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Irrigation water quality may improve in arid regions of China

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Abstract: The stability and safety of water environment are the foundation of agricultural development. The possibility of salinization and desertification in the oasis agricultural area is much higher than that in other areas, for the population density, lack of water resources and high salinity. Therefore, it is necessary to study the water environment of irrigation water in this area, so as to make a reasonable water resource utilization and protection plan. In the agricultural irrigation period (from Apr. to Sep.) and non-irrigation period (from Oct. to Mar. of the next year), there were 9 sampling points set up from the source area to the oasis of the middle and lower reaches in Shiyang River Basin. Evaluating the irrigation water quality of surface water by ion concentration, SAR and end-member mixing diagram. The results shown: (1) the dilution effect of precipitation has a decisive influence on the ion concentration of surface water in the watershed. Due to the overlapping of irrigation period and rainy season, rainfall dilution makes irrigation water quality better. (2) There are spatial differences in hydrochemical types. The upstream hydrochemical type is mainly Ca-HCO_3 type. The hydrochemical type of the middle and lower reaches is Ca (Na) - HCO_3 mixed type. The upstream surface water is very suitable for agricultural irrigation, and the middle and downstream oasis area is suitable. (3) Surface rock weathering and evaporation crystallization are the main factors affecting the hydrochemical characteristics of surface water. Due to changes in the underlying surface environment in a short time, it is unlikely that the water quality will deteriorate. (4) In recent years, with the increase in precipitation caused by climate change and the strict environmental protection policies, the risk of deterioration of irrigation water quality is greatly reduced, surface water may be more suitable for agricultural irrigation.

Keywords: Inland River Basin; Oasis; Shiyang River; Irrigation water quality

1 Introduction

The water resource is an important material basis for human survival and development (Van der Hoek et al., 2001; Zhang et al., 2012). As an important part of geochemical cycle in arid area, river is the connecting channel of material and energy cycle between land and ocean (Stallard and Edmond, 1981; Berner andBerner, 2012; Zhu et al., 2012), and also the main source of water for Industry and agriculture (Stigter et al., 2006; Dograceci et al., 2012). Whether the surface water environment is healthy or not directly determines the sustainability of local social and economic development. Under the background of global climate change, the hydrochemical characteristics of surface water are controlled by natural processes such as rock weathering, atmospheric precipitation, evaporation crystallization and groundwater recharge (Gibbs, 1970; Meybeck and Helmer, 1989; Thomas et al., 2015). The interference of human activities is also accompanied by the evolution of the surface water environment. The sustainable development of the surface water environment is a topic of common concern for human society (Pant et al., 2018).

Hydrochemistry studies can reveal the quality of drinking water, agricultural water, and industrial water (Burt et al., 1993; Haygarth and Jarvis, 2002; Fučík et al., 2012). Hydrochemical parameters is base in evaluating water quality suitable for irrigation (Al-Bassam and Al-Rumikhani, 2003). Excessive salt in irrigation water is one of the main constraints for agricultural development in arid areas (Wang et al., 2004). Irrigation with poor quality water may bring excessive harmful elements to the soil and affect its fertility. The quality of irrigation water restricts the yield of crops through its impact on the soil environment and becomes a key factor affecting the growth of crops (Fipps, 2003). Scholars have carried out a lot of research work in the areas where agricultural activities are concentrated. Based on understanding the hydrochemical characteristics of irrigation water, it is an urgent problem to explore an effective research method to evaluate water resources reasonably and guide agricultural production activities. Giridharan et al. (2008) found that the groundwater quality was mainly controlled by the dissolution and ion exchange of carbonate and silicate minerals by analyzing the main ion components of groundwater in the cooum river area of India. The suitability of groundwater for agricultural irrigation in the study area was analyzed by using single indicators such as sodium adsorption ratio (SAR) and residual sodium carbonate (RSC). Varol and Davraz (2015) used R-type factor analysis to study the water-rock interaction during the formation of groundwater chemical composition in the tefenni plain of Turkey. By comparing the change rule of Na% in the wet season and the dry season, it was found that the groundwater quality in the dry season was more unfavorable to agricultural irrigation. Zouahri et al(2015) using the USSL classification method, found that the risk of soil salt damage caused by groundwater irrigation was higher in western european plain, while the risk of soil alkali damage was lower. Pang et al (2010) studied the effect of brackish water irrigation on Soil in northern China. The results showed that brackish water significantly increase soil salt content in different depths. Zhang et al (2012) believed that in Songnen plain, surface water and shallow groundwater are suitable for irrigation, but the harm of sodium salt needs to be controlled. Zhang et al(2018) evaluated the suitability of groundwater irrigation in Sichuan Basin and found that the water quality of shallow surface groundwater is good and suitable for irrigation. From shallow to deep, the water quality of groundwater gradually becomes poor, and the middle and deep groundwater is not suitable for long-term agricultural irrigation. Besides, Wilcox classification (Alam and Aslam, 2012), salinity and alkalinity method (Li et al., 2013), and other research methods related to irrigation water quality evaluation. In the early stage, many research results used a single water quality evaluation index to evaluate the irrigation water quality respectively (Al-Bassam and Al-Rumikhani, 2003; Sadashivaiah et al., 2008; Tank and Chandel, 2010). The evaluation results lacked integrity and comprehensiveness.

