

Hydrochemistry Characteristics of Groundwater with the Influence of Spatial Variability and Water Flow in Hetao Irrigation District, China

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Research Article

Keywords: Groundwater resources, hydro-chemical characteristics, control mechanisms, water quality assessments, hydro-geochemistry, Hetao Irrigation District.

Posted Date: November 30th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1033631/v1>

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Abstract

Groundwater is an important resource of water in arid and semi-arid agricultural regions. This study considered the spatial differentiation of geographical features and the concentration of groundwater flow. The upstream of the Hetao Irrigation District Shenwu Irrigation Area (SWIA) and the downstream Wulate Irrigation Area (WLTIA) were selected as the study area, and a total of 85 groundwater samples (42 from SW and 43 from WLTIA) were collected. The aims of the study were to analyze the chemical composition and main control mechanisms of groundwater, and to evaluate the suitability of groundwater irrigation in the study area from the perspective of salt and alkali damage. Geological and environmental factors increase the spatial variability of groundwater chemical characteristics in the Hetao Irrigation District. In addition the groundwater of the study area is weakly alkaline, with the flow of groundwater; the solute content of downstream (WLTIA) is higher than that of upstream (SWIA); SWIA is mainly fresh water (47.62%); and WLTIA is mainly brackish water (65.12%). The main water chemistry types are Cl-Na type, Cl-SO-Ca-Mg type, Na^+ and Cl^- have obvious advantages in WLTIA, and they are the main contribution indicators of groundwater TDS in the study area. Rock weathering, ions exchange and evaporate crystallization are the main controlling factors for groundwater in the Hetao Irrigation District. Na^+ mainly originates from the dissolution of evaporate salt rock and silicate rock, and Ca^{2+} from the dissolution of gypsum and carbonate. The order of contribution of different rocks is evaporation rock > silicate rock > carbonate rock, and the contribution rates of human activities and atmospheric input are small. The groundwater quality of the upstream SW is better than that of the downstream WLTIA. However, due to the high chemical ion concentration of the groundwater, most of the groundwater cannot be directly used for irrigation, which may cause salt and alkali damage. Therefore, when using groundwater irrigation, either drip irrigation or irrigation water aeration pretreatment can be used to avoid damages such as reduced soil permeability and compaction.

1. Introduction

Groundwater is an important component of water resources, and serves as important support for human survival and development [Li et al., 2018], especially in arid and semi-arid areas where precipitation and surface water are scarce. Groundwater plays a decisive role in agricultural production [Li et al., 2016b]. In recent years, the amount of water diversion from the Yellow River to the Hetao Irrigation District has dropped sharply, and the use of groundwater has become increasingly important in agricultural and domestic water. The quality of water directly affects the quality of farmland soil environment, crop growth and residents' drinking water safety [Zhao et al., 2018]. In fact, agricultural water has higher requirements than industrial water and domestic water [Li et al., 2018]. Crop growth has specific threshold of the ions content in irrigation water, excessive solute might affect the yield, germination rate and quality of crops, especially in soil salinization areas [Pradhan et al., 2021]. If an ion in the groundwater exceeds the specific threshold, it might cause harm to crops or soil when it is used for irrigation.

The study of hydrochemical characteristics is a direct factor to measure the environmental quality of groundwater [Wei et al., 2021], and is also the core of groundwater quality evaluation [Hao et al., 2020]. Research regarding the characteristics of groundwater chemical composition, water quality and control factors can reveal the formation process and succession of groundwater mechanism, and scientific use and management of groundwater resources [Zhao et al., 2017]. The chemical composition of groundwater is affected by the combined effects of natural factors and human activities [Chen et al., 2017], and the cross-effects of multiple factors render groundwater management more complicated [Li et al., 2017]. The Piper three-line diagram, Gibbs model, ion correlation, and Na end member diagram are important methods for exploring the chemical composition of water. Scholars throughout the world have carried out numerous studies using these methods in wetlands [Li et al., 2021], alluvial fans [Tang et al., 2019a] and basins [Sun et al., 2018] karst areas [Tang et al., 2019b], the results of which are of great significance to the efficient use and management of water resources. In addition, the ion content of groundwater plays an important role in crop growth [Dou et al., 2021]. Poor irrigation water quality will inhibit crop growth, thereby resulting in soil compaction, reduced permeability, and salinization [Zhao et al., 2018]. For example, excessive Na^+ can cause sodium damage, soil permeability reduction, and inhibit crop absorption of water and nutrients [Tahmasebi et al., 2018]. In addition, excessive Mg^{2+} can cause magnesium damage, which makes the soil alkaline and affects crop yield [Xu et al., 2019], etc. Therefore, the suitability evaluation of irrigation water quality has important practical significance for agricultural production. At present, the more common irrigation water evaluation indicators include sodium percentage ($\text{Na}\%$), sodium adsorption ratio (SAR), residual sodium carbonate (RSC), magnesium hazard (MH), permeability index (PI), etc.

The Hetao Irrigation District is the largest irrigation district in Asia, with a large amount of arable land and extensive distribution of salt groundwater. For many years, scholars have taken the depth of groundwater burial and water quality in variables or the evaluation factors to perform research on water saving and salt control, irrigation system and crop high yield [Wang et al., 2019; Shi et al., 2020], while research on groundwater chemical composition and main driving factors remains relatively limited. Existing related research on

groundwater in the Hetao Irrigation District are often considered from the overall perspective of the region, and seldom consider the differences of the water chemical ions composition and sources in the irrigation area. In addition, there is a lack of in-depth discussion and evaluation of groundwater environmental quality through groundwater chemical ions.

Based on this, this paper selected the Shenwu Irrigation Area in the upper reaches and the Wulate Irrigation Area in the lower reaches of the Hetao Irrigation District as the study areas. In the paper, mathematical statistical analysis, hydrogeochemical analysis and other methods are applied to compare and analyze the chemical characteristics and main control mechanisms, and to identify the source of ions of groundwater in the main drainage and drainage control areas of the Hetao Irrigation District. Three evaluation indicators including sodium adsorption ratio (SAR), residual sodium bicarbonate (RSBC) and potential salinity (PS) were selected to evaluate the suitability of groundwater for irrigation. The results of this research study will help the irrigation district to formulate effective water quality protection measures and appropriate irrigation management strategies. The study results are expected to provide new insights for groundwater environmental protection and scientific irrigation, and provide guidance for the research of brackish water (salt water) irrigation in the Hetao Irrigation District.

2. Study Area

2.1 Location and climate characteristics

The Hetao Irrigation District is located in the western section of Inner Mongolia. It is the largest irrigation area in Asia with only one diversion port. The total control area is 11900 hectares. The climate has the characteristics of an arid and semi-arid continental climate, with an annual average precipitation of approximately 160 mm, and an evaporation rate up to 2,240 mm. The average groundwater depth and salinity of in the irrigation area are 1.83 m and $3.38 \text{ g}\cdot\text{L}^{-1}$, respectively. Affected by irrigation, the shallowest depth after autumn irrigation is only 1.56 m, which was noted in the statistical data of the Hetao Irrigation District Irrigation Administration (1998-2019).

The Shenwu Irrigation Area is located in the upstream of the Hetao Irrigation District, and it is also an important water diversion control area of the Hetao Irrigation District. The longitude range is between $106^{\circ}52'$ and $107^{\circ}04'$, and the latitude range is $40^{\circ}28'$ to $40^{\circ}08'$. Its total area is 2.87 million mu. The main water diversion channels in the study area include the Dongfeng Main Channel and the First Main Channel, and the First and Second Main Drains are its main drainage channels.

The Wulate Irrigation Area is located in the downstream of the Hetao Irrigation District, and is the main drainage control area of the Hetao Irrigation District. The longitude range is from $108^{\circ}06'12''$ to $109^{\circ}39'$, and the latitude range is $40^{\circ}27'$ to $41^{\circ}10'$, with a total area of 30.7 million mu. The main irrigation drains in the area include the Changta Diversion Channel, Changji Main Channel, Tabu Main Channel, and the Sanhu River Main Channel. The main drainage channels include the Eighth, Ninth and Tenth Drainage Channels.

