Pol. J. Environ. Stud. Vol. 29, No. 1 (2020), 371-395
DOI: *10.15244/pjoes/103029*

Original Research

Hydrochemistry Characteristics and Water Quality Assessment for Irrigation along the Second Songhua River in the South of the Songnen Plain, Northeast China

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Received: 17 November 2018
Accepted: 19 January 2019

Abstract

In view of changes in the water environment in Songnen Plain and water quality problems in recent years, the Second Songhua River Basin was used as our research object. To conduct the water environment investigations, 11 surface water samples and 76 shallow groundwater samples were collected. Multiple methods, such as isotope hydrological analysis, principal component analysis, and irrigation water quality parameter (SSP, SAR, RSC, MAR, KR) analysis were used to systematically apply water chemistry analysis and its evolutionary process, and water quality evaluation for irrigation. The results showed that Ca^{2+} and HCO_3^- were the main ions in the water body. The regional groundwater was recharged by atmospheric precipitation, and the surface water received both atmospheric precipitation and groundwater recharge. The hydrogeological process included the weathering and dissolution of carbonates, and the ion exchange reaction. In addition, the major reaction of local groundwater was the weathering and dissolution of silicate. Water quality was affected by agricultural fertilizer and domestic sewage. The water downstream of the basin, if used for irrigation, might accelerate the formation of alkaline and saline soil, neither of which help crop growth. The water upstream of the watershed in the region was suitable for irrigation.

Keywords: chemical information of water, statistical analysis, isotope hydrology, assessment of irrigation water

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Introduction

Surface water and groundwater are the main water resources on earth. The interaction between the two affects the chemical components of the water and records the formation, transformation, and migration of water bodies under the action of human activities to a certain degree [1-4]. The mutual conversion of surface water and groundwater is a hotspot of research in the field of terrestrial water circulation and water resources [5-7]. Understanding the interaction between surface water and groundwater is critical for the management of water resources [8] and analysis of ecohydrology [9]. In irrigated areas, surface water and groundwater flows become more complicated with the impacts of surface water diversion, groundwater pumping and irrigation [10]. This plays a decisive role in basin water recontradiction between the supply and demand of water resources, and basin ecological environment source evaluation, scientific management of development and utilization, relieving construction.

The sustainability of irrigated agriculture in many arid and semiarid areas of the world is at risk because of a combination of several interrelated factors, including a lack of fresh water, lack of drainage, the presence of high water tables, and salinization of soil and groundwater resources [11]. Water transfer projects have been launched across the globe to alleviate water shortage problems in arid regions and promote development, such as in Australia, the United States, Canada, China, and India [12]. In the study area, the river-lake connectivity project has been carried out since 2015, aimed at improving the state of the environment, and the connected surface water will be referenced for irrigation in agricultural areas. In order to avoid the occurrence and deterioration of such problems, it is necessary to evaluate the applicability of irrigation water resources.

Songnen Plain is located in the central part of the northeastern Plain, which is one of the main bases for grain production and animal husbandry, and one of the three major plains in northeastern China [13]. In recent years, the rapid expansion of urban areas, the increasing scale of industry, and the increase of the area of paddy fields along the mainstream of the Songhua River have resulted in a continuous increase in the demand for water resources. With the current amount of exploitation and utilization, water quality is a concern [14-15]. The contribution to the total amount of sewage in the Songhua River system is about 30%, and the pollution effect coefficient for the Songhua River basin is about 0.4 [15]. For example, excessive pumping of groundwater will bring about runoff from the river and floodplains toward over-exploited areas, which could result in abnormal hydro-chemical conditions. Furthermore, the toxic substances from agricultural irrigation and fertilization would infiltrate the groundwater together with the runoff, threatening the safety of drinking groundwater. The water quality for the downstream of the second Songhua River, for example, from the water quality of the Linjiang Bridge has been classified as Category III. The impact factor was the potassium and permanganate index, and occasionally mercury exceeded the standard. The water quality for the monitoring section of Zhenjiangkou and Songhuajiang Village has reached Grade V. The over-standard items were the chemical oxygen demand, ammonia nitrogen, BOD_5, petroleum, and so forth. The water quality of the Yinma River has been evaluated as Grade V. The major pollutants were chemical requirements, volatile phenols, and oils [16-18].

According to the environmental functions and protection objectives of surface waters, they are divided into five categories according to the level of function.

Class I water is mainly used in source water and national nature reserves.

Class II water is mainly used in the first-grade protection zone of centralized drinking water surface water sources, cherished aquatic habitats, fish and shrimp spawning grounds, and feeding grounds for juveniles and young fish.

Class III water is mainly used in the secondary protection areas of centralized drinking water surface water sources, fish and shrimp wintering fields, migratory passages, aquaculture areas, and other fishery waters and swimming areas.

Class IV water is mainly suitable for general industrial water areas and recreational water areas where the human body is not in direct contact with the water.

