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Original Research

Hydrochemical Characteristics, Ion Source Analysis and Irrigation Water Quality Evaluation of Rivers in Huaibei Plain

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Abstract

The river is an important irrigation water source in the Huaibei Plain. Hydrochemical composition of river water is the result of the interaction with the environment during its development. With the development of regional industry and agriculture, hydrochemistry of rivers have been affected to varying degrees. Therefore, it is very important for river environment management and agricultural production to analyze river hydrochemistry, ion source and irrigation water quality evaluation. In order to understand hydrochemistry characteristics and assessment for irrigation purposes in Huaibei Plain, Sui River and Tang River were selected as the research objects. Twenty-three river water samples were collected and analyzed for major cations and anions. In this study, mathematical statistics, Piper diagrams, Gibbs diagrams, and ion ratio-coefficient were used to analyze hydrochemistry of samples. Sodium salt concentration and F^-, Cl^- ion concentrations irrigation suitability evaluation systems were used to evaluate rivers. The concentration of pH varied from 8.30 to 9.34 with an average value of 8.62 of Sui River, while that of Tang River ranged from 7.51 to 8.46 with an average value of 8.12. The TDS value of Sui River is relatively high, with a mean value of 1142 mg/L, while that of Tang River is 571 mg/L. Piper diagram shows that chemical type of Sui River changes from Na-Ca-Mg-HCO_3-SO_4-Cl type in upstream to Mg-Na-SO_4-Cl type in downstream. In contrast, the chemical type of Tang River was converted from Ca-Mg-HCO_3-Cl type in upstream to Na-Mg-Ca-SO_4-HCO_3-Cl type in downstream. Gibbs diagram shows that hydrochemical composition of two rivers is mainly affected

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by rock weathering. The main rock dissolution types are carbonate and halite dissolution, while silicate and gypsum dissolve less. Ion ratio-coefficient diagram display human activities have a significantly stronger impact on Sui River than Tang River. The main affected ions are NO_3^- and SO_4^{2-}. Through field investigation, it is speculated that high SO_4^{2-} in Sui River may be related to waterproof materials used in small factories in downstream. SAR, SC, PI and RSC irrigation suitability evaluation evaluation results show that all sampling points are suitable for irrigation. While the evaluation of irrigation water quality based on concentration of F^- and Cl^- suggests that caution should be taken when sample S6 and sample S7 are used for irrigation.

Keywords: river, hydrochemistry, source analysis, irrigation

Introduction

Irrigation water quality is the key to improve the quality of agricultural products, ensure food safety and ensure people's health [1]. Huaibei Plain is an important production base of grain, cotton and oil in China. Its water resources are seriously short and uneven in spatial and temporal distribution. The per capita water resources are only 1/6 of the world's per capita water resources. At the same time, the agricultural irrigation water consumption is large, and the agricultural irrigation water mainly depends on Huai River and its tributary, and also groundwater. With the economic development of cities in Huaibei plain and the increase of urban population, industrial sewage, farmland pollutants and other pollutants discharge into Huai River and its tributaries, the ecological environment of Huaibei Plain is damaged, and the quality of farmland irrigation water is polluted [2, 3]. Such as, Wu Hongling et al. [4] analyzed water quality monitoring data of five rivers in Huaibei Plain, and found that the concentration of total nitrogen and fluoride improved year by year from 2015 to 2017. Zhang Longjiang et al. [5] investigated the water levels, Cl^-, NO_3^- of surface water and shallow groundwater in Fuli section of Sui River, and adopted correlation analysis method to find that due to the hydraulic effect of surface water and groundwater, the water pollution of the Sui River affects the shallow water near the river. In order to manage river environment, the river chief system has been implemented in China. To protect water resources, prevent and control water pollution, improve water environment, restore water ecology as the main task, such as launched to clean up sewage points, clear the riverbed silt, river banks afforestation and so on. Based on this, we want to know the water quality of river and whether its irrigation conditions after the implementation of the river chief system.

The chemical composition of River water is the result of interaction between river and environment during its development. It reflects the hydrochemical characteristics of rivers in the basin [6, 7]. Hydrochemical characteristics are important indicators of river water quality evaluation and river ecosystems [8]. The chemical composition of river is affected by regional natural factors such as geology (rock weathering, soil erosion, groundwater, etc.), climate (rainfall, evaporation), and human activity (agricultural activities, industrial production, urban sewage), etc. [9-11]. Therefore, the chemical characteristics of the river can reflect the basic characteristics of the basin to a certain extent. The study of water chemical characteristics, especially the ion source analysis, can provide a reference for scientific and effective improvement of water quality.

In order to provide reliable basis for regional water environment management and ensure the safety of agricultural production water, we systematically collected water samples from Sui River and Tang River in Suzhou area of Huaibei Plain, analyzed water chemical characteristics, ion sources, and carried out irrigation water quality evaluation.

Study Area

The Sui River and Tang River are both tributaries of Huai River and belong to Hongze Lake drainage system. Both rivers flow from west to east through Yongqiao District, Suzhou City, Anhui Province. The landforms on both sides of rivers are dominated by plains and hills. The hills are mainly concentrated in the north of Sui River. The hilly bedrock is mainly Sinian-Ordovician limestone and a small amount of sandstone and shale. The plain slopes gently from north to south and from west to east with a gradient of 1/5,000 to 1/10,000. And, the soil types are mainly sandy silt soil, sandy black soil, black lime soil, mountain red soil, etc. [12]. In terms of climate, it is located on the southern edge of warm temperate zone and belongs to warm temperate zone and semi-humid monsoon climate. In general, four seasons are distinct and monsoon is obvious. The annual precipitation is 770~900 mm abundant, but the distribution is uneven. Spring precipitation only accounts for about 8% of annual precipitation, and spring droughts often occur. Precipitation in summer is highly concentrated, accounting for about 50% to 60% of the year. The average annual evaporation is 900~1050 mm [12]. In study area, there are frequent agricultural activities along the river basin, and it is an important production base of commercial grain and greenhouse vegetables in China.