2.2 Hydrogeological settings

The aquifer in the Hetao Irrigation District is mainly composed of fine-grained alluvial lacustrine deposits formed during the Late Jurassic Period. There are also Holocene-upper Pleistocene lacustrine deposits and alluvial-flood deposits in the area, and lacustrine deposits in the upper part of the middle Pleistocene. The surface layers of the soil are composed of cohesive soil layers containing sandy loam, loam and clay with thicknesses ranging between 4 and 15 m. The bottom layers are composed of thick layers of fine sand and thin clay layers with thicknesses of approximately 50 m. The sand layers contain gravel layers, which are distributed in the depth ranges of 10 to 15 m and 30 to 40 m. The upper part of the Middle Pleistocene series is lacustrine with a stable distribution, which is mainly composed of clay and portions of sandy loam.

The SWIA is mainly dominated by forest and grassland areas. The aquifer is dominated by sandy soil, with good permeability and smooth groundwater flow. The WLTIA is mainly cultivated land, and the aquifer is mainly clay and fine sandy soil. The groundwater flow is slow, or even not flowing, and the groundwater is vulnerable to the recharge of Wuliangshuai. Both irrigation areas have independent drainage structures. The main discharge mode of groundwater is evaporation, and the recharge mode is agricultural irrigation. There are no natural surface rivers in the two irrigation areas. The artificial surface rivers are seasonal rivers composed of ditches for agricultural irrigation. The groundwater resources are deeply affected by the irrigation practices in the region, and exhibit seasonal fluctuations throughout the year.

3. Materials And Methods

3.1 Sample collection and analysis processes

In this study, a total of 85 groundwater samples were collected in September of 2018, including 42 groups in the SWIA and 43 groups in the WLTIA. The sampling well depths were less than 30 m, and the sampling point positions were accurately located using a handheld GPS. The sampling point positions are detailed in Fig. 1. The sample collection and processing procedures used in this study followed the groundwater environmental monitoring technical specifications. The EC values of groundwater samples were measured in-situ using a portable multi-parameter analyzer (DZB-712). The groundwater samples used for the determination of hydro-chemical components were packed in dry 500 mL polyethylene bottles. The sampling bottles were repeatedly rinsed with deionized water for drying and back-up use prior to collecting the samples. The groundwater samples were rinsed three times before sealing the bottles in order to prevent any influencing effects caused by other impurities. The collected groundwater samples were sent to Bayannaer Water Resources Research Institute for content determinations within 24 hours, strictly following the standard determination method proposed by the Ministry of Health of the People's Republic of China (GB/t5750-2006). The pH levels were determined using a glass electrode method. The K^+ and Na^+ content levels were determined using flame atomic absorption spectrophotometry, and the Cl^- , Ca^{2+} , SO_4^{2-} , Mg^{2+} and HCO_3^- content levels of the samples were obtained using a traditional titration method.

The reliability of groundwater samples was analyzed by calculating the charge balance errors (CBE %). The calculation method of CBE % [Li et al., 2018c] was as follows:

$$CBE\% = \frac{\sum \text{cation} - \sum \text{anion}}{\sum \text{cation} + \sum \text{anion}} \quad (1)$$

The concentration units of anion and cation were meq/L, and the CBE% results were within $\pm 5\%$, which indicated that the data were reliable. Therefore, the determination results of the groundwater samples in this study had met the necessary requirements.

The forward succession model was used to estimate the contribution rate of different sources, its basic principle is the law of conservation of mass. The derivation process of the dissolved ion concentration of different salt rocks is as follows:

$$X_g = X_a + X_p + X_c + X_e + X_s \quad (2)$$

$$Cl^-_g = Cl^-_e + Cl^-_a \quad (3)$$

$$SO_4^{2-}_g = SO_4^{2-}_e + SO_4^{2-}_a \quad (4)$$

$$NO_3^-_g = NO_3^-_a + NO_3^-_p \quad (5)$$

$$Na^+_g = Na^+_s + Na^+_e + Na^+_a + Na^+_p \quad (6)$$

$$Ca^{2+}_g = Ca^{2+}_s + Ca^{2+}_e + Ca^{2+}_a + Ca^{2+}_c \quad (7)$$

$$Mg^{2+}_g = Mg^{2+}_s + Mg^{2+}_a + Mg^{2+}_c \quad (8)$$

$$K^+_g = K^+_s + K^+_a \quad (9)$$

In the formula, X_g , X_a , X_p , X_c , X_e and X_s respectively represent the measured concentration of an ion, atmospheric input contribution, human activity contribution, carbonate contribution, evaporate contribution, and silicate contribution concentration. Na_p is ignored. This study takes $(Ca^{2+}/Na^+)_s=0.25$, $(Mg^{2+}/Na^+)_s=0.4$.

3.2 Groundwater quality assessments

In the Hetao Irrigation District, the groundwater resources are widely used to irrigate farmland areas and personal gardens, with some directly used for drinking. Its quality directly affects the environmental conditions of the soil and crop growth rates, and agricultural development. Therefore, the evaluation results of the groundwater quality can intuitively reflect the chemical compositions of the groundwater and its impact on the soil environment. The evaluation results can also provide effective references for local residents and managers. In this study, three evaluation indexes were selected to evaluate the suitability of groundwater irrigation in the study area,

namely the SAR (sodium absorption ratio), RSBC (residual sodium bicarbonate levels) and PS (potential salinity). The calculation method was as follows:

$$PS = Cl^- + \frac{1}{2}SO_4^{2-} \quad (10)$$

$$RSBC = HCO_3^- - Ca^{2+} \quad (11)$$

$$SAR = \frac{Na^+}{\sqrt{Ca^{2+} + Mg^{2+}}} \quad (12)$$

$$TDS = 640 * EC \quad (EC < 5dS \cdot m^{-1}) \quad (13)$$

$$TDS = 800 * EC \quad (EC > 5dS \cdot m^{-1}) \quad (14)$$

In the formula, the ion concentration unit is $meq \cdot L^{-1}$.

4. Results And Discussion

4.1 Chemical parameters of the groundwater

Ion content levels can reflect the basic hydro-chemical characteristics of groundwater [Li et al., 2018c]. The main physical and chemical parameters of the groundwater in the SWIA and WLTIA are shown in Table 1. It can be seen in the table that the groundwater in the two irrigation areas was weakly alkaline. The pH range of groundwater in the SWIA was between 7.21 and 8.32 (mean: 7.72), and the pH range of groundwater in the WLTIA was between 7.27 and 8.81 (mean: 7.85). The pH values in the study area were mostly within the standard range (6.5 to 8.5) stipulated by WHO [WHO, 2011] and China's groundwater environment quality. Only fresh water ($TDS < 1,000 \text{ g} \cdot L^{-1}$) is suitable for drinking [WHO, 2004], since high TDS can alter the taste of water [Christensen et al., 2018]. Fresh water ($TDS < 1 \text{ g} \cdot L^{-1}$) accounted for 47.62% of the water in the SWIA, and brackish water ($1 < TDS < 3 \text{ g} \cdot L^{-1}$) accounted for 65.12% of the water in the WLTIA. In addition, salt water ($3 \text{ g} \cdot L^{-1} < TDS$) accounted for 14.29%, while brackish water accounted for 38.09% of the water in the SWIA. In the WLTIA, it was determined that brackish water accounted for 18.60%, and fresh water accounted for 16.28%. This study found that the ion content and TDS of the WLTIA were higher than those of the SWIA. The main reason for this was that the WLTIA was located in the downstream, thus the ion content and TDS displayed significant enrichment. At the same time, the permeability of the soil aquifer in the WLTIA was lower, resulting in the basic stagnation of groundwater flow. The groundwater resources in that area were affected by such factors as the recharge of the Wuliangshuai and the fault zone produced by the Wula mountain uplift, which were consistent with the known facts [Liu et al., 2014].

From the coefficient of variation, it could be seen that the order of anions and cations were $Cl^- > SO_4^{2-} > HCO_3^-$, $Na^+ > Mg^{2+} > Ca^{2+}$. These findings indicate that Cl^- and Na^+ were the main salinization ions in the SWIA and WLTIA, respectively, both of which were sensitive to environmental changes. However, the variation coefficients of HCO_3^- and Ca^{2+} in the two irrigation areas were observed to be small, which indicated that the distributions of HCO_3^- and Ca^{2+} were stable in the study area, and they have been mainly affected by certain geological factors. Most of the Cl^- , Na^+ and HCO_3^- contents of the groundwater in the two irrigation areas were determined to exceed the drinking limits proposed by WHO ($250 \text{ mg} \cdot L^{-1}$, $200 \text{ mg} \cdot L^{-1}$, and $300 \text{ mg} \cdot L^{-1}$, respectively), indicating that the groundwater in the area was not suitable for human consumption. In addition, the abnormally high values of chemical ions in the water in some areas showed that sewage irrigation practices had certain impacts on the groundwater in the study area.