Class V water is mainly used in general agricultural water areas and general landscape waters.

The study of the water chemical information of the interaction between the unconfined groundwater and surface water is the basis for understanding water quality degradation. In order to solve the above problems, 11 surface water and 76 groundwater samples of the Second Songhua River were collected in 2012-2014. The hydro-chemical concentrations and chemical properties of the surface water and groundwater in the area were characterized via SPSS 17.0 in this paper. The particular purpose of this study is to (1) understand the relationship between the surface water and unconfined groundwater with the aid of isotope hydrology; (2) discuss the hydro-chemical evolution of the surface water and unconfined groundwater; and (3) assess the quality of the surface water and groundwater in the district for irrigation functions.

Study Area

Study Site Description

The study area is located in the southern part of Songnen Plain (121°27′-128°12′E, 43°36′-49°45′N) in northeastern China (Fig. 1c). The study area has the Changbai Mountains in the east, the Daxingan

(Greater Khingan) Mountains in the west, and the Songliao watershed divide in the south. The total area includes Jilin Province and Inner Mongolia Province in the district. The research region has a semi-humid and semi-arid continental monsoon climate. The mean annual precipitation is 350-600 mm, with 70-80% of precipitation occurring during June to September. The average annual temperature is about 4.0-5.5ºC. The

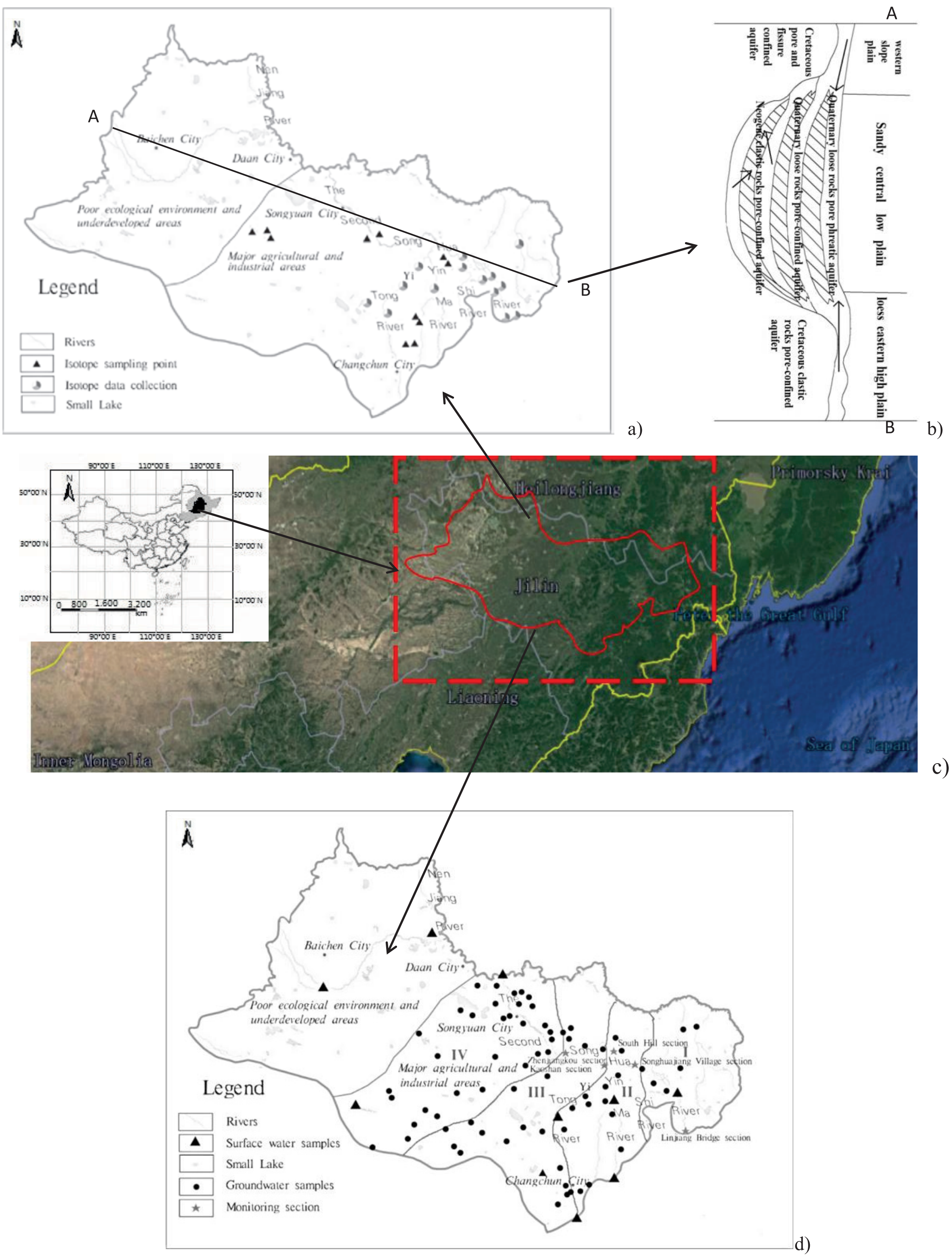

Fig. 1. Groundwater and surface water isotope sampling sites and collection data in the study area (a). Hydrogeological profile (b). The location of the study area (c). The water sampling sites and surface water system (d). To the west of the dividing line, near Da'an city on the map, is the western part of Jilin Province. The ecological environment is harsh, and the climate is dry. To the east, mainly showing the area along the Second Songhua River, agriculture is developed and the climate is semi-humid and semi-arid.