Sampling and Analysis

Sampling and Pretreatment

In March 2021, river water samples were collected along Sui River and Tang River. A total of 12 samples from Sui River and 11 samples from Tang River were collected. The locations of the sampling points were shown in Fig. 1.

When sampling, a 550 ml polyethylene plastic bottle was used, which was cleaned with purified water in advance. Before sampling, the bottle was rinsed three times with river water, and then river water was taken out with a river water sampler and filled with bottles. The pH value and TDS value are obtained by using a portable pH and TDS test pen on site. After samples were brought back to laboratory, they were filtered with a 0.45 μm microporous membrane, and then placed in a 4ºC refrigerator for testing. All pretreatments are completed in Anhui Province Coal Mine Exploration Engineering Technology Research Center.

Analysis Indicators and Analysis Methods

Hydrochemical analysis indicators include pH value, TDS value, Na^+, K^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, HCO_3^-, CO_3^{2-}. CO_3^{2-} and HCO_3^-.

The pH value and TDS value are obtained by using a portable pH and TDS test pen during sampling process. HCO_3^- are obtained by acid-base titration. The content of other anions and cations was analyzed by ion chromatography (Thermo Fisher ICS-900), and the recovery rate was 96.1%~104.2%. All analyses are completed in Anhui Province Coal Mine Exploration Engineering Technology Research Center.

Hydrochemical Characteristics Analysis Method and Irrigation Water Quality Evaluation Method

Mathematical statistics, Piper diagram, Piper diagrams, Gibbs diagrams and ion ratio coefficient were used to analyze the water hydrochemistry and ion source analysis.

Methods based on sodium salt concentration and $F^-$and Cl^- concentrations were used to evaluate the quality of irrigation water.

Result and Discussion

Ionic Composition Characteristics

The statistical analysis results of two rivers' chemical indicators are shown in Table 1. The charge balance coefficient of inorganic ions in water (NICB = $(TZ^+-TZ^-)/TZ^+\times100\%$) ranged from -10% to 10%,

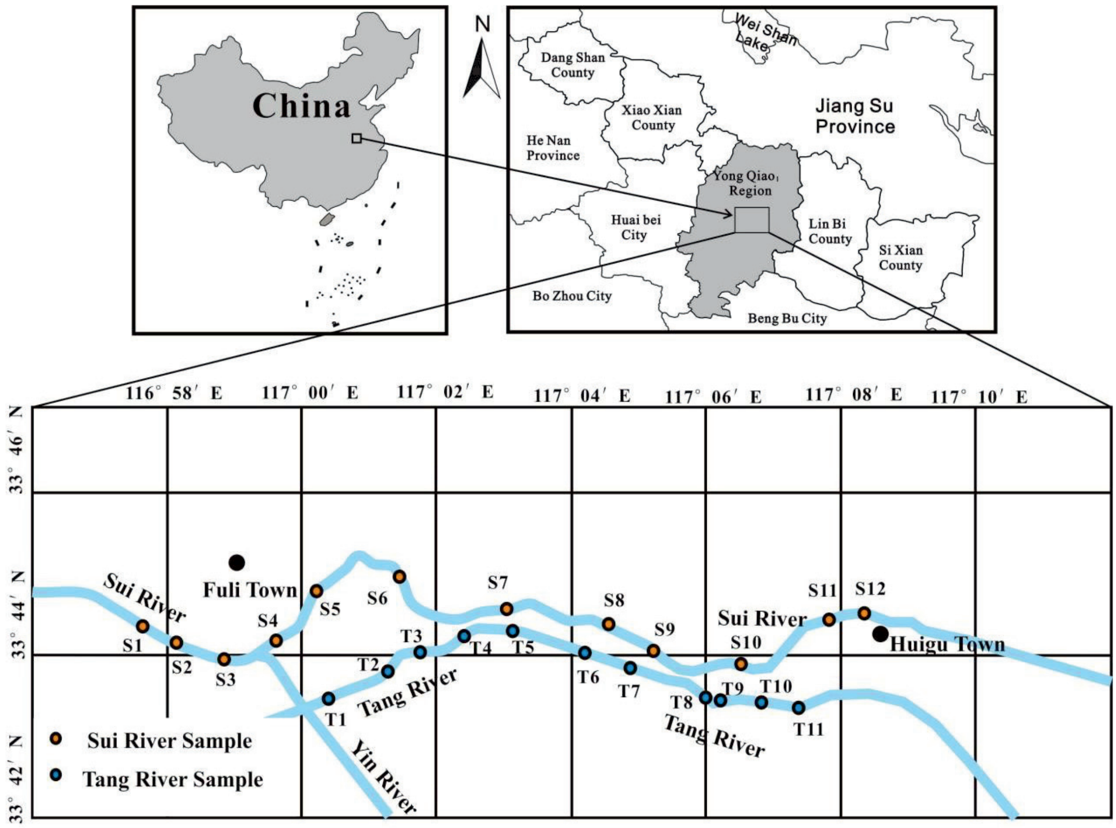

Fig.1. A map of the study region with the sampling sites.

Table 1. Statistics of chemical composition of Sui River and Tang River (mg/L).