The orders of the average concentrations of anions and cations in the SWIA and WLTIA were as follows: $Cl^- > SO_4^{2-} > HCO_3^-$ and $Na^+ > Mg^{2+} > Ca^{2+}$. The concentrations of anions and cations in the WLTIA were found to be higher than those in the SWIA. As shown in Fig. 2, the dominant cations in both irrigation areas were Na^+ . It has been suggested that the maximum sodium content in irrigation water should be only 60% [BIS, 1991]. In the present study, Na^+ accounted for 63.96% and 63.87% of the total cations in the two irrigation areas. Comprehensive evaluations were required prior to the commencement of irrigation processes. The variation range of the Cl^- concentrations in the SWIA was large, ranging from $0.09 \text{ g} \cdot L^{-1}$ to $6.65 \text{ g} \cdot L^{-1}$. There were found to be 22 samples which exceeded the $250 \text{ mg} \cdot L^{-1}$ limit set by WHO (2008). Meanwhile, the HCO_3^- content was relatively concentrated (0.11 to $1.74 \text{ g} \cdot L^{-1}$) and higher than the Cl^- content. Only 10 samples were observed to be below the limit of $300 \text{ mg} \cdot L^{-1}$. The content levels of Cl^- in the WLTIA ranged from 0.07 to

25.88 mg·L⁻¹, and the exceeding rate was 81.40%. The concentration of HCO₃⁻ ranged from 0.14 to 1.25 mg·L⁻¹, with only four samples not exceeding the 300 mg·L⁻¹ limit. The chloride content levels were found to be high and unstable, which may have been related to rock weathering, sedimentary rock dissolution, soil leaching, and domestic sewage [Prasanth et al., 2012].

4.2 Types of hydro-chemical groundwater

The chemical ion compositions and evolution characteristics of the groundwater were determined using a Piper Diagram (Fig. 3). In the cation triangle diagram, the SWIA and WLTIA groundwater cations are mainly concentrated in the lower right corner of the diagram, and the dominant cation is Na⁺. In the anion triangle diagram, the SWIA anions are mainly concentrated in the middle, and each anion shows a non-dominant type. The distribution of WLTIA anions is relatively dispersed, partially concentrated in the Cl-terminal, and partially concentrated in the non-dominant area of anions. The main hydro-chemical types of the two irrigation areas were Cl-Na types and Cl-SO₄-Ca-Mg types. Because of water flow, the proportion of Na⁺, Cl⁻ and HCO₃⁻ in groundwater increases significantly from upstream to downstream in the Hetao Irrigation District, and the downstream area (WLT) is more dispersed than the upstream (SW) ion composition, and the chemical composition of water varies greatly. This is mainly because the groundwater in the downstream area is not only affected by water flow, but also by a variety of other factors, such as the recharge of rock fissure water in Wula Mountain, deep groundwater upwelling in the uplift fault zone, groundwater retention and accumulation, etc.

4.3 Hydro-chemical control mechanisms

The Gibbs Diagram is widely used in groundwater chemistry research, most often to macroscopically reflect the natural formation mechanisms of regional groundwater [Li et al., 2016b]. The Gibbs Diagram is mainly divided into three control mechanisms: evaporation concentration, rock weathering, and atmospheric precipitation [Gibbs, 1970]. As shown in Fig. 4, the majority of the groundwater sample locations in the SWIA were in a rock weathering zones, with a small portion located in evaporation and concentration zones. Meanwhile, the majority of the groundwater samples obtained in the WLTIA were affected by evaporation and concentration levels, which indicated that the chemical composition of the groundwater in the area was jointly affected by rock leaching [Li et al., 2016c] and evaporation crystallization. Compared with the WLTIA, the SWIA is more affected by rock weathering, this is mainly due to the fact that the SWIA mostly was an alluvial plain formed by the Yinshan Mountains, the groundwater flow was smoothly, and was recharged by the fissure water of the Yinshan rock formations. The farmland irrigation areas in the WLTIA accounted for a large proportion. The groundwater flow was poor and the burial depths of the groundwater were shallow. In addition, the lack of rainfall increased the evaporation intensity in the area. Another portion of the sampling points were distributed outside the Gibbs Diagram, which indicated that the groundwater in the study area was affected by human factors to some extent [Yuan et al., 2019]. Due to the shallow groundwater depths in the region, it was easily infiltrated by rainwater and irrigation water, such as the water used in agricultural irrigation, fertilization and industrial development processes. In addition, the sampling points of the two areas are all far away from the atmospheric precipitation control area, which is mainly due to the perennial drought and low rainfall in the study area, resulting in minimal impact of precipitation on groundwater.

By the relationship between Ca²⁺/Na⁺ and HCO₃⁻/Na⁺, Mg²⁺/Na⁺, the influence of weathering and dissolution of different rocks on groundwater solute can be identified [Gailla et al., 1999]. As can be seen in Fig. 5, the majority of the sampling points in the two study areas were distributed between the evaporite and carbonate rock, with some approaching the silicates. These findings indicated that the sources of the groundwater hydro-chemical components in the study area were complex and affected by many factors. This was mainly controlled by the actions of the evaporite and silicate rock. However, the carbonate rock also affected the chemical compositions of the groundwater in the study area to some extent.

4.4 Sources of major ions

The main sources of Na⁺ can be determined according to the ratio relationships between the Na⁺ and Cl⁻. For example, if the ratio is 1, then the sources come from the dissolution of evaporated salt rock. However, if the ratio is greater than 1, then the sources can be known to have originated from the weathering of silicate rock [He et al., 2021]. Fig. 6(a) illustrates that the majority of the sampling points in the two examined irrigation areas were located near to or on the right side of the 1:1 ratio line. Therefore, the groundwater in the study area was mainly affected by the dissolution of evaporated salt rock and the weathering of silicate rock. Only a small number of points in the WLTIA were found to be located above the 1:1 line. The advantage of Na⁺ over Cl⁻ in the SWIA may have been that the rock minerals are continuously dissolved and Na⁺ is released during the process of groundwater runoff. At the same time, Ca²⁺ in the water replaces Na⁺ in the soil, causing the concentration of Na⁺ to be greater than that of Cl⁻ [Li et al., 2014]. In addition, the HCO₃⁻ concentration in the SWIA irrigation area is quite large, which reduces the advantage of Cl⁻.

It was determined that if the $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratio was approximately 1, then the dissolution of gypsum was the main source of the groundwater in the region [Chen et al., 2019a; Chen et al., 2019b]. As shown in Fig. 6(b), most of the sampling points of SWIA are located above the 1:1 straight line, as the cation displacement reaction reduces the Ca^{2+} concentration. Some sampling points of the WLTIA are located below the 1:1 line. It can be seen that the Ca^{2+} in this area is not only affected by gypsum dissolution, but carbonate dissolution is also an important source of Ca^{2+} .

In addition, it was determined that if the $(\text{HCO}_3^- + \text{SO}_4^{2-})$ to $(\text{Ca}^{2+} + \text{Mg}^{2+})$ was approximately 1, then the dissolution of carbonate and sulfate minerals was the main process affecting the chemical compositions of the groundwater in the region [Li et al., 2016c; Li et al., 2018a]. As detailed in Fig. 6(c), the majority of the sampling points in the two irrigation areas were located below the ratio line, indicating that the $\text{HCO}_3^- + \text{SO}_4^{2-}$ had obvious advantages for $\text{Ca}^{2+} + \text{Mg}^{2+}$. This may have been due to silicate weathering and ion exchanges. However, a small number of the samples were above the ratio line in the WLTIA, which suggested that reverse cation exchanges played a certain role in controlling the groundwater in the WLTIA [Xu et al., 2019]. At the same time, if the value of $(\text{Ca}^{2+} + \text{Mg}^{2+} - \text{SO}_4^{2-} - \text{HCO}_3^-) / (\text{Na}^+ + \text{K}^+ + \text{Cl}^-)$ was approximately -1, then it was determined that the groundwater in the study area had undergone ion exchange adsorption processes [Li et al., 2016a]. As shown in Fig. 6(d), the slopes of the two irrigation areas $(\text{Ca}^{2+} + \text{Mg}^{2+} - \text{SO}_4^{2-} - \text{HCO}_3^-) / (\text{Na}^+ + \text{K}^+ + \text{Cl}^-)$ were 0.93 and 1.01, respectively, both of which were close to 1. This indicated that cation exchanges were dominant in both irrigation regions, while a small portion of reverse cation exchanges also existed in the WLTIA.