average temperature in January is -16 to -26ºC, while the average temperature in July is 21-23ºC. Evaporation from the water surface is between 700 and 1100 mm.

The Second Songhua River has a total length of 790 kilometers and an area of approximately 7.8 km^2, which accounts for 14% of the basin. The Songhua River has two sources, the north and the south. The northern source originates from the Nenjiang River. The southern source originates from the Tianchi of Changbai Mountain. The Second Songhua (the southern source river), which flows from southeast to northwest, and the Nenjiang merge in the center of the area and then become the Songhua, which flows from west to east. It is the main commodity grain production area and industrial area in the three northeastern provinces. The Yitong and Yinma rivers in the south of the central low plain, and the Taoer and Huolin rivers in the slope plain in the west, are the Ersong tributaries in the study area. The surface water system distribution of the basin in the area is shown in Fig. 1d).

In Fig. 1d), three monitoring sections can be seen located in the main stream of the Second Songhua, and one further section lies in the branch (the merged site of the Yitong and Yinma rivers). These monitoring sections are Songhuajiang Village, South Hill, Kaoshan Bridge, and Zhenjiangkou section. The four water quality monitoring sections divide the surface river into four areas along the direction of the flow, upstream (above the South Hill section), tributaries (including the Yinma and Yitong rivers), and downstream (below the Zhenjiangkou section) of the main stream. The corresponding four aquifer sub-areas are also formed: I, II, III, and IV (Fig. 1d).

According to Fig. 1d), a boundary shows up, the west area has a poor environmental state, while the major agriculture and industry developments are distributed in the east. One of the purposes of this study is to judge whether the water resources in the research region are suitable for irrigation water; therefore, the groundwater sampling points in the agricultural developed areas are relatively dense.

A comparative analysis of the use of pesticides and fertilizers in the study area from 2008-2012 showed that the use of agricultural fertilizers increased year by year, from 2,890,040 tons in 2008 to 3,430,422 tons in 2012, indicating that in recent years, with the increase of agricultural output in the region, the application rate of chemical fertilizers and pesticides also increased. Due to their extensive use in the region, some of them infiltrated into the soil and groundwater with rainfall, thereby affecting the groundwater environment. Table 1 shows the area distribution of various land types in the six administrative regions of the study area in 2010.

Geology and Hydro-Geology

The study area is underlain by alluvial, lacustrine, and aeolian deposits. Under the control of neotectonic movements and geomorphological conditions, the Quaternary strata of the study area formed obvious differences between the western slope plain, the central low plain, and the eastern high plain (Fig. 1b). In the western slope plain, there are more depositional features of the internal structure, mainly ice water accumulation and flood alluvium, and the lithology is mostly coarse-grained sandy soil which is thinning from east to west. In the lower central plain, the lower Pleistocene river and lake gravelly soil, the Middle Pleistocene lake-phase cohesive soil, and the Upper Pleistocene river-lacustrine sandy soil are generally piled up. The overlying Holocene sediments are more common – mainly aeolian deposits and fluvial deposits – and the swampy deposits are distributed like dots. In the high plains of eastern China, the neotectonic movement takes a block-like elevation south of the South Songhua River, and is dominated by the alluvial loess in the middle and upper Pleistocene and the subtropical clay in Chonghu Lake [7, 13, 16-18].

Songnen Plain is a large-scale underground water collection basin. It is a complete groundwater flow system consisting of Tertiary Eocene, the Oligocene Yi'an Formation, the Miocene Da'an Formation, the Pliocene Taikang Formation, and the Lower Pleistocene. Since Songnen Plain is also a basin containing multiple aquifers, each aquifer has its own relatively independent water flow system. Therefore, shallow water, middle water, and deep groundwater flow systems that are related to each other and relatively independent are

Table 1. Land use in various regions of the study area in 2010 (km^2).

Cities	Cultivate land	Woodland	Grassland	Building Site	Unused Land	Total
Songyuan	9147	2934	6175	896	871	20023
Baicheng	9473	3065	7362	409	841	21150
Changchun	9815	899	3779	1668	109	16270
Jilin	363	331	128	63	0	885
Siping	1057	0	46	113	0	1216
Neimeng						2685
Total	29855	7229	17490	3149	1821	62229

formed on the section. The overall flow of groundwater in the basin converges from the recharge area on both the western and eastern sides to the discharge center of the basin, and finally flows out of the basin through Songnen River and the subsurface flow of the valley. In this study, we mainly focus on shallow groundwater aquifers.