Name	Number	Index	pH	TDS	Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	HCO_3^-	CO_3^{2-}	NO_3^-	SO_4^{2-}	TH
Sui River	13	Min	8.30	656	76.7	5.33	39.2	36.6	0.61	117	65.8	-	-	204	344
		Max	9.34	1987	226	21.1	180	130	3.25	361	347	19.6	9.57	954	1048
		ave.	8.62	1142	137	12.3	88.9	86.8	1.45	197	274	5.18	6.26	444	587
		C.V. (%)	3.79	33.4	29.2	34.2	58.5	33.6	66.9	39.5	35.9	160	57.7	62.3	46.2
Tang River	11	Min	7.51	353	25.7	4.98	22.1	52.8	0.39	51.8	258	-	-	10.6	275
		Max	8.46	731	117	22.8	50.0	82.5	0.92	132	361	-	-	223	354
		Ave.	8.12	571	72.9	11.3	37.7	66.0	0.68	98.1	297	-	-	121	322
		C.V. (%)	3.56	23.2	53.5	38.9	29.8	16.3	29.4	33.2	14.4			79.3	8.93
Yangtze River [12]				206	8		7.60	34.1		2.90	134			11.1	
Yellow River [13]				486	57.0	3.04	26.2	64.1		64.2	218			106	
Huai River [14]				214	24.8	3.70	10.0	27.7		22.5	86.4			27.5	

Note: pH, C.V. are dimensionless, „-" means not detected.

indicating that anion and cation charges were basically balanced. It can be seen from Table 1 that pH value of Sui River ranges from 8.30 to 9.34, with an average value of 8.62. The pH value of Tang River ranges from 7.51 to 8.46, with an average value of 8.12, which is lower than pH value of Sui River. The TDS value of Sui River is relatively high, with an average value of 1142 mg/L. The C.V. value of TDS value is relatively large, which is 33.4%, indicating that it may be greatly affected by human activities. The average TDS value of Tang River is 571 mg/L, and the C.V. value is 23.2%, which was lower than that of Sui River, indicating that it was less affected by human activities than Sui River. Compared with other rivers in the world, it is found that the average TDS value of the two rivers is higher than the average TDS of the world rivers (69 mg/L) and Amazon River (44mg/L) [13], Yangtze River (222 mg/L) [14], Huaihe (214mg/L) [15]. It is speculated that it is related to the time of sampling in dry season. In terms of hardness, the TH of Sui River varies greatly, ranging from 44 to 1048 mg/L, while the hardness of Tang River does not change much, with an average value of 322 mg/L, which is lower than that of Sui River.

In Sui River , the relationship between average cation concentration is $Na^+>Mg^{2+}>Ca^{2+}>K^+$. The equivalent concentration of Na^+ accounts for 26.8%~41.6% of total cations, with an average value of 34.8% and an average concentration of 137 mg/L. The equivalent concentration of Mg^{2+} accounted for 27.1%~53.4% of total amount of cations, with an average value of 38.7% and an average concentration of 59.3 mg/L. The relationship between the mean value of anion concentration is $SO_4^{2-}>HCO_3^->Cl^->CO_3^{2-}>NO_3^->F^-$, indicating that SO_4^{2-} and HCO_3^- are the dominant anions. The SO_4^{2-} equivalent concentration accounted for 29.9%~62.7% of total anions, with an average value of 44.38% and an average concentration of 455 mg/L. The coefficient of variation of SO_4^{2-} reached 62.3%, also reflecting greater impact of human activities on Sui River [16]. The HCO_3^- equivalent concentration accounted for 6.8%~39.4% of total anions, with an average value of 25.8% and an average concentration of 275 mg/L. NO_3^- concentration is range from 0 to 9.57 mg/L, with an average value of 6.26 mg/L in Sui River, Otherwise NO_3^- concentration in Tang River is below the detection limit of ICS-900. Compared with results of Wu Hongling et al. [4], the NO_3^- concentration is reduced. In general, Na^+, Mg^{2+}, SO_4^{2-} and HCO_3^- contributed the most to TDS value. Compared with Yangtze River, Yellow River and Huai River in China, the mean concentrations of Na^+, Mg^{2+}, SO_4^{2-} and HCO_3^- are significantly higher (Table 1).

In Tang River, the relationship between average cation concentration is $Na^+>Ca^{2+}>Mg^{2+}>K^+$. The equivalent concentration of Na^+accounts for 15.5%~41.2% of total cations, with an average value of 30.9% and an average concentration of 72.9 mg/L. The equivalent concentration of Ca^{2+} accounts for 22.8%~53.5% of total cations, with an average value of 34.8% and an average concentration of 66.0 mg/L.

The equivalent concentration of Mg^{2+} accounts for 26.1%~34.2% of total cations, with an average value of 31.4% and an average concentration of 37.7 mg/L. The relationship between mean value of anion concentration is $HCO_3^->SO_4^{2-}>Cl^->F^-$, indicating that HCO_3^- is the dominant anion. The HCO_3^- equivalent concentration accounted for 32.8%~70.6% of total anions, with an average value of 49.7% and an average concentration of 297 mg/L. The SO_4^{2-} equivalent concentration accounted for 2.8%~37.2% of total anions, with an average value of 23.1% and an average concentration of 121 mg/L, which lower than that of Sui River. The coefficient of variation of SO_4^{2-} is 79.3%, which also indicated that it was also affected by human activities. In the Tang River, Na^+, Ca^{2+}, HCO_3^-, SO_4^{2-} and Cl^- contribute the most to TDS value. Compared with Yangtze River, Yellow River and Huaihe River, the mean concentrations of Na^+, Mg^{2+}, SO_4^{2-} and HCO_3^- are slightly higher, but it is significantly lower than those of the Sui River (Table 1).