The amount of water in the arid area is very limited. The oasis supported by the inland river concentrates almost all human activities in the arid area and bears huge pressure of population, resources and environment. Due to the natural background of low precipitation and high evaporation and the discharge of agricultural and industrial pollutants, many studies have confirmed that the water quality in the inland river basin take a turn for the worse (Ji et al., 2006; Zhang et al., 2010). Still, most of the sampling points in the relevant studies are concentrated in the cities and towns with dense human activities. Because the hydrological system will continue to migrate and transform, it has certain self-purification capabilities, only from the perspective of the whole water cycle can we systematically understand and view the water environment of the basin, and accurately evaluate whether the surface water can support the agricultural production of the basin.

In this paper, Shiyang River Basin, which has the densest population and the most pressure on water resources in China, is selected as the research sample. Based on a large number of hydrochemical data collected in the Shiyang river basin, (1) the hydrochemical characteristics are analyzed by the surface water in the source area, catchment area and dissipation area of the basin to determine whether the surface water in different areas are suitable for irrigated. (2) We analyzes the main control factors of the water environment in the basin. (3) Forecast the development trend of irrigation water quality in the future. This study can quantitatively reveal the spatiotemporal characteristics of the hydrochemistry characteristics of the surface water in the inland river in the arid area, and improve the understanding level of the suitability of the surface water irrigation in the inland river in the arid area.It can predict the water quality change in the future, which is beneficial to the developmenthe agricultural development, ecological environment protection, farmland water conservancy facilities construction and rational utilization of water resources in Shiyang River Basin.

2 Study area

Shiyang River basin, located in the east of the Qilian Mountains, is one of the three basins originating from the northern slopes of the Qilian Mountains. In the south isthe Qinghai Tibet Plateau. In the north are the Tengger Desert and Badain Jaran Desert (101 ° 41 ′ - 104 ° 16 ′S, 36 ° 29 ′ - 39 ° 27 ′ N). The basin is located at the junctionof the eastern monsoon area and the non-monsoon area, where the ecological environment is extremely fragile (Fig. 1). The altitude of the basin is between 1254-5217m, which belongs to the temperate continental climate. The temperature vary widely, the rainfall is rare, and the surface evaporation is strong. The surface water of the basin mainly comes from the precipitation in the mountain area and the melting water of ice and snow. With the change of altitude, there are alpine meadow, subalpine shrub, shrub grassland, desert vegetation, and other vegetation types from the river source area to the oasis in the middle and lower reaches. Shiyang River basin covers an area of about $4.16 * 10^4$ km^2, with a total cultivated land area of $4.17 * 10^5$ hectares. At present, the total population of the basin is 2.27 million, and the proportion of multiple planting is 50%. The agricultural water consumption accounts for 85.7% of the total water consumption, the large agricultural water consumption is the main reason for the overload of water resources in the Shiyang River Basin. The increase of agricultural irrigation water leads to a series of ecological problems, such as the decline of groundwater level, vegetation degradation, soil salinization and land desertification ，this area is one of the most serious ecological problems in China (Su et al., 2019).