Due to the uplift belt in the east of the study area, a loess-like undulating high plain and a sandy wavy high plain are formed, and a local clay soil underlies a thin layer of gravel. The aquifer is mainly composed of pore phreatic aquifer, pore-confined aquifer, and inter layer confined aquifer. The groundwater depth is 5~30 m. The central low plain has the characteristics of a basin, and it has accumulated thick Cretaceous and Tertiary clastic rocks and thick Quaternary loose sediments. The terrain is low and the permeability in the aerated zone is good. The groundwater level is less than 10 m, the main distribution is confined aquifer, and the pore phreatic aquifer is locally distributed. In the western mountain front sloping plain, sand-gravel fan-shaped land also constitutes a very water-rich storage structure. The main part is pore phreatic aquifer, and the water depth is less than 5 m.

Material and Methods

Water Sampling and Analysis

To achieve this paper's objectives, 11 surface water and 76 shallow groundwater (depth<30 m) samples, 11 surface water and 11 groundwater isotopic samples were collected between July and August in 2012-2014 (Fig. 1a), and tested in the laboratory of the Heilongjiang Province Hydro-Geology and Environmental Geology Investigation Institute. The location of the sampling points is illustrated in Fig. 1a), d). Field test indicators include water temperature, pH, EC, Eh, DO, and turbidity. The laboratory test index includes TH, TDS, Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, NO_2^-, F–, SiO_2, Cu, Mn, Zn, As, Pb, Cd, TCr, Al, I^-, Fe, DBS, and COD_{Mn}.

The samples were collected in 500 ml sterilized polythene bottles. Each bottle was rinsed with distilled water before pouring in the sample water. The bottles were labeled and airtight. On the field, the latitude and longitude of each sampling point were taken with GPS, and the approximate depth of the wells was noted from the well owner's records. For all samples collected, parameters such as pH, electrical conductivity (EC), and total dissolved solids (TDS) were measured in the field. The electrical conductivity (EC), total dissolved solutes (TDS), pH, and temperature for the rivers, hand-dug wells and boreholes were measured at each sampling point with a radiometer conductivity meter (PHM82) and a standard pH meter.

For the rivers, the water samples were collected from the middle of the rivers to ensure perfect mixing of the water. For sampling of the hand-dug wells, prior to sampling, each well was pumped for a few minutes until it purged out approximately twice the well volume, or until steady-state chemical conditions (pH, TDS, EC, salinity, and temperature) were obtained. The above was done to ensure that the sampled water from the hand-dug wells was from the casing or open wells, and the sampled water from the boreholes was from the aquifer. Water samples were collected in two separate polyethylene bottles in order to analyze for major ions and trace elements. Consequently, 2 ml HNO_3 50% was added into water samples for trace element analysis to preserve precipitation.

$K^+$and Na^+ were tested using the flame photometric method; Ca^{2+}, Mg^{2+}, and total hardness were tested by the EDTA complex titration method; Cl^- was tested by the standard solution titration with silver nitrate method; pH was tested by a pH meter; and SiO_2 and anions such as SO_4^{2-}, and F^-, NO_3^-, and NO_2^- were tested by the spectrophoto metric method. The concentrations of trace metals such as Fe and Mn were analyzed by atomic absorption. The concentrations of trace elements Cu, Zn, As, Pb, Cd, TCr, Al, and I^- were measured using inductively coupled plasma and mass spectrometry, which was linearly calibrated from 10 to 100 lg/L with custom multielement standards (SPEX CertiPrep, Inc., NJ, USA) before use. The concentrations of DBS and COD_{Mn} were measured by the methylene blue spectrophotometric method and acid potassium permanganate method. The stable isotope (d2H and d18O) compositions of the waters (rivers and hand-dug wells) were measured using a liquid-water stable isotope analyzer (based on off-axis integrated cavity output spectroscopy (OA-ICOS) via laser absorption). D and ^{18}O were tested by the Laboratory of Geographical Resources Institute of Geographic Sciences and Natural Resources Research, CAS. Quality assurance and quality control were conducted according to the "Standard for Assessment and Investigation of Groundwater Pollution" (DD2008-01), using the method of adding standard recovery and extracting repeated sampling to control quality.

Analysis accuracy was assessed through the ion balance error, which was found to be in the range of ±5%, indicating the accuracy and quality of the analytical data.

$$BE = \left[\frac{(TCC - TCA)}{TCC + TCA}\right] \times 100 \tag{1}$$

Where TCC and TCA are the concentrations of total cations and total anions in meq /L, and BE denotes the percentage of ionic balance error.