Spatially, TDS value and ionic concentrations of two rivers changed regularly along flow direction. Fig. 2a) shows that chemical composition of Sui River changes with flow direction. Chemical composition of S1-S5 samples in upstream are similar, while ionic concentrations of S6-S10 samples in downstream increases significantly. By the S11-S12 samples, its ionic composition falls to be similar to that of S1-S5 samples. Becsuse of S6-S10 samples have inconsistent increase in ion composition, the dominant cations transition from Na^+, Ca^{2+} to Mg^{2+}, Na^+ with the flow direction and the anion composition changes from HCO_3^- rich to SO_4^{2-} rich. After investigation, it was found that aquaculture and industrial activities in S6-S10 samples' point are more active than other areas. Therefore, the change of chemical composition of river may be related to it. Fig. 2b) shows that chemical composition of Tang River changes with flow direction. The composition of T1-T6 samples in upstream has little change and T7-T11 samples in downstream are basically similar. While chemical composition of upstream and downstream are significantly different. In downstream, SO_4^{2-} content increased significantly, while HCO_3^- decreased.

Types of Water Chemistry

Piper diagram can present a large number of water samples to show their water chemistry characteristics [17-18]. The ion content characteristics of Sui River and Tang River samples are plotted in Fig. 3. It can be

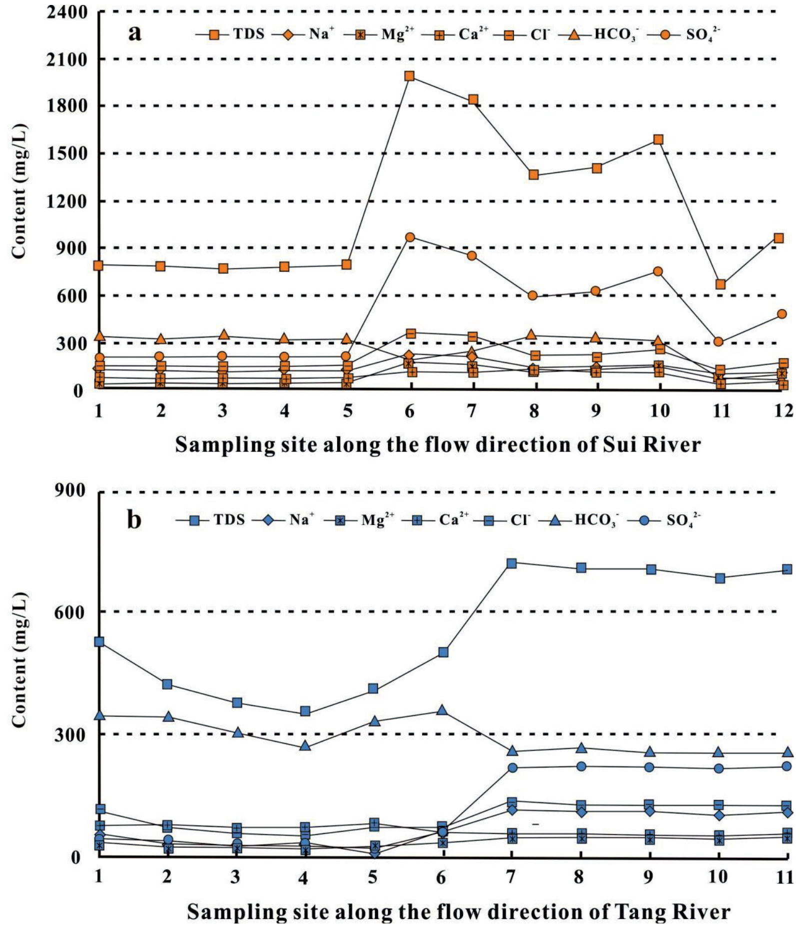

Fig. 2. Major ions concentrations at the Sui River a) and the Tang River b) sampling sites.