Fig.1 The Shiyang River Basin, in the east of Qilian Mountains, showing location of oasis agricultural irrigation area and sampling points

3 Data and methods

From June 2015 to October 2017, surface water samples were collected in Shiyang River Basin. According to the planting type and structure of crops in the study area, the sampling time was divided into irrigation period (from Apr. to Sep.) and non-irrigation period (from Oct. to Mar. of the next year). The sampling period is once a month, 323 samples are collected. The location of the sampling points is shown in Fig. 1. The sample bottle is a 100 ml polyethylene plastic bottle that has been cleaned by deionized water in advance, then load the sample, and then seal and freeze it. All samples were transported to the National Key Laboratory of cryosphere, Northwest Institute of ecological resources and environment, Chinese Academy of Sciences by freezing and stored in cold storage at -15°C. Two days before the analysis, the sample was taken out and melted naturally at room temperature (about 23°C). Before the test, filter with 0.45 μm filter membrane, analyze the concentration of main cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, and NH_4^{+}) by Dionex-600 ion chromatography; analyze the concentration of main anions (Cl^{-}, NO_3^{-}, and SO_4^{2-}) by Dionex-2500 ion chromatography, with the accuracy of $ng.g^{-1}$ and the test data error of < 5%. DDS-307 water quality analyzer is used to measure pH, TDS and other indicators of water.

The meteorological data (temperature and sunshine duration) involved in this study were selected from the data of Wuwei meteorological station located in the study area, and the starting year was 1960. The relevant meteorological data involved in the study are all from China Meteorological Data Service Center(*http://data.cma.cn/*).Runoff and precipitation data are from Shiyang River Basin Water Resources Management Bureau(*http://slt.gansu.gov.cn/syhglj/*).In this paper, the Penman-Monteith model (P-M) recommended by the world food and Agriculture Organization (FAO) is used as the theoretical basis, and combined with the actual situation in the region, the potential evaporation in the study area is estimated. The calculation formula is:

$$Eq.1\ ET_0=\frac{0.48\Delta(R_n-G)+\gamma\frac{900}{T+273}U_2(e_s-e_a)}{\Delta+\gamma(1+0.34U_2)}$$

Among them, ET_0 is potential evapotranspiration (mm); △ is slope of saturated water vapor pressure curve (kPa °C^{-1}); R_n is net radiation (MJm^{-2}day^{-1}); G is soil heat flux (MJm^{-2}day^{-1}); γ is dry and wet surface constant (kPa°C^{-1}); t is average temperature (°C); U_2 is wind speed at 2m (ms^{-1}); e_s is saturated vapor pressure (kPa); e_a is actual vapor pressure (kPa).

The suitability of irrigation water depends on the type and concentration of dissolved salts, in which sodium plays an important role (Subramani et al., 2005). Generally, high sodium content in irrigation water will lead to the replacement of Ca^{2+} and Mg^{2+} by Na^{+}. The migration of Ca^{2+} and Mg^{2+} in the soil reduces the permeability of the soil, thus causing damage to crops such as calcium deficiency, skewness, and tilt, and affecting crop yield. Therefore, the irrigation suitability of river water can be evaluated by estimating the percentage of sodium ion (Na^{+}%) and the sodium adsorption ratio (SAR).

Sodium adsorption ratio (SAR) is an important parameter to indicate the Na^{+} content in irrigation water or soil solution, and also an important index to measure the degree of soil alkalization caused by irrigation water. The higher SAR value is, the stronger Na^{+} absorption capacity of soil is. High concentration of Na^{+} will lead to poor permeability of soil surface, lower germination rate of crops, serious diseases and insect pests, and affect the growth and development of crops. Irrigation water can be divided into five categories according to Na^{+}% (excellent: < 20%, good: 20-40%, suitable for irrigation: 40-60%, suspicious: 60-80%, unsuitable: > 80%) (Richards, 1954; Thomas et al., 2015). The calculation formula is:

$$Eq.2\ SAR=\frac{Na^{+}}{\sqrt{\frac{Ca^{2+}+Mg^{2+}}{2}}}$$

$$Eq.3\ Na^{+}\%=\frac{Na^{+}+K^{+}}{Na^{+}+K^{+}+Ca^{2+}+Mg^{2+}}\times 100\%$$

the unit of each ion is meq L^{-1}

Combined with the analysis and test data, the piper diagram is used to explore the ion composition and hydrochemical types of the study area. The contribution proportion of rock weathering and the specific impact of human activities on hydrochemistry are explained by the end-member mixing diagram and principal component analysis (PCA).

