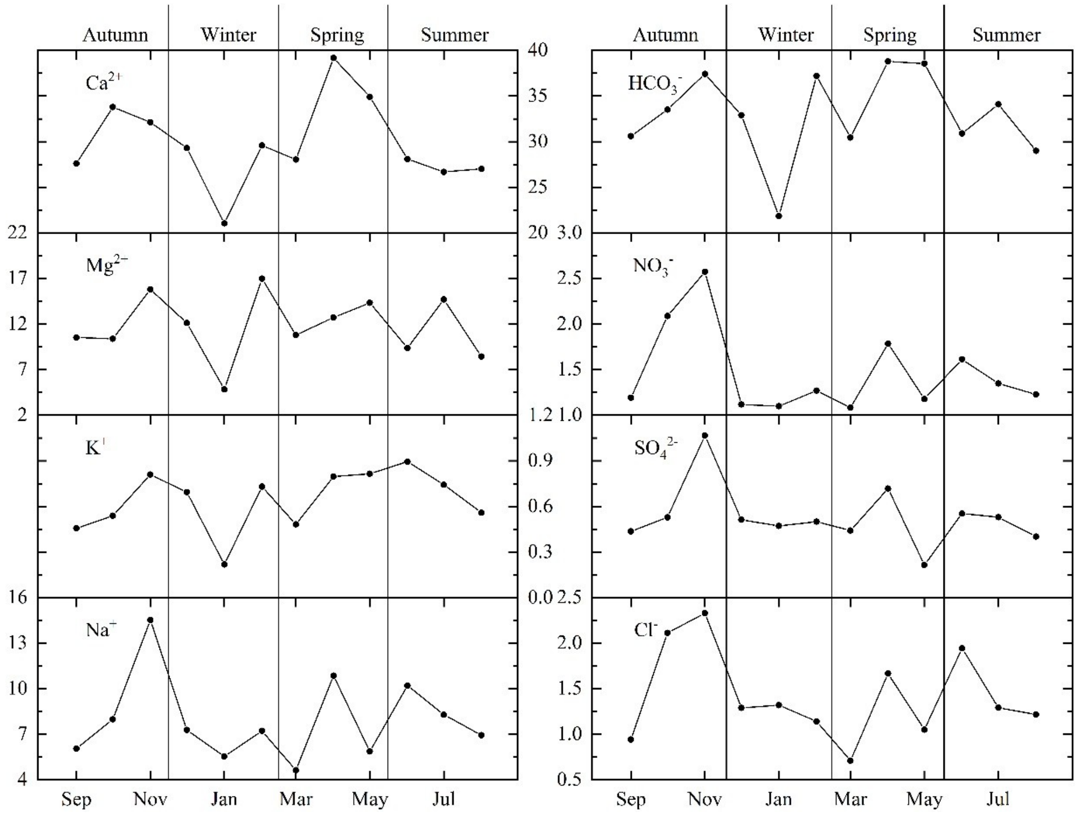

Figure 10. Annual variation of main ion concentration in the Xiying River ($mg \cdot L^{-1}$).

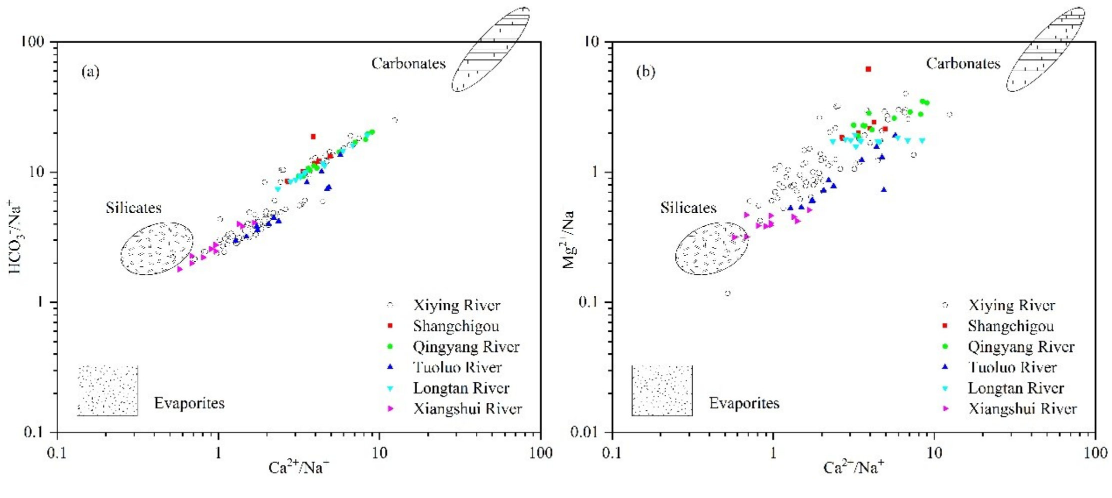

Figure 11. Ion ratio diagram of the Xiying river and its tributaries.