4.5 Quantitative estimation of contribution rate of different factors

In this study, the forward succession model was used to quantify the contribution rates of atmospheric input, human activities and weathering of different rocks (Table 2), and the results are consistent with the conclusions obtained by the Gibbs model. The contribution rates of atmospheric input and human activities to groundwater solutes are small, both at 5%. The weathering of rocks is the main source of chemical ions in groundwater, among which evaporative rocks have the largest contribution rate, and the order of the contribution rates of different rocks is evaporate rock > silicate rock > carbonate rock. In the Loess Plateau, carbonate rocks have the largest contribution rate [Li et al., 2019; Liu et al., 2021]. This is mainly due to the poor fluidity of groundwater in the Hetao Irrigation District and the long-standing issue of salinization. The high concentrations of Na^+ and Cl^- make evaporate salt rocks the main source of rocks. The average contribution rate of the SWIA is 49.78%, and that of downstream WLTIA is 50.14%. From upstream to downstream, the groundwater flows continuously to dissolve the components in the soil, thus resulting in a significant increase in the concentration of Na^+ and Cl^- in the groundwater in the downstream area, and the contribution rate of evaporate rock and carbonate rock is increasing.

5. Discussion

5.1 Contribution of major ions to saline groundwater

According to the correlation between the groundwater TDS and ions in the study area (Fig. 7), the contribution of different ions to groundwater salinization can be determined. Among the anions, Cl^- contributed the most to TDS. HCO_3^- and SO_4^{2-} increased first and then slowed down with the increase of TDS, and when $\text{TDS} > 2500 \text{ mg}\cdot\text{L}^{-1}$, the content was almost unchanged. It can also be seen that Na^+ and Cl^- in groundwater are the main contribution indicators of TDS, and their excessive contents is the main cause of groundwater salinization in the study area. The contribution of Mg^{2+} and Ca^{2+} are relatively small, but with the increase of TDS, their contents also show an upward trend, which is more consistent with the results of Zeng (2021). This study and the research performed by Li (2014) have indicated that Na^+ and Cl^- of groundwater in the lower reaches of the Hetao Irrigation District show significant enrichment, and the WLTIA groundwater has obvious advantages in Na^+ and Cl^- , which lead to the widespread distribution of brackish water in this area. The SWIA is dominated by fresh water, but the results show that most groundwater is not suitable for irrigation. The main reason for this is that the concentration of groundwater HCO_3^- is generally high in this area, yet the contribution of HCO_3^- to TDS is relatively small, which results in the groundwater in this area being mainly freshwater, while its ion content is still at a relatively high level.

5.2 Impacts of human activities

With the rapid development of industry and agriculture, the intensification of human activities has greatly affected the content of groundwater components. The Hetao Irrigation District is an alluvial plain formed by the diversion of the Yellow River. It has been an important agricultural region for many years. Due to the fact that there are no natural rivers in the area, there are fewer available water resources. The drought and lower rain conditions in the area have required the local farmlands to be irrigated using the Yellow River

water for more than 2,000 years. From 2009 to 2018, the average annual water diversion into the SWIA and WLTIA was 505 and 438 million m³, respectively, and the drainage volume was only 0.07 and 0.87 million m³ (Fig. 8), and the average salt accumulation is 2.64×10⁵ t and 1.862.64×10⁵ t respectively. Issues such as the silting up of drainage ditches and small hydraulic gradients have made the drainage volumes decrease in this area, the discharged salt load is small, and a large amount of salt accumulates inside the area. The groundwater buried depths are now less than 3 m in the two irrigation areas, which respectively account for 76.21% and 80.11% of the total area (Fig. 9). The chemical components of groundwater rise to the soil during the non-irrigation period with evapotranspiration, and are leached into the groundwater again during the irrigation period or heavy rainfall season. Then they carry the soluble salt from agricultural fertilization and industrial discharge into the groundwater, which leads to the problem of the groundwater salinization being aggravated.

5.3 Discussion on the suitability of saline groundwater for irrigation

When groundwater is used for irrigation, salt and alkali damage must be considered [Li et al., 2013]. Especially in areas where the problem of soil salinization is prominent, more caution must be taken in regard to irrigation water. SWIA and WLTIA are the main water diversion and drainage control areas in the Hetao Irrigation Area, thus the evaluation of water quality is particularly important for guiding farmland irrigation. In the present study, the RSBC (residual sodium bicarbonate), PS (potential salinity) and SAR (sodium adsorption ratio) were used to assess the salt and alkali damage of groundwater when it is used for irrigation in the study area.

RSBC [Gupta et al., 1987] was proposed by Gupta in 1987, which divides water quality into five alkaline levels. SWIA and WLTIA have 8 and 13 samples respectively belonging to non-alkaline water, and these water samples will not produce alkali damage when used for irrigation. The groundwater in the study area is mostly low alkaline and above (80.95% and 69.77%, respectively), which may increase the content of alkaline substances in the soil when used for irrigation. Unfortunately, the water quality of the two irrigation areas with high alkaline and above accounted for a relatively large proportion (16.66% and 34.89%), and the alkaline hazard to the soil is extremely serious, thus it is not recommended to be used for irrigation (Table 3).

PS is an important indicator for judging whether the salinity of groundwater is suitable for irrigation [Gupta et al., 1987], and its classification methods are shown in Table 4. The PS value of the SWIA domain varies from 3.75 to 61.95 meq·L⁻¹, with an average value of 13.50 meq·L⁻¹. All samples in the area domain belong to the category of "suspicious and harmful." The PS value of the WLTIA domain varies from 2.75 to 96.65 meq·L⁻¹, with an average value of 20.13 meq·L⁻¹, and only one sample in the area is excellent water quality. This indicates that, if only the PS index is considered, then most of the groundwater in the two areas is not suitable for irrigation. The excessively high content of soluble salt ions in the shallow groundwater increases the PS, which may be mainly due to the excessively high levels of Cl⁻ and Na⁺ in the groundwater.

If the SAR of irrigation water is high, it may cause damage to soil permeability and structure, thereby inhibiting crop water absorption [Tang et al., 2019b]. According to SAR, water quality can be divided into four levels: excellent (SAR<10), good (10<SAR<18), suspicious (18<SAR<26), and unsuitable (SAR>26) [Ravikumar et al., 2011]. The evaluation results can be displayed in the USSL diagram. The abscissa of the USSL diagram is EC, and the ordinate is SAR. EC represents salt damage, SAR represents alkali damage, the SAR value of SWIA irrigation area varies from 1.49 to 35.55 (mean value 7.79), and the variation range of WLTIA groundwater SAR value is 1.02~35.40 (average 8.55). It can be seen from Fig. 10 that only one sample of the SWIA and WLTIA are located in the C2S1 area, which belongs to medium-salt, low-sodium water and is suitable for irrigation. Most of the groundwater samples of the two areas are concentrated in the C3S1 area. Among these samples, the SWIA accounts for 59.52%, and the WLTIA for only 37.21%. This type of water belongs to high-salt, low-sodium water, which can only be used for irrigation of crops with strong salt tolerance or soil with good drainage conditions. In addition, 19.05% and 37.21% of the sampling points of the SWIA and WLTIA were discretely distributed in the C4 region, thus indicating that these samples would lead to serious salt and alkali damage problems if they were to be used for irrigation, which in turn may affect soil permeability and inhibit water absorption of crops.

At present, salt water irrigation and drip irrigation are considered to be important ways by which to alleviate the lack of water resources in agricultural concentrated areas, and these methods are widely used throughout the world. In recent years, many scholars have carried out saline (or slightly saline) water irrigation experiments in the Hetao Irrigation District. In order to ensure the sustainable development of local agriculture and soil safety, and to reduce soil CO₂ emission and increase the scale of the carbon pool, some scholars have suggested that 2.0 g·L⁻¹ brackish water be used for drip irrigation [Wei et al., 2021]. However, long-term use of salt water (brackish water) for irrigation may reduce the oxygen content in the soil and deteriorate the soil environment, thereby inhibiting plant growth [Zhu

et al., 2021]. Oxygen-enhancing treatment for irrigation water can effectively increase crop yield, and the suitable dissolved oxygen concentration of irrigation water differs with different salinities [Sun et al., 2020]. Cycle irrigation with brackish and fresh water may cause accumulation of soil salinity, but the amount of salt accumulation had no impact on crop growth within three years [Guo et al., 2017].