4 Results and analysis

4.1 Hydrochemical characteristics

All the samples in the study area are weakly alkaline, with pH value between 7.86-9.39, the average value of 8.03 and coefficient of variation of 5%, indicating that the pH value changes slightly in the water of the study area and is relatively stable, with slight changes between different sampling points. The total dissolved solids (TDS) in the study area ranged from 180-793 mg L^{-1}, and the coefficient of variation was 53%, which reflected that there were great spatial differences in the water characteristics of the whole basin. From upstream to middle and downstream, the total dissolved solids value increases, salinity rises, and ion concentration also rises.

The soluble cations in natural water are mainly Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, and the soluble anions are mainly Cl^{-}, SO_4^{2-}, HCO_3^{-}, and NO_3^{-}. Under the condition of weak alkalinity, the concentration of CO_3^{2-} is very little, which is less than 5% of the total amount of weak acid ions, so it is ignored. According to the principle of solution neutralization, the anion and cation are balanced, i.e.:

$$Eq.4\ \Sigma Z*mc=\Sigma Z*ma$$

$$Eq.5\ 2c¿$$

according to this, HCO_3^{-} ion concentration is calculated.

Statistical analysis of the hydrochemical parameters of the water in the study area (Table 1). It can be seen that the order of anion concentration in the study area during the irrigation period is: $HCO_3^{-} > SO_4^{2-} > Cl^{-} > NO_3^{-}$, and the average ion concentration is 46.42mg/L, 28.77mg/L, 6.59mg/L and 3.60mg/L respectively. The order of cation concentration is: $Ca^{2+}>Na^{+}>Mg^{2+}>K^{+}>NH_4^{+}$, and the average ion concentrations were 30.94mg/L, 14.97mg/L, 12.61mg/L, 1.27mg/L and 0.36mg/L, respectively. In the non-irrigation period, the order of ion concentration from large to small is the same as that in the irrigation period, but there are differences in numerical value. Among them, the concentration of NH_4^{+} is the most obvious, and the ion concentration increases by 72% compared with the irrigation period. However, there are few NH_4^{+} in the natural water, most of which are related to human factors. Therefore, it can be judged that the use of agricultural fertilizer have an impact on the ion concentration in the study basin.

Table 1 Descriptive statistics of hydrochemistry characteristics of surface water in irrigation and non-irrigation periods in Shiyang River Basin (mg L^{-1})

4.2 Ion composition

Project the sample into the Piper diagram(Piper, 1994), and the results show that the main types of water in Shiyang River Basin are mainly carbonated water. In the cation diagram(Fig. 2), the sample mainly falls into the lower-left corner, indicating that the main cation is Ca^{2+}. From the source area (M1-M5) to the middle and lower reaches of the agricultural oasis area (O1-O4), the main cations have a trend from Ca^{2+} to Na^{+} gradually. This feature is reflected in both irrigation and non-irrigation periods. In the anion diagram, water samples are concentrated in the lower-left corner, and HCO_3^- is the dominant ion. SO_4^{2-} control a small number of samples in the upstream irrigation period and the middle and downstream non-irrigation period. The area where river water samples fall in the diamond obviously reflects that the main hydrochemical type in the study area is Ca-HCO_3 type, and part of the samples in the middle and lower reaches of non-irrigation period gradually change to Ca(Na)- HCO_3 mixed type. In addition, it can be seen from the cation triangle diagram that the water environment in mountainous area is relatively stable, and the relative concentration of Na^{+} in irrigation period and non irrigation period is almost the same; however, the relative content of Na^{+} in the water of oasis area in the lower reaches has obvious difference in irrigation period and non irrigation period, which shows that Na^{+} is stable and small in irrigation period, and fluctuates greatly in non irrigation period. On the whole, the water quality in irrigation period is better and stable.