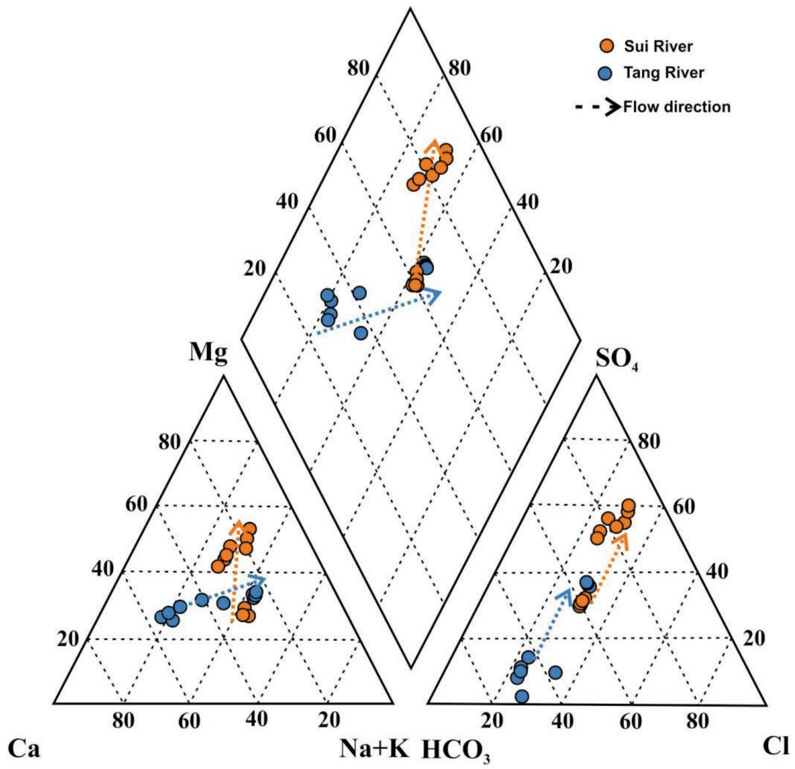

Fig. 3. Piper diagram of the Sui River and the Tang River

seen that the chemical type of Sui River has changed from Na-Ca-Mg-HCO_3-SO_4-Cl type in upstream to Mg-Na-SO_4-Cl type in downstream. It shows that the upstream may be affected by natural processes such as carbonate and evaporite mineral dissolution, while human activities are strongly affected in downstream. The chemical type of Tang River changes from Ca-Mg-HCO_3-Cl type in upstream to Na-Mg-Ca-SO_4-HCO_3-Cl type in downstream . It also shows that the upstream may be affected by natural processes, while human activities are strongly affected in downstream. To sum up, there are differences in hydrochemical types of

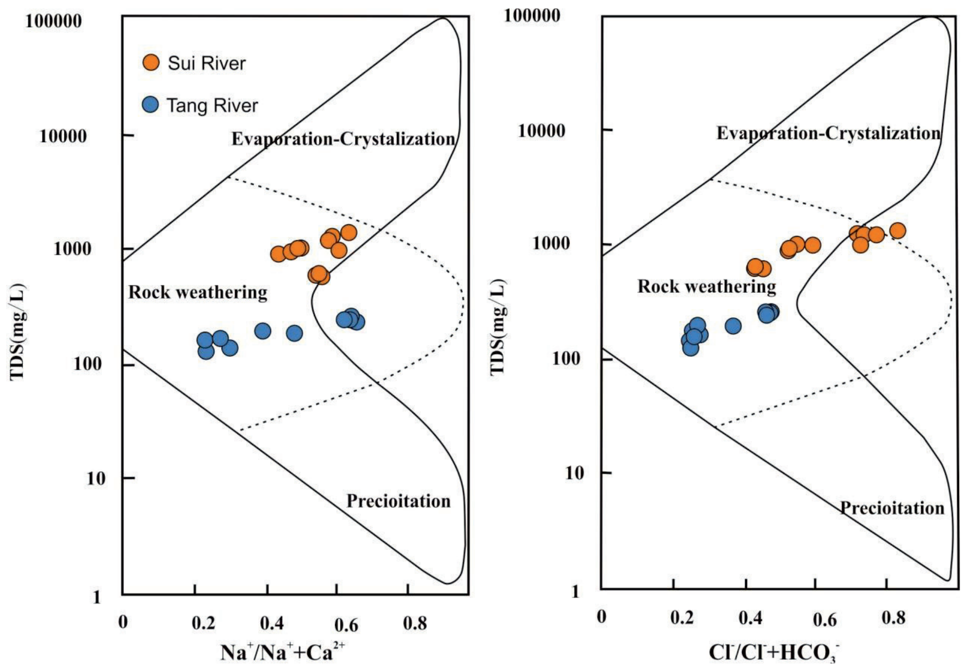

Fig. 4. Gibb´s plot of the Sui River and the Tang River.

upstream and downstream of the two rivers, which are related to human activities.

Analysis of Ion Sources and Control Factors

The chemical composition of riveris the result of the combined action of various factors such as atmospheric precipitation, rock weathering, and human activities. In order to identify different sources of each ion, the Gibbs model was used to qualitatively determine the source of chemical composition of river water, including evaporative crystallization, rock weathering and atmospheric input. And then the correlation analysis and ion proportional coefficient analysis were used to reveal the relationship between the various ions in river water, which used to determine its ion source.

Water-Rock Interaction

The Gibbs diagram can qualitatively identify the controlling factors of water chemical composition, whether it is atmospheric precipitation, rock weathering or evaporation - crystallization [19]. The samples data in the study were plotted on a Gibbs semi-logarithmic coordinate model (Fig. 4). It can be seen from Fig. 4 that most of samples of two rivers fall on rock weathering endmembers. It indicates that the main ion source of Sui River and Tang River is controlled by rock weathering. However, some samples in downstream of Sui River fall in the transition zone between evaporation and rock weathering, indicating that they may be affected by human factors and cation exchange [20].

The correlation between (Ca^{2+} + Mg^{2+}) - (HCO_3^- + SO_4^{2-}) and (Na^+-Cl^-) can be used to evaluate the alternating cation adsorption between Ca^{2+}, Mg^{2+} and Na^+ that occurs in aquifers [21]. Fig. 5 shows that the correlations of (Ca^{2+} + Mg^{2+}) - (HCO_3^- + SO_4^{2-}) and (Na^+-Cl^-) of Sui River and Tang River are very poor, and slope of the fitted line deviates from -1. Therefore, alternate adsorption of ions did not play a significant role in the formation of chemical composition of Sui River and Tang River.