The evaluation results of irrigation water in this study indicate that both SWIA and WLTIA groundwater may lead to salt and alkali damage if used for irrigation. It can be seen that there are certain risks when shallow groundwater of the Hetao Irrigation District is directly used for irrigation. Caution is necessary when using it for irrigation, and soil with better air permeability can effectively reduce risks such as that of soil compaction. At the same time, it is necessary to adopt drip irrigation, cycle irrigation with brackish and fresh water, and aeration treatment of irrigation water when salt water (brackish water) is used for irrigation, so as to increase the utilization efficiency of salt water (brackish water), and to reduce the use of salt water (brackish water). The secondary salinization risk caused by salt water irrigation and the possible alkali damage caused by salt water (brackish water) cannot be ignored.

6. Conclusion

Groundwater plays an important role in agricultural development. Human activities and environmental factors exert great impacts on the groundwater environment. However, unreasonable utilization of groundwater resources will not only reduce soil quality, but also affect crop yields. In this study, the spatial differentiation of groundwater and water flow pooling were considered, and the chemical characteristics, main control mechanisms and water quality in the Hetao Irrigation District of Inner Mongolia were analyzed. Based on the obtained results, the following conclusions were drawn.

Affected by many factors, including geological factors and groundwater runoff conditions, the hydrogeochemical characteristics of groundwater in the Hetao Irrigation District exhibit great spatial variability. With the flow of groundwater, groundwater salinization in the downstream areas is significant. The SWIA is dominated by fresh water (47.62%), while the WLTIA is dominated by brackish water (65.12%). The SWIA has no obvious dominant anion, WLTIA uses Cl^- as the dominant anion, and both cations are dominated by Na^+ . Na^+ and Cl^- are the main contributing indicators of groundwater salinization in the study area. The main hydrochemical types are $\text{Cl}\cdot\text{Na}$ and $\text{Cl}\cdot\text{SO}\cdot\text{Ca}\cdot\text{Mg}$. The content of each ion in WLTIA is higher than that in the SWIA, particularly Na^+ and Cl^- .

Rock weathering, ion exchange and evaporative crystallization are the main controlling factors for groundwater in the Hetao Irrigation District. Among them, Na^+ mainly originates from the dissolution of evaporative rock and silicate rock, and Ca^{2+} from the dissolution of gypsum and carbonate. The order of the contribution rate of different rocks is evaporative rock > silicate rock > carbonate rock, and the contribution rate of human activities and atmospheric input is small.

As the water flows, the concentration of groundwater solutes rises, and the groundwater quality of the upstream SWIA is superior to that of the downstream WLTIA. However, due to the high ion concentration in groundwater, most of the shallow groundwater in the Hetao Irrigation Area cannot be directly used for irrigation, which may cause salt and alkali damage. When using the groundwater to irrigate farmland, it is necessary to fully evaluate and pretreat the groundwater, such as using drip irrigation or increasing oxygen for irrigation water, the main goal of which is to avoid the reduction of soil permeability and compaction.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

The datasets generated and/or analysed during the current study are not publicly available due the test data is restricted to the relevant personnel of the project and is not allowed to be disclosed to the public but are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests" in this section.

Funding

This research was funded by the Research and demonstration of key technologies for farmland conservation and soil fertility improvement in the northern agro-pastoral zone (201802065), Inner Mongolia Autonomous Region Science and Technology Plan Project (201802084), Inner Mongolia Science and Technology Major Project (zdx2018059).

Authors' contributions

Hongying Yuan: Formal analysis, Investigation, Writing-original draft, Visualization. **Shuqing Yang:** Conceptualization, Methodology, Writing - review & editing, Supervision, Project administration. **Bo Wang:** Investigation. **Tiankai Han:** Investigation.

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Tables

Table 1 Physicochemical groundwater characteristics and statistical features

Project	SWIA					WLTIA				
	Minimum	Maximum	Mean	Standard deviation	Coefficient of variation	Minimum	Maximum	Mean	Standard deviation	Coefficient of variation
pH	7.21	8.32	7.72	0.26	0.03	7.27	8.81	7.85	0.31	0.04
TDS/ mg·L ⁻¹	0.26	13.06	1.84	2.41	1.31	0.33	56.4	3.6	8.53	2.37
Cl ⁻ / mg·L ⁻¹	0.09	6.65	0.54	1.06	1.96	0.07	25.88	1.36	3.95	2.90
SO ₄ ²⁻ / mg·L ⁻¹	0.07	2.40	0.47	0.53	1.13	0.07	15.13	0.69	2.27	3.29
HCO ₃ ⁻ / mg·L ⁻¹	0.11	1.74	0.43	0.27	0.61	0.14	1.25	0.58	0.23	0.40
Ca ²⁺ / mg·L ⁻¹	0.02	0.36	0.09	0.06	0.66	0.01	0.80	0.14	0.14	0.09
Mg ²⁺ / mg·L ⁻¹	0.02	0.61	0.09	0.10	1.13	0.01	1.28	0.14	0.19	1.36
Na ⁺ / mg·L ⁻¹	0.07	4.38	0.5	0.79	1.57	0.05	22.93	1.09	3.47	3.18

Table 2 Contribution rate of groundwater chemical composition source

项目	硫酸盐/%	氯化物/%	其他/%			
			碳酸盐	硫酸盐	氯化物	其他
SW	4.23	3.15	18.89	49.78	23.95	92.62
WLT	5.55	2.27	19.52	50.14	22.52	92.18

Table 3 Classification of the quality of the groundwater for irrigation processes based on the RSBC

Evaluating indicator	Range	Remark on quality	Sample number and percentage	
			SWIA	WLTIA
RSBC [meq·L ⁻¹]	<0	Non-alkaline	8 [19.05%]	13 [30.23%]
	=0	Normal	0 [0%]	0 [0%]
	0-2.5	Low alkalinity	18 [42.86%]	10 [23.26%]
	2.5-5	Medium alkalinity	9 [21.43%]	5 [11.63%]
	5-10	High alkalinity	3 [7.14%]	12 [27.91%]
	>10	Very high alkalinity	4 [9.52%]	3 [6.98%]

Table 4 Classification of the quality of the groundwater for irrigation processes based on the PS values

PS [meq·L ⁻¹]	Water quality	Sample number and percentage	
		SWIA	WLTIA
<3.0	Excellent to good	0 [0%]	1 [2.33%]
3.0–5.0	Good to injurious	6 [14.29%]	1 [2.33%]
>5.0	Injurious to unsatisfactory	36 [85.71%]	41 [95.35%]