Fig.2 Piper diagram of ion composition of irrigation water in different regions and periods

***4.3** Hydrochemical evaluation of irrigation water*

The SAR value of Shiyang River Basin is between 1.28-3.00 in the irrigation period and between 1.63-3.22 in the non-irrigation period. The average pH value of the basin is 7.98. According to the range of SAR value, it can be concluded that most of the water in the study basin can be directly used for agricultural irrigation. SAR values in irrigation period are lower than that of the non-irrigation period in most sampling points(Fig. 3a), which shows that crops and coastal vegetation have a certain absorption effect on Na^{+}. In Hongyashan reservoir, SAR values in irrigation period are higher than that of the non-irrigation period, Hongyashan reservoir is an artificial reservoir in Shiyang River Basin. During the irrigation season, the Hongyashan Reservoir has a storage capacity of 127 million cubic meters（ 60 million cubic meters of water from the Yellow River ，30 million cubic meters from the Xiying river ，23million cubic meters from Shiyang river）. The water from the Yellow River and the upper reaches of Shiyang River enters the Hongyashan Reservoir by the water delivery project, which reduces the SAR values of the Hongyashan Reservoir, making the water in the Hongyashan Reservoir more suitable for irrigation (Zhu et al., 2018).

The total average value of Na^+% in the study area is 19.86%, which indicates that the quality of irrigation water is good as a whole. On the spatial scale (Fig. 3b), the percentage of sodium ion in the water in the upstream mountainous area is all below 20%. After entering the mountain front oasis, the percentage of sodium ion in the water rises sharply, and the values are all above 20%. Therefore, the water in the upstream mountainous area is more suitable for agricultural irrigation, and the irrigation suitability of water from the mountain pass to the oasis area decreases gradually. In general, the water quality of the mountain reaches of Shiyang River Basin is good, and the problem of declining irrigation water quality mainly exists in the rivers from Wuwei city to Hongyashan reservoir(O1-O4). The irrigation suitability of surface water in Qilian mountain area is very good.

Fig.3 Spatial variation trend of SAR(a) and Na^+%(b) during irrigation and non-irrigation periods in Shiyang River Basin

5 Discussion

5.1 Ion source and main control factors of irrigation water

The end-member mixing diagram is a common method to explore the relationship between the main ion composition and lithology of river water. It can further explore the contribution of bedrock weathering and dissolution to the ion composition characteristics and changes of water and identify the control effect of rock properties on water (Gaillardet et al., 1999; Yang et al.,2018; Ma et al.,2019). The contribution rate of rock weathering to ion source can be determined by the ratio of Ca^{2+}/Na^+, Mg^{2+}/Na^+ and HCO_3^-/Na^+ normalized by sodium ion equivalent concentration. When HCO_3^-/Na^+=2 ± 1, the composition of the rock is mainly affected by silicate rock. The HCO_3^-/Na^+ ratio of sample points in the study area mainly falls into the range of 2 ± 1, so it can be concluded that the ions in Shiyang River Basin mainly come from silicate weathering. Also, in the agricultural oasis area during the irrigation period, some samples are affected by evaporite (Fig. 4). Therefore, the weathering and dissolution of silicate is the main source of surface water in Shiyang River Basin, and the weathering of carbonate also contributes the water in mountainous area. The chemical composition of some water in the middle and lower reaches of the irrigation period is affected by the weathering and dissolution of evaporite.

Based on the river water samples in the basin, principal component analysis (PCA) is used to further determine the source of the main ions in the samples (Table 2). Three principal components were extracted and 89.6% of the total variance was explained. The three principal components accounted for 67.338%, 12.168% and 10.076% of the total variance respectively. The first principal component has a strong positive correlation with Na^+, Mg^{2+}, Ca^{2+}, HCO_3^-, SO_4^{2-}, K^+ and Cl^-, and most of these ions come from nature, so it can be concluded that the first principal component represents the natural environment background of the basin. The second principal component has a strong positive correlation with NH_4^+ and NO_3^-. However, NH_4^+ and NO_3^- are mainly influenced by human factors, so it can be considered that the second principal component represents human activities such as industrial pollution, domestic sewage discharge and the use of agricultural fertilizer. The third principal component showed a strong positive correlation with NH_4^+ and a significant negative correlation with NO_3^-. It can be considered that the third principal component shows the different vegetation on both sides of the river, and the utilization and transformation of nitrogen elements are different. The relative contribution of the three main components to the total variance decreased gradually, indicating that the natural environment background of the study area still dominates the hydrochemical characteristics of the basin, and human activities, land use types and crop planting structure have a certain impact on the surface water environment in the middle and lower reaches of the Shiyang River Basin.