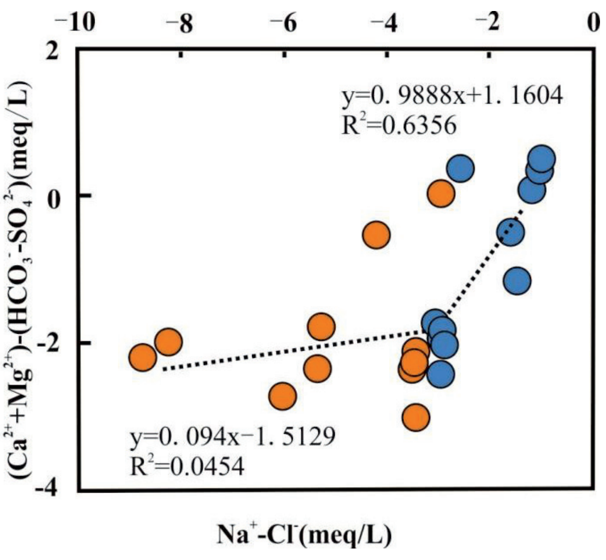

Fig. 5. Scatter plot of (Ca^{2+}+Mg^{2+})-(HCO_3^-+SO_4^{2-}) vs (Na^+-Cl^-).

Usually, the possible sources of Na^+, K^+ and Cl^- are dissolution of halite, silicate and cation exchange, etc. [22, 23]. The above analysis has ruled out a significant effect of cation exchange on chemical composition of two rivers, so, the other two sources may be. When Na^+ mainly comes from dissolution of halite, the ratio of Na^+ vs Cl^- should be 1. Fig. 6a) shows that samples of Sui River and Tang River are basically located near the 1:1 line of Na^+/Cl^-, implying that Na^+ and Cl^- are mainly from dissolution of halite.

Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-} in surface water mainly come from dissolution of calcite, dolomite, gypsum, etc. According to ion ratio-coefficient, the rock weathering information can also be reversed [15, 19]. When they originate from dissolution of calcite and dolomite, the ratio of (Ca^{2+} + Mg^{2+})/HCO_3^- is theoretically 1, but when there is simultaneous dissolution of gypsum, then the ratio of (Ca^{2+} + Mg^{2+}) / (HCO_3^-+SO_4^{2-}) is 1 [10, 20]. It can be seen from Figure 6b that most of samples are located above the line with (Ca^{2+} + Mg^{2+})/HCO_3^- ratio of 1:1, while samples in Sui River deviates further from the ratio of 1:1 line. It shows that Ca^{2+} and Mg^{2+} in Sui River are partly derived from dissolution of carbonates, and most samples require additional anion to balance Ca^{2+} and Mg^{2+}. For Tang River samples, dissolution of carbonates is the main source of Ca^{2+}, Mg^{2+}, HCO_3^-, and only a small part of Ca^{2+}, Mg^{2+} comes from other minerals. The dissolution of sulfate minerals (such as gypsum) was added, and samples of Tang River fall near the line with a ratio of (Ca^{2+} + Mg^{2+}) / (HCO_3^- + SO_4^{2-}) of 1:1 (Fig. 6c). Therefore, the existence of gypsum dissolution is further demonstrated. Most of samples of Sui River locate at low of the line with a ratio of (Ca^{2+} + Mg^{2+}) / (HCO_3^- + SO_4^{2-}) of 1:1 (Fig. 6c), which indicates the dissolution of sulfate minerals and excess of SO_4^{2-}. The scatter plot of Mg^{2+} to SO_4^{2-} (Fig. 6d) shows that SO_4^{2-} has a significant positive correlation with Mg^{2+}. It suggests that SO_4^{2-} is more likely to come from magnesium sulfate minerals. It also indicates that carbonate is not the only source of Mg^{2+}. The content of magnesium sulfate minerals in natural is extremely little, and it is a common waterproof material in industry. So, it is speculated that this phenomenon may be related to the discharge of sewage from small processing plants around Sui River.

The Impact of Human Activities on Chemical Composition of Rivers

Recently, in Fuli-Huigu section of the Sui River and Tang River basins, waste medicine, waste water and waste residues produced by greenhouse agriculture, animal husbandry, and small processing plants have had a certain impact on water quality. Along Sui River, in addition to agricultural and animal husbandry

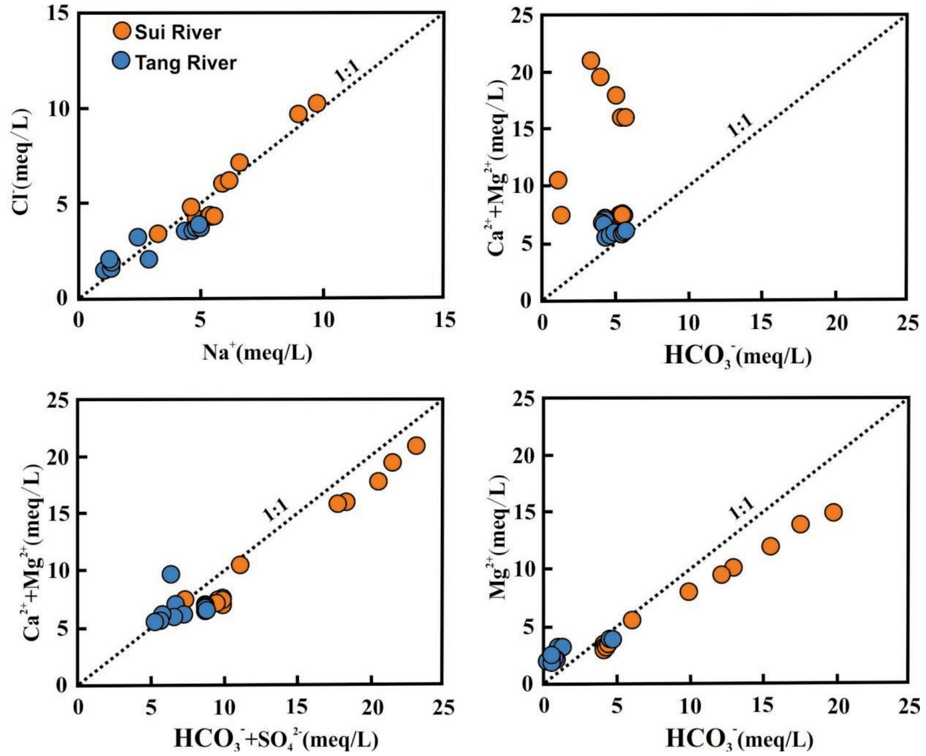

Fig. 6. Scatter plot of a) Na^+ vs Cl^- b) $Ca^{2+}+Mg^{2+}$ vs HCO_3^- c) $Ca^{2+}+Mg^{2+}$ vs $HCO_3^-+SO_4^{2-}$ d) Mg^{2+} vs SO_4^{2-}.