Figures

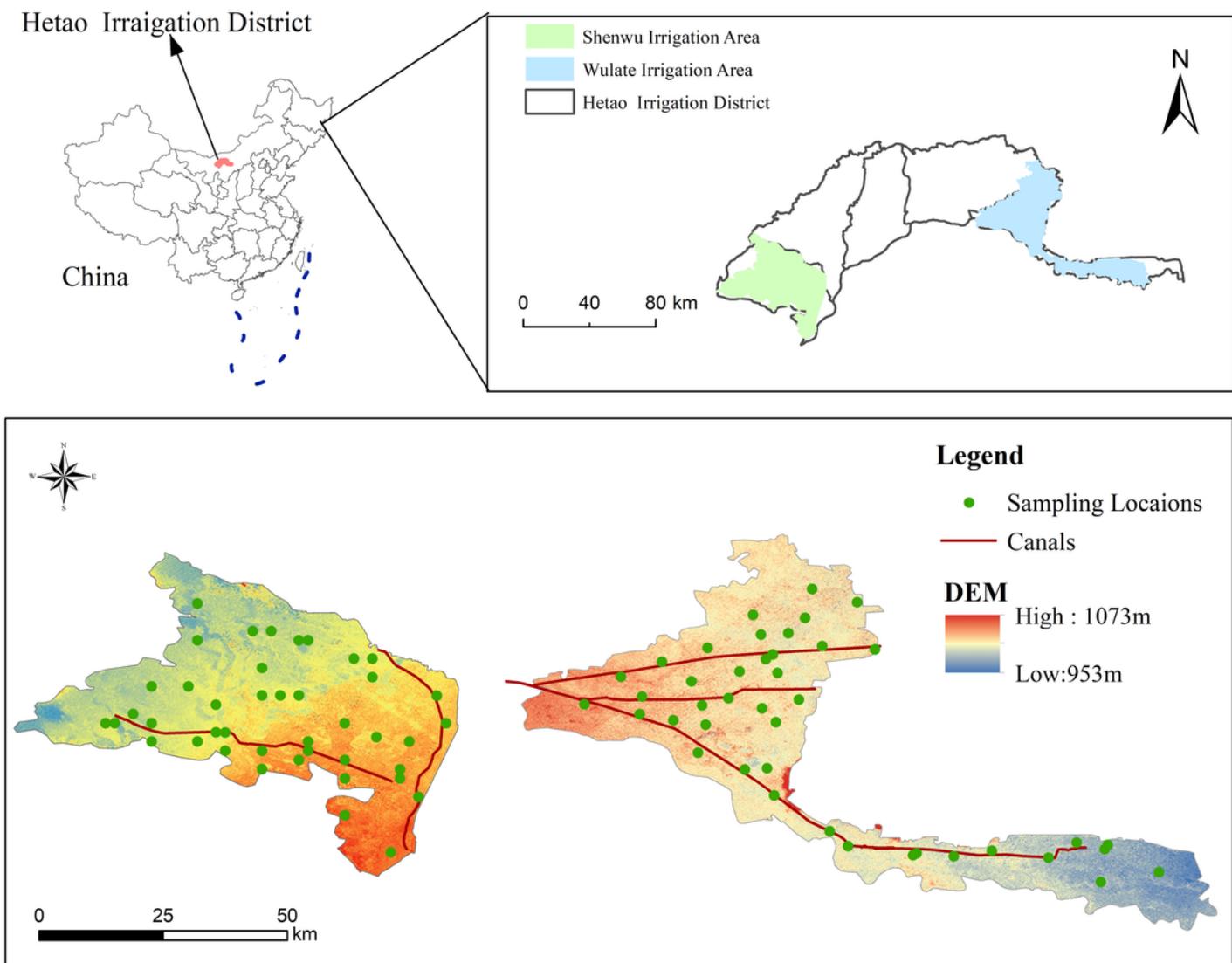


Figure 1

Study area and sampling locations

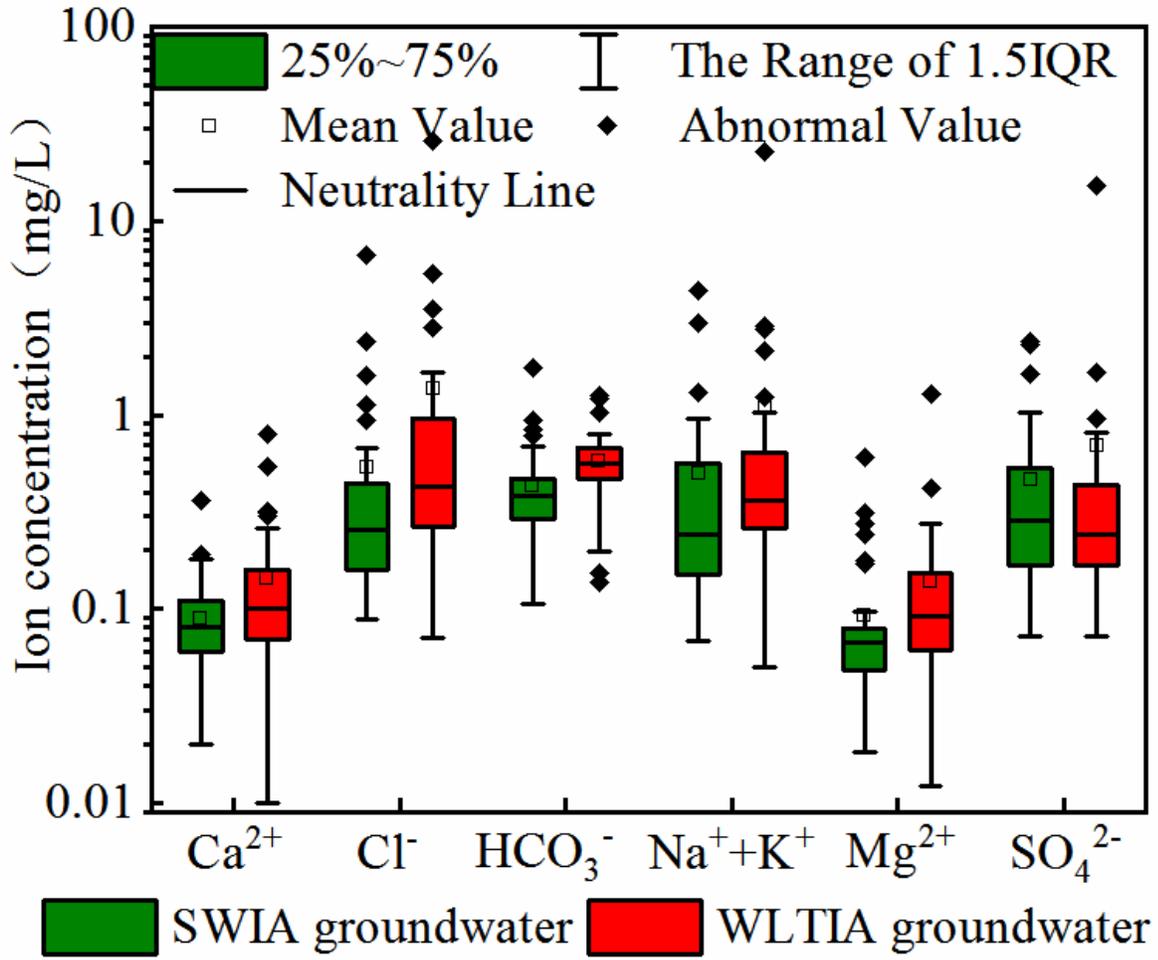


Figure 2

Box plots of the major ions in the Shenwu and Wulate Irrigation Districts

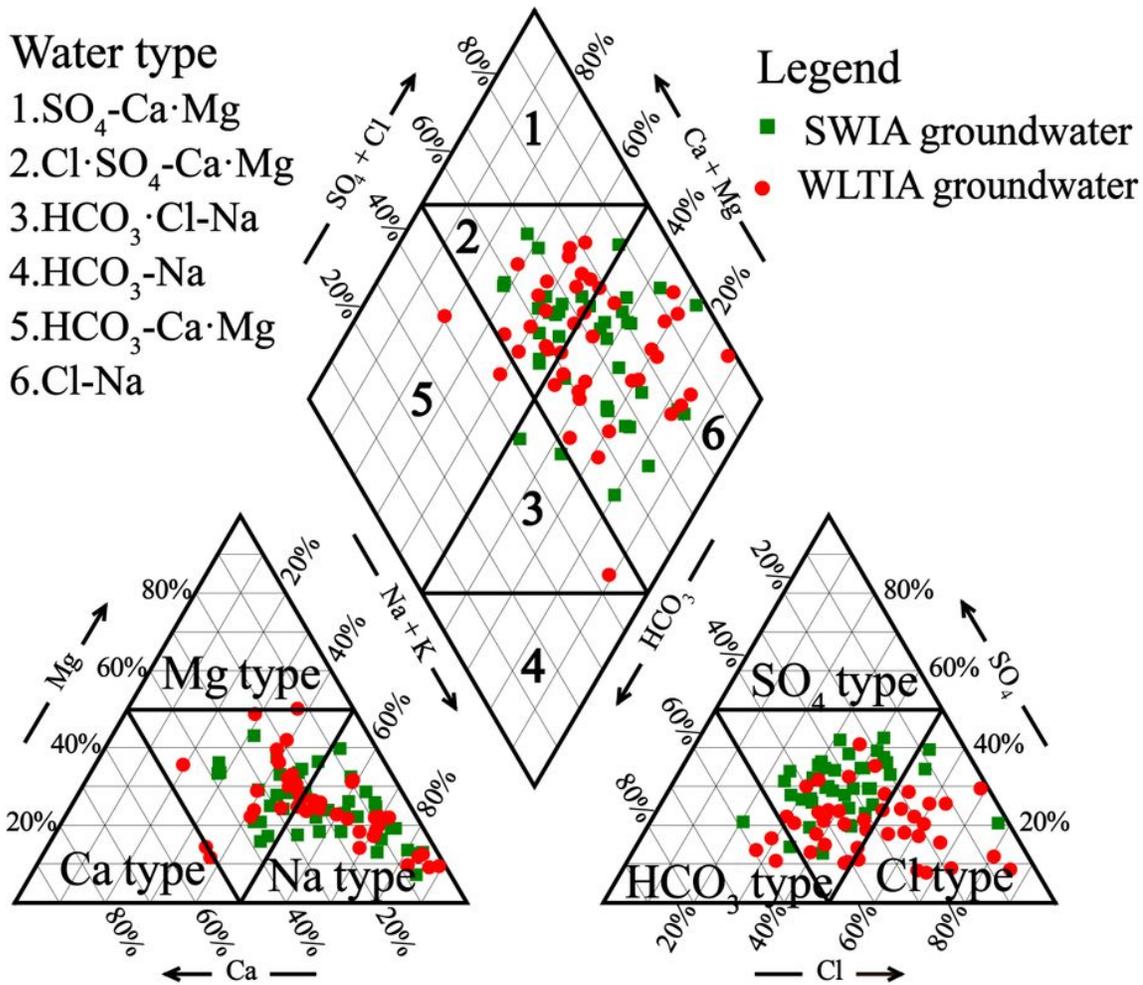


Figure 3

Piper diagram of the chemical compositions of shallow groundwater

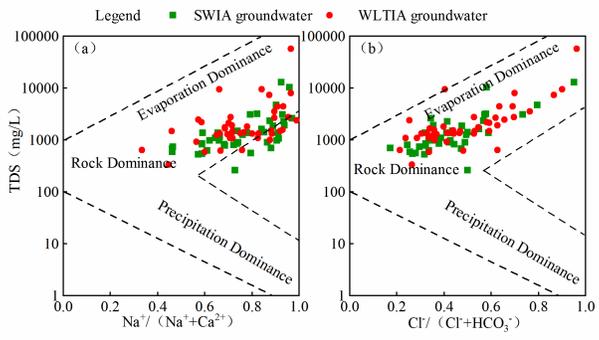


Figure 4