Fig.4 End-member mixing diagram of Shiyang River Basin in irrigation and non-irrigation periods normalized by sodium ion equivalent concentration

Table 2 Principal Component Load

5.2 The possible impact of climate change on irrigation water quality

Since the 20th century, global climate change has had a profound impact on the water cycle process and water environment characteristics in different basins (Allan R and Soden B, 2008). Due to less precipitation and strong evaporation of arid inland river basins, agriculture is highly dependent on surface and groundwater whose salinity is generally higher than that of humid and semi-humid regions. Therefore, changes in water quality caused by climate change have a great impact on agriculture in arid oasis. From 1960-2016, the temperature in the Shiyang River Basin has been rising at a rate of 0.45℃/10a(Fig.5), the rainfall increasing rate is 1.6mm/10a(Fig.5), the potential evaporation has dropped by 2.3mm/10a(Fig.5). and the runoff has increased significantly in the Shiyang River Basin. Using the scenario assumptions proposed for carbon emissions in the fifth assessment report of the IPCC, two greenhouse gas concentration scenarios (RCP4.5 and RCP8.5) were selected and the assessment concluded that during the period 2020-2099 (Wang, 2017), the annual average The temperature rise rate under the PCR8.5 scenario is 0.68℃/10a, and under the RCP4.5 scenario is 0.23℃/10a. The annual average precipitation rate is 9.65mm/10a under the RCP8.5 scenario and 6.33mm/10a under the RCP4.5 scenario.

An increase in temperature will increase local evaporation and lead to a decrease in water volume in the basin, and an increase in precipitation will increase the water volume in the basin. If the concentration caused by the increase in evaporation are stronger than the dilution caused by the increase in precipitation, there is a risk of a decline in the quality of irrigation water in the basin, On the contrary, the quality of irrigation water will be further optimized.

Fig.5 Runoff (a), temperature(b), sunshine duration (c), potential evaporation(d) and precipitation (e) variation diagram of Shiyang River Basin (Wuwei meteorological station) (runoff data: 1993-2016; precipitation data: 1986-2016; temperature, sunshine duration and potential evaporation: 1960-2018)

5.3 Influence of basin water pollution on irrigation water quality

Since 1999, the discharge of sewage increased first and then decreased in the SRB, and fell below 0.4 million tons in 2009. In 2015, the proportion of sewage purification treatment in the basin reached 100%. Since 2009, the chemical oxygen demand has increased first and then decreased, and fell below 3 million tons in 2017(Table 3). Ammonia nitrogen emissions increased first and then decreased, and fell below 5,000 tons after 2016. The proportion of polluted river sections dropped from 12.5% in 2011 to 4.3% in 2018. There is no eutrophication in the surface water bodies in the SRB.

In the future, due to (1) a further reduction in urban sewage discharge and a further increase in the proportion of purification treatment; (2) the government will further control the use of pesticides and fertilizers. The risk of deterioration of irrigation water quality due to water pollution is greatly reduced.

Table 3 Changes in water pollution indicators in the Shiyang River Basin

6 Conclusion

The ion concentration of surface water in the irrigation period is lower than the non-irrigation period, which is related to the dilution effect of precipitation in basin, The main hydrochemical type of the runoff producing area is Ca-HCO_3 type. As Na^+ is gradually enriched along the course, part of the water types of the middle and lower reaches of the river change to Ca (Na) -HCO_3 mixed water, this process is mainly affected by evaporation and crystallization. The surface water is generally of good quality in the Shiyang River Basin, suitable for agricultural irrigation, and the upstream water quality is better than the middle and lower reaches. Global climate forecasts indicate that the temperature in arid areas will increase in the future, and the precipitation will increase, which means that the uncertainty of changes in water quality affected by evapotranspiration and rainfall dilution in the basin's surface water will increase. In addition, in recent years, more stringent water pollution prevention and control measures has implemented in Shiyang River basin , and the irrigation water quality is more likely to be further improved in the Shiyang River Basin.

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Authors Contributions

Conceptualization, Guofeng Zhu and Huiying Ma conceived the idea of the study, Yu Zhang analyzed the data, Huiying Ma wrote the paper ，Liyuan Sang analyzed samples in laboratory, Qiaozhuo Wan collected samples in Shiyang River Basin ，Zhiyuan Zhang collected samples in Shiyang River Basin and Yuanxiao Xu and analyzed samples in laboratory. All authors discussed the results and revised the manuscript.

Additional Information

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Data Availability Statement

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