production, industrial activities are frequent. In contrast, two sides of the Tang River are mainly agricultural and animal husbandry, with no typical industrial activities. General coal mine and factory wastewater often have higher TDS value, SO_4^{2-} concentration. Potassium fertilizers and compound fertilizers used in agricultural production will increase the concentration of K^+, Cl^- and NO_3^- in surface water [24] confirmed that ratios of SO_4^{2-}/Ca^{2+}, NO_3^-/Ca^{2+}, $Cl^-/Na^+$and NO_3^-/Na^+ would increase when affected by human activities. Fig. 7 shows the relationship between Cl^-/Na^+ vs NO_3^-/Na^+, SO_4^{2-}/Ca^{2+}vs NO_3^-/Ca^{2+} in rivers. It can be seen from Fig. 7a) ratio of NO_3^-/Na^+ in Tang River is 0, revealing that human agriculture and aquaculture activities have limited influence on water quality of Tang River. Ratio of NO_3^-/Na^+ in Sui River is between 0 and 0.03. The highest value of NO_3^-/Na^+ ratio is near Fuli Gate in upstream, suggesting this point is affected by obvious human activities. It is speculated that high NO_3^- content is related to breeding industry, fruit and vegetable planting industry and discharge of domestic sewage from high-density residents near Fuli Gate. It is found from Fig. 7b) that SO_4^{2-}/Ca^{2+} ratio of Tang River is significantly lower than that of Sui River as a whole. The high SO_4^{2-}/Ca^{2+} value samples of Tang River is located in downstream, which is basically consistent with the obvious change of Sui River. Field investigation found there are many small factories in downstream of Sui River. Spatially, chemical composition of Tang River, which is far away, also changed. It is because wastewater from waterproof materials of the small factories along Sui River changed chemical composition of the adjacent Tang River through hydraulic connection with the groundwater. In general, human activities have little impact on chemical composition in upstream of Tang River, while chemical composition of water in downstream of Tang River and Sui River may be related to discharge of sewage from small factories.

In conclusion, source analysis of ions shows that waters of Sui River and Tang River are the result of combined action of rock weathering and human activities. The rock weathering types are mainly related to carbonate dissolution, evaporite dissolution and a very small part of gypsum dissolution. This conclusion is consistent with the results of previous studies on surface water near the study area [25]. The impact of human activities on chemical composition of Tang River is obviously weaker than that of Sui River. The main influencing factors in upstream of Sui River are planting, aquaculture, and residential sewage discharge, and the influencing ion is mainly NO_3^-. The main influencing factor in downstream is related to industrial activities, and the influencing ion is mainly SO_4^{2-}.

Irrigation Suitability Analysis of Surface Water

Evaluation of Irrigation Water Quality Based on Sodium Salt Concentration

Sui River and Tang River water are often used to irrigate crops in dry season. Excess sodium and salinity concentrations in irrigation water can lead to sodium

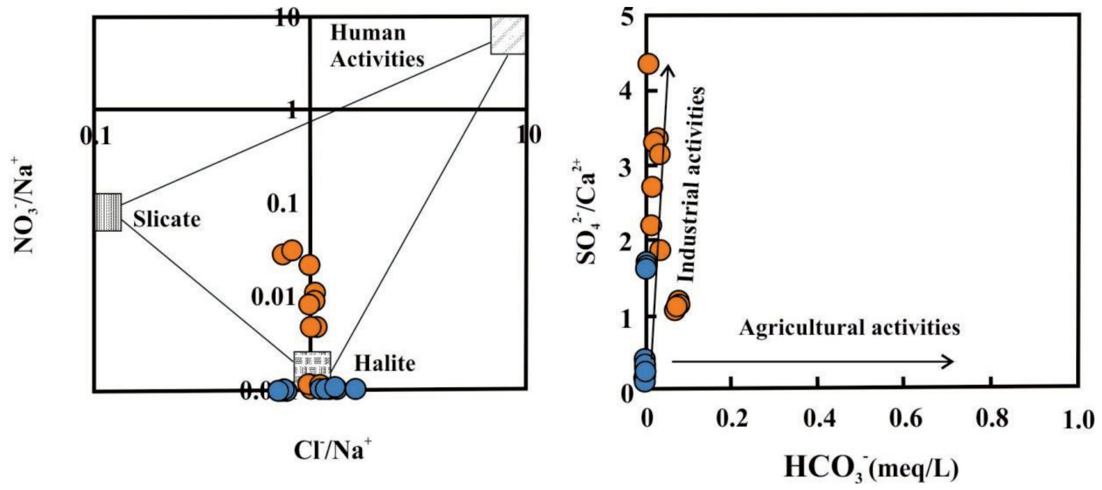

Fig. 7. Scatter plot of a) NO_3^-/Na^+ vs Cl^-/Na^+, b) NO_3^-/Ca^{2+} vs SO_4^{2-}/Ca^{2+}.

Table 2. Scoring grades of irrigation water applicability.