Gibbs Diagram of the study area

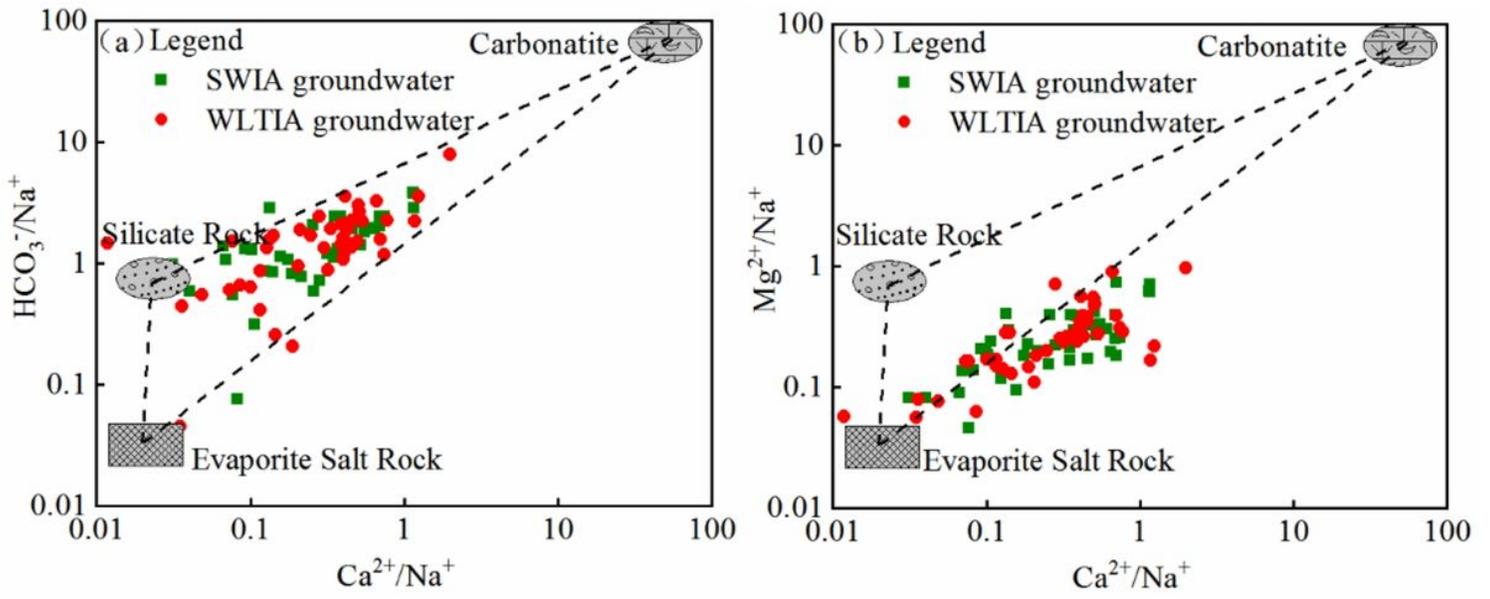


Figure 5

Relationships among the $\text{Ca}^{2+}/\text{Na}^+$, $\text{HCO}_3^-/\text{Na}^+$, and $\text{Mg}^{2+}/\text{Na}^+$ of the study area's groundwater resources

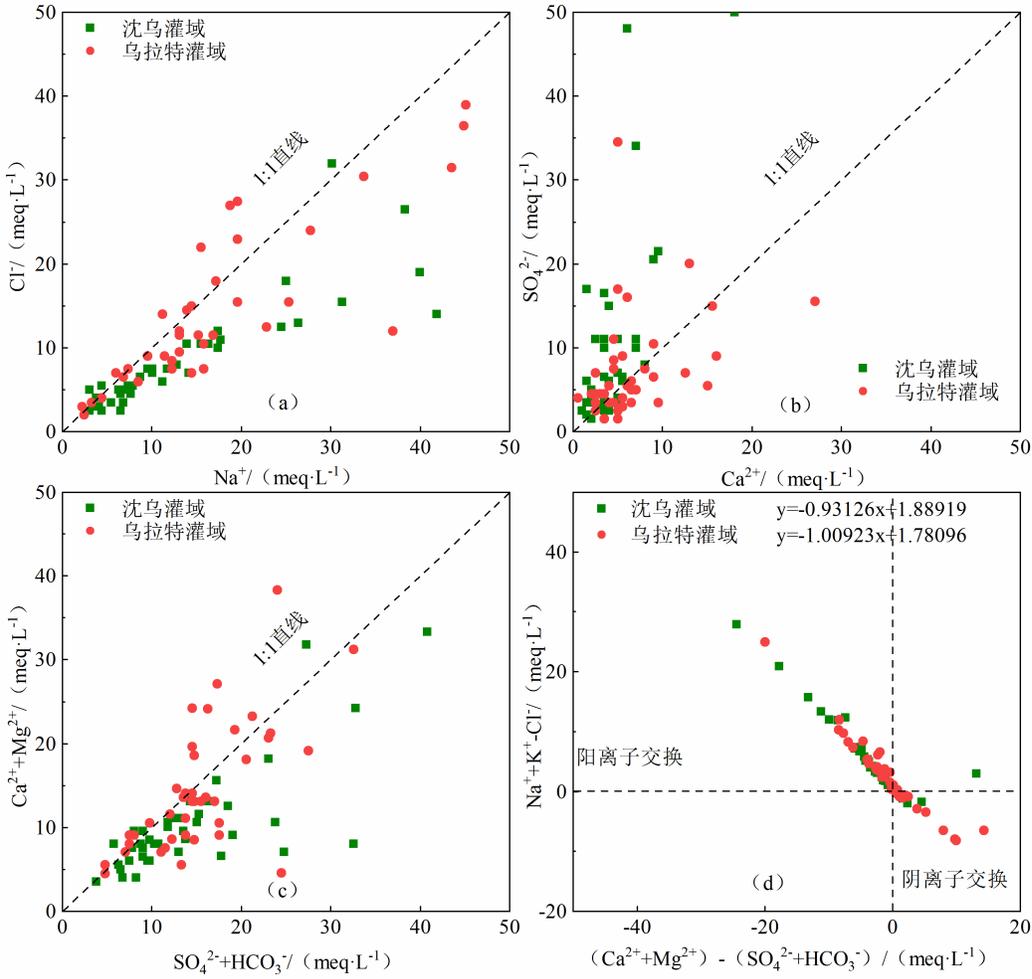


Figure 6

Ion correlation diagram of the shallow groundwater resources in the Shenwu and Wulate Districts