Data Analysis

In this study, isotope hydrology, the Piper diagram, the principal component analysis method, the Gibbs plot, the CAI-1 index, and the assessment of water quality for irrigation with the aid of SSP (%Na) [19], SAR (sodium absorption ratio) [20], RSC (residual sodium carbonate) [21], MAR (magnesium adsorption ratio) [22], and KR [19] were used.

The principal component analysis method, which reflects the characteristics of ion composition and ion proportion in water, was used in this paper to determine the geochemical process of groundwater. In the analysis, the principal component analysis method is further used to simplify the data structure and reduce indicators that have no indicative significance, while losing minimal data information. The original variables are converted into new principal components using orthogonal transformation, and there is no correlation between them as each principal component is a linear combination of partial raw variables. The exact principle component is such that the maximum variance is dedicated to the first component, the second greatest variance to the second component, and so on. To provide information based on the most meaningful parameters with minimum loss of the original information, the axes defined by PCA rotate, and new variables can be created. In this study, factor analysis alongside principle component analysis methods are put to use in the water quality assessment. There are two ways to determine the number of principal components, when the cumulative contribution rate of K principal components reaches a certain eigenvalue (generally 70% or more), the first K principal components are retained; the principal component with an eigenvalue ≥1 is selected.

The soluble sodium percentage (SSP) is used to evaluate the sodium hazard [23]. Todd (1980) defined the soluble sodium percentage (SSP), or Na%, as follows:

$$SSPorNa\% = \frac{(Na^{+} + K^{+}) \cdot 100}{(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+})} \tag{2}$$

For evaluating water quality for irrigation purposes, the sodium or alkali hazard expressed by the sodium adsorption ratio (SAR) is widely used. If the water sample is high in Na+ and low in Ca^{2+}, the ion exchange complex may become saturated with Na+, which destroys the soil structure [21]. The SAR value of irrigation water quantifies the relative proportion of Na+ to Ca^{2+} and Mg^{2+}, and is computed as follows:

$$SAR = \frac{Na^{+}}{\sqrt{Ca^{2+} + Mg^{2+}/2}} \tag{3}$$

…where Na^+, Ca_2^+, and Mg_2^+ are defined as the concentrations of Na, Ca, and Mg ions in the water, respectively [23]. The residual sodium carbonate (RSC) is computed by taking the alkaline earths and weak acids, as follows:

$$RSC = (CO_3^{2-} + HCO_3^{-}) - (Ca^{2+} + Mg^{2+}) \tag{4}$$

The magnesium adsorption ratio (MAR), also known as the magnesium hazard (MH), was calculated as follows:

$$MAR = \frac{Mg^{2+} \cdot 100}{(Ca^{2+} + Mg^{2+})} \tag{5}$$

Lastly, Kelley's ratio (KR) [24] is described as follows:

$$KR = \frac{Na+}{(Ca^{2+} + Mg^{2+})} \tag{6}$$

All ionic concentrations are in the milli equivalent per liter (meq/L). All these parameters and individual chemical parameters had been compared with national and international standards in order to assess the groundwater suitability.

The Piper diagram is one of the most effective graphic representations in the study of groundwater quality, helping the understanding of the groundwater geochemical characteristics. In this paper, the water chemical analysis software AquaChem V4.0 was used to draw the Piper diagrams of the selected samples, which can directly reflect the general chemical characteristics of water samples and their relative contents. Major ion compositions (including Ca, Mg, K, Na, and Cl^-, SO_4^{2-}, and HCO_3^-, the units of which are the milligram equivalent) were used to identify the water types with the help of the AquaChem software (version 4.0).

The mixing ratio of precipitation with surface water and groundwater during the rainy season was calculated using the multisource mass balance model [25]. For isotopic mass balance studies involving a two-component mixture, the fraction of surface water in the mixture is defined as:

$$YG + YP = YM \tag{7}$$

$$YG\delta G + YP\delta P = YM\delta M \tag{8}$$

…where YG and YP are the percentage contribution of the groundwater and precipitation to the mixture YM. δG, δP, and δM are the isotopic compositions of the groundwater, precipitation and admixture, respectively. Substituting Equations (8) in (9) and (10) for YG and YP provides the contribution of the groundwater and precipitation component to the surface mixture.

$$YG = YM\left(\delta M - \delta P\right)/\left(\delta G - \delta P\right) \tag{9}$$

$$YP = YM\left(\delta G - \delta M\right)/(\delta P - \delta G) \tag{10}$$

Differences in the isotopic composition of the surface water, rainfall, and groundwater result in relatively high precision for detecting the mixing proportion of groundwater in the surface water [26].

The index value of the CAI-1 (choro-alkaline index) [27] indicates whether the ion exchange between

Table 2. Abbreviations that appear in the abstract and in the body of the article.

Abbreviation	Full name	Abbreviation	Full name	Abbreviation	Full name
SSP	Soluble sodium percentage or Na%	DBS	Sodium dodecyl benzene sulfonate	DO	Dissolved oxygen
SAR	Sodium adsorption ratio	TH	Total hardness	TCr	Total Cr
RSC	Residual sodium Carbonate ratio	TDS	Total dissolved solids	TCC	Total concentration of cation
MAR	Magnesium adsorption ratio	EC	Electrical conductance	TCA	Total concentration of Anion
KR	Kelley's ratio	Eh/ORP	Oxidation reduction potential	WHO	World Health Organization

the surface water, groundwater, and its environment exists. The calculation formula is as follows:

$$CAI - 1 = \frac{[Cl - (Na + K)]/Cl}{Cl} \qquad (11)$$

…where all ionic concentrations are expressed in terms of mg/L.

The categories are based on the Environmental Quality Standards for surface wate (GB3838-2002). The list of abbreviations in the paper is found in Table 2.

For the data appearing in Figs 9 and 11, the corresponding indicators are shown in Tables 5 and 6 in the supplementary materials.

Software

Major ion compositions were used to identify the water types with the help of the AquaChem software (version 4.0). SPSS (version 17.0) was used to calculate the statistical principle components among anions and cations of the surface water and groundwater samples. MAPGIS (version 6.7) was used for the mapping of the sample locations, and to show the spatial distribution.

Results and Discussion

The groundwater chemistry depends on different hydro-geochemical processes that the groundwater undergoes over space and time. The variation of water quality is due to the combined effects of natural and anthropogenic factors, the natural factors include such things as the geological structure where groundwater is stored, the composition of the precipitation, the interaction between the groundwater and aquifer minerals such as in oxidation/reduction, cation exchange, precipitation/dissolution of minerals, and mixing of waters. The anthropogenic factors include leaching of fertilizers, manure, and biological and micro-biological factors. The interaction between the surface water and groundwater can also affect water chemistry.

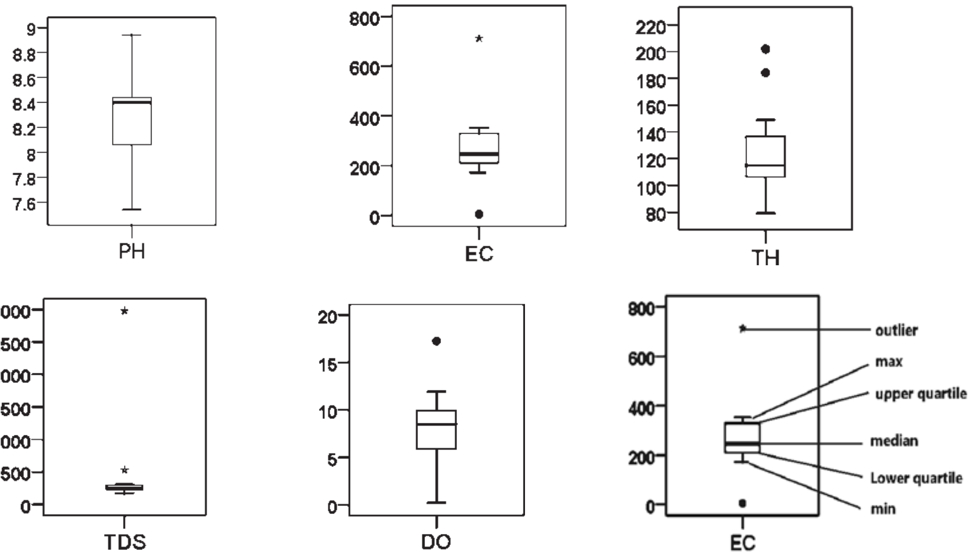

Fig. 2. Box and whisker plot of the pH, EC (us/cm), DO (mg/L), TH (mg/L), and TDS (mg/L) data for the surface water samples in the study area

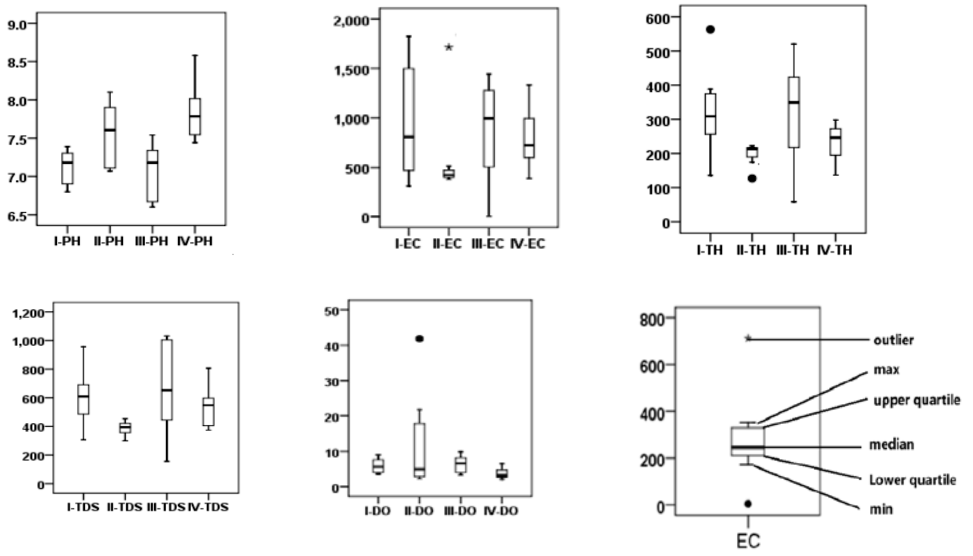

Fig. 3. Box and whisker plots of the pH, EC (us/cm), DO (mg/L), TH (mg/L), and TDS (mg/L) data for the groundwater samples in the study area.

Physicochemical Characteristics and Water Type

The pH value of the surface water in the study area is from 7.54-8.94, the average value is 8.24 (Fig. 2, Table 7), and the pH distribution range of shallow groundwater I-II-III-IV is 6.8-7.39, with an average of 7.12, 7.07-8.10 with an average of 7 .55, 6.55-8.59 with an average of 7.65, and 7.26-9.07 with an average of 7.97 (Fig. 3, Table 8), indicating that the overall environment of the area is alkaline.

The EC range of the surface water is 4.23-712 us/cm with an average of 282.65 us/cm (Fig. 2, Table 7), and the EC range of the subarea groundwater is 309-1826 us/cm, 377-1715 us/cm, 3.51-2360 us/cm, and 3.36-2194 us/cm (Fig. 3, Table 8), respectively. With a mean value of 529.62-747.06 us/cm, the average EC of the surface water is lower than the average EC value of each subarea of groundwater. Surface water directly receives the influence of atmospheric precipitation, while the groundwater is recharged by atmospheric precipitation, and is also affected by the regional runoff path. The EC of the surface water and groundwater is basically lower than the WHO permissible limits (1000 us/cm).

The DO and Eh values in the water body represent the redox state of the water environment. In general, the Eh value of groundwater is lower than that of the surface water as it is in contact with the atmosphere. The on-site measurement of Eh is difficult, in order to measure the true value of the water body. The value given is for reference only, and no specific analysis is made. The TDS from 92% of the surface water and groundwater samples is less than 1 g per liter, which suggests weak mineralized water. In general, the TDS in the overall water body comes from the natural environment and sewage discharge. The total hardness is the dissolved amount of calcium and magnesium ions in the water body. The value of the TDS for the surface water in the study area is 168-2979 mg/L, the TH is from 79.26-201.94 mg/L (Fig. 2, Table 7), the total TDS distribution in groundwater is 155-2107 mg/L, and the TH is 58.25-978.64 mg/L (Fig. 3, Table 8). The TDS of the surface water is greater than that of the groundwater,

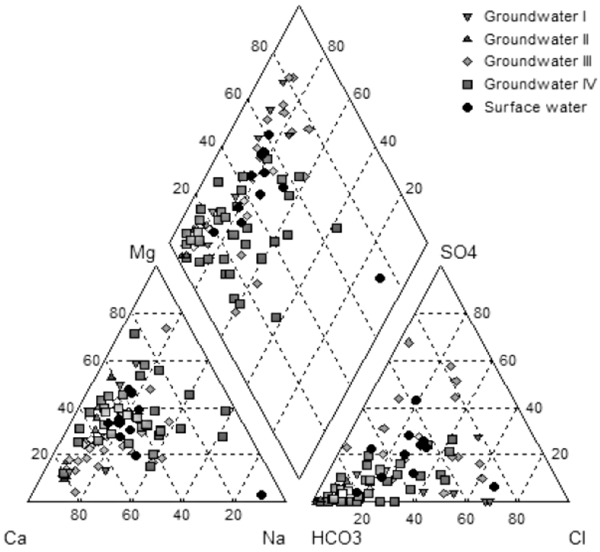

Fig. 4. Piper plot of analyzed surface water and groundwater in this region. Groundwater I controls the area between the Linjiang Bridge and Songhuajiang Village section, Groundwater II controls the area between the South Hill Section and Songhuajiang Village section, Groundwater III controls the area between the South Hill Section and Zhenjiangkou section, and Groundwater IV controls the area below Zhenjiangkou Section. The site of each section is illustrated in Fig. 1.

whereas the TH is less than the distribution of groundwater. It is speculated that surface water is more affected by effluent discharge than groundwater.

The concentration of chloride ions in the surface water sampling point (in Fig. 1d) in the eastern part of Da'an City is as high as 801.79 mg/L. The sampling point is located in the lower reaches of the second Songhua River, and the TDS index concentration is as high as 2979 mg/L. According to the "Environmental Quality Standards for Surface Water" (GB3838-2002), the COD_{Mn} and DBS indicators of the sampling point are 192.5 times and 1.5 times that of the standard value of class III, respectively, and the concentrations of the remaining indicators are the maximum values (beyond the Class III standard limit) in almost all the surface water sampling points. In particular, the high arsenic and high fluorine problems are more serious. The location of the sampling point is in the arid saline-alkali area of the study area, and the water temperature at the time of sampling was 30.6ºC, which may explain the problem. The concentration of each indicator of the surface water sample is concentrated by evaporation. These results show that the water problem in the lower reaches of the Second Songhua River is more serious.

Hydrogeochemical facies are helpful to find the chemical characteristics of water with respect to cation-anion pairs. These are masses of water that have various hydrogeochemical characteristics. The chemical differences between the surface water and the groundwater were illustrated using Piper Trillinear diagrams, shown in Fig. 4.

The Piper plot of the surface water points in the study area (Fig. 4), revealing that four of the samples were Ca-Mg-HCO_3, while of the remaining seven water points, four are Mg-Ca-HCO_3, and three are Mg-Na–HCO_3, Na-Mg-HCO_3, and Na-Cl, respectively. The Piper plot of the regional groundwater point reveals that the 76 sampling points are dominated by Ca-HCO_3, Ca-Mg-HCO_3, and Ca-Na-HCO_3-type water, followed by Ca-Na-Cl, Ca-HCO_3, and Ca-Mg-Cl, Ca-Na-HCO_3, and other scatter distributions.

According to the main water chemistry characteristics in the study area revealed by the Piper three-line diagram (Fig. 4), the main cations in the water samples are Ca^{2+} and Mg^{2+}, and the anion is mainly HCO_3^-, the distribution of HCO_3-Ca and HCO_3-Na. Ca type water accounts for more than 60% of the total (Fig. 5).

Isotopic Hydrology Analysis

The isotopic composition measurements for the surface water and the groundwater were plotted in Fig. 6. The $\delta^{18}O$ and δD isotopic composition measurements of the surface water (Table 9) ranged from –11.80‰ to –5.44‰ with a mean of –9.76‰, and from –81.98‰ to –51.63‰ with a mean of –72.58‰, respectively. The $\delta^{18}O$ and δD isotopic composition measurements of the groundwater (Table 9) ranged from –10.50‰ to –9.30‰ with a mean of –9.94‰, and from –77.50‰ to –69.30‰ with a mean of –73.16‰, respectively.

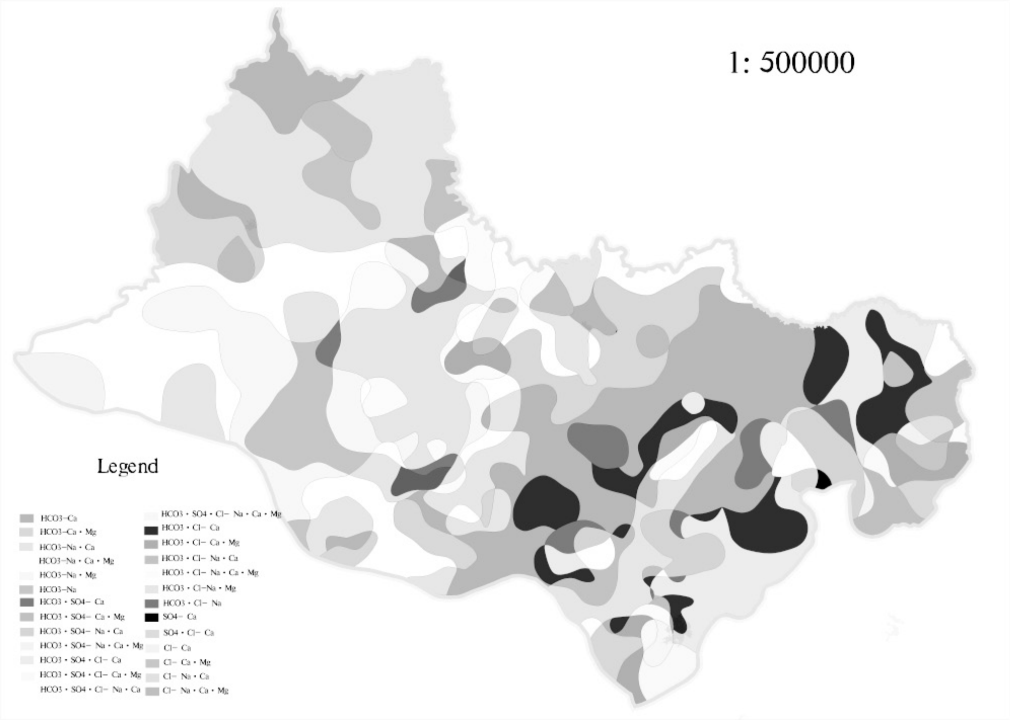

Fig. 5. Each code on the map corresponds to the phreatic water environment unit and the corresponding lithology distribution, and the map of the study area showing hydrogeochemical types.