Evaluation parameters	Reference value	Level
SAR / $(mmol \cdot L^{-1})^{1/2}$	<10	Very applicable
	10~18	More applicable
	18~26	Applicable
	>26	Not applicable
PI / %	>75	I (Very applicable)
	25~75	II (Applicable)
	<25	III (Not applicable)
SC / %	<20	Very applicable
	20~40	More applicable
	40~60	Applicable
	60~80	Not sure
	>80	Not applicable
RSC/ $meq \cdot L^{-1}$	<1.25	Very applicable
	1.25~2.50	Applicable
	>2.50	Not applicable

hazard and salinity hazard. The sodium ions in water replace calcium and magnesium ions in soil, resulting in a decrease in phosphorus content and permeability, which hardens the soil. Four evaluation systems can be used to evaluate surface water: sodium adsorption ratio method (SAR), sodium content method (SC), permeability index method (PI) and residual sodium carbonate method (RSC) [26, 27]. The classification criteria of the four evaluation systems are shown in Table 2. The calculation formulas of SAR, SC, PI and RSC are as formulas (1) to (4), and the ion concentration units involved in the formulas are all $meq \cdot L^{-1}$.

$$SAR = Na^+ / \sqrt{(Ca^{2+} + Mg^{2+})/2} \quad (1)$$

$$SC = \frac{100 \times \ K^+ + Na^+}{(K^+ + Na^+ + Ca^{2+} + Mg^{2+})} \quad (2)$$

$$PI = \frac{100 \times (Na^+ + \sqrt{HCO_3^-})}{(Na^+ + Ca^{2+} + Mg^{2+})} \quad (3)$$

$$RSC = HCO_3^- - (Ca^{2+} + Mg^{2+}) \quad (4)$$

The Sui River and Tang River waters were evaluated by four irrigation suitability evaluation systems including SAR, SC, PI and RSC. The results are shown in Table 3. The evaluation results of SAR, SC, PI and RSC for irrigation suitability are generally good, among which, the evaluation results of SAR and

Table 3. Applicability evaluation results of Sui River and Tang River.

Indicators		SAR	SC	PI	RSC	Comprehensive
Sui	Mean level	Very applicable	Applicable	II (Applicable)	Very applicable	Applicable for irrigation
River	Max. level	Very applicable	Applicable	II (Applicable)	Very applicable	Applicable for irrigation
Tang	Mean level	Very applicable	Applicable	II (Applicable)	Very applicable	Applicable for irrigation
River	Max. level	Very applicable	Applicable	II (Applicable)	Very applicable	Applicable for irrigation

RSC surface water irrigation suitability of rivers are all very suitable, and the evaluation results of SC and PI are suitable. So, concentrations of K^+, Na^+, Mg^{2+}, Ca^{2+} and HCO_3^- of Sui River and Tang River are suitable for irrigation.

Evaluation of Irrigation Water Quality Based on F^- and Cl^- Ion Concentrations

According to China's farmland irrigation water quality standard (GB5084-2005), farmland irrigation water quality is divided into Class I (water crops), Class II (dry crops) and Class III (vegetables). GB5084-2005 only restricts the limits of F- and Cl- in conventional ions. The three types of irrigation water limits are specified as $F^- \leq 3$mg/L, $Cl^- \leq 350$mg/L. Cl^- concentration of sample S7 was 361 mg/L, and F^- concentrations of S6 and S7 were 3.24 mg/L and 3.25 mg/L, respectively, all exceeding the limit. Therefore, the river water at these two sampling points is not suitable for water cropping, dry cropping and vegetable irrigation, and attention should be paid to it. All other samples were suitable for irrigation.

Comprehensive evaluation results of SAR, SC, PI and RSC irrigation suitability and evaluation results based on Chinese farmland irrigation water quality standard limit show that S6 and S7 should be cautious when used for irrigation, and other samples are suitable for irrigation.

Conclusion

The hydrochemical analysis of rivers water and groundwater from Sui River and Tang river, Huaibei Plain, China reveals that the processes of water-rock interaction, human pollution and almost suitability for irrigation. All the parameters concentration can meet the demand for inhabitant and suitable for drinking. The chemical type of Sui River changed from Na-Ca-Mg-HCO_3-SO_4-Cl type in upstream to Mg-Na-SO_4-Cl in downstream, otherwise Tang River's water chemical type changed from Ca-Mg-HCO_3-Cl type in upstream to Na-Mg-Ca-SO_4-HCO_3-Cl type in downstream. That is because of human pollution comes from industrial activities. The plots of NO_3^-/Ca^{2+} vs SO_4^{2-}/Ca^{2+} also support this view. Gibbs diagram suggests that the dominant influence is related to water-rock interaction. The scatter plot of Na^+ vs Cl^-, $Ca^{2+} + Mg^{2+}$ vs HCO_3, $Ca^{2+} + Mg^{2+}$ vs $HCO_3^- + SO_4^{2-}$ and Mg^{2+} vs SO_4^{2-} show that rock weathering types are mainly carbonate dissolution, evaporite dissolution and a small part of gypsum dissolution. Meanwhile, alternate adsorption of ions has no contribution to hydrochemical components. The computed values of SAR, SC, PI and RSC standards illustrates that all the samples are within the zone of water suitable for irrigation. The evaluation of irrigation water quality based on concentration of F^- and Cl^- shows that caution should be vigilant when S6 and S7 were used for irrigation. Compared with the previous research data before the implementation of the river chief system, the data results show that the water quality is improved, and almost all water is suitable for irrigation.

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Conflict of Interest

The authors declare no conflict of interest.

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