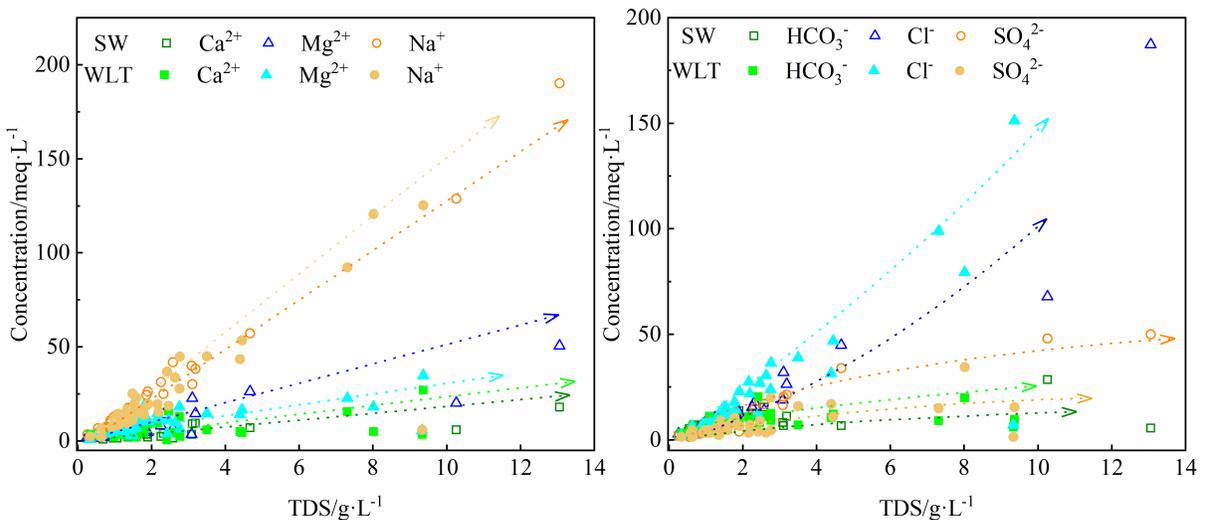


Figure 7

The relationship between TDS and ions of groundwater

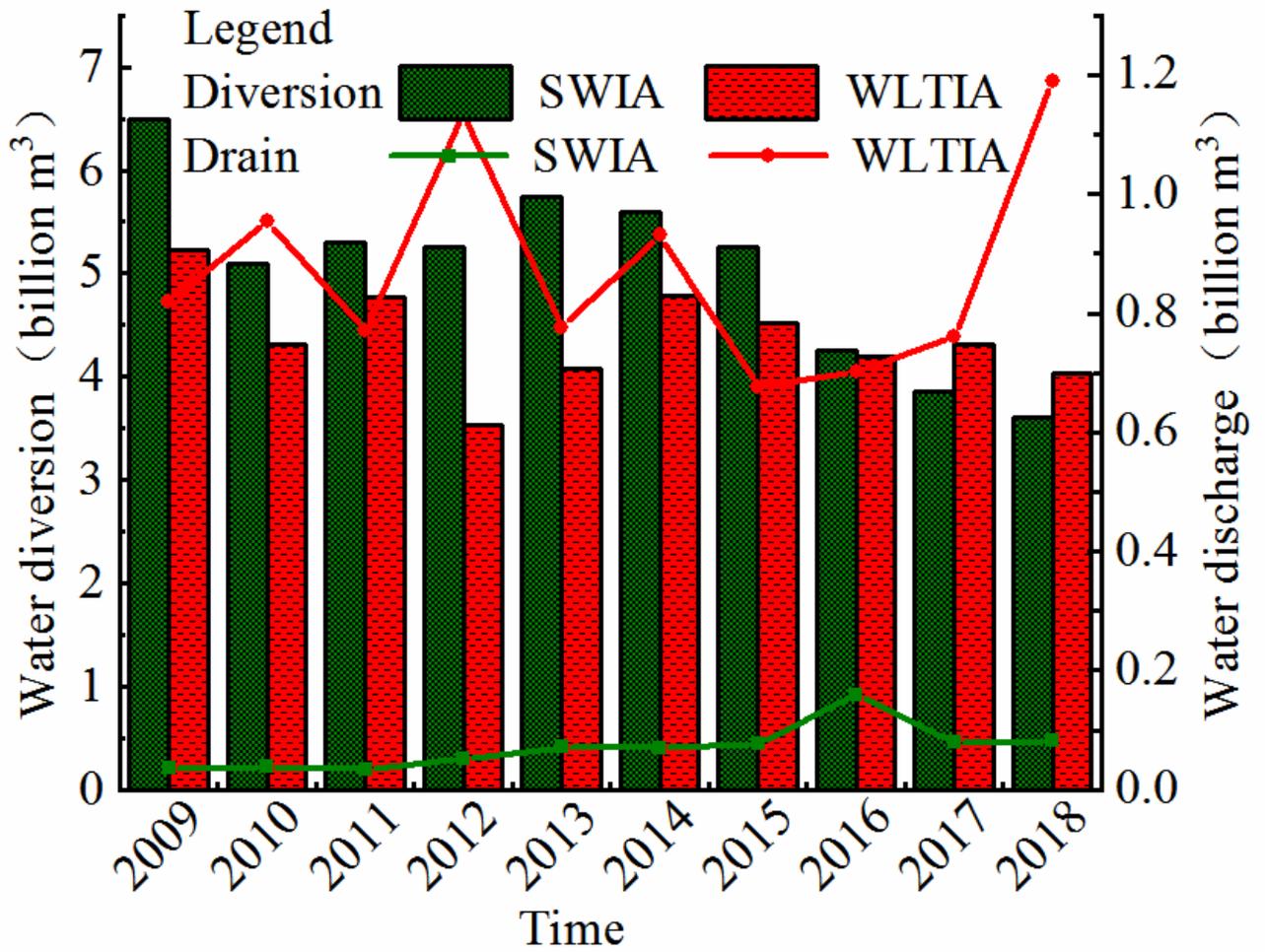


Figure 8

Changes in the diversion and drainage processes of the Shenwu and Wulate Districts

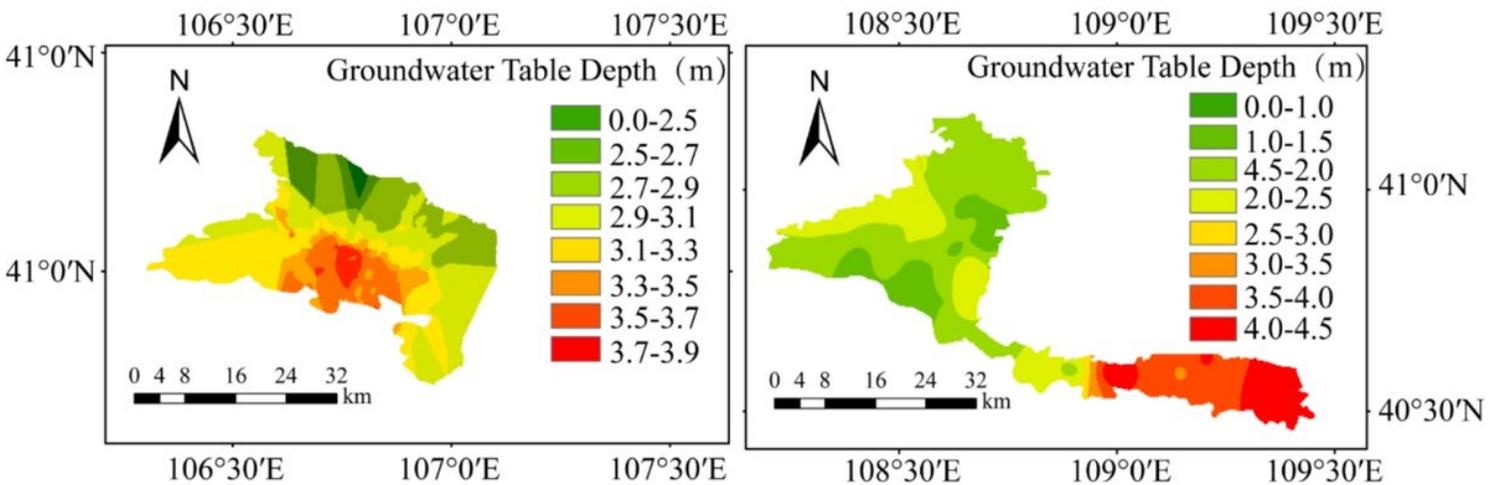


Figure 9

Spatial distribution map of the groundwater table depths in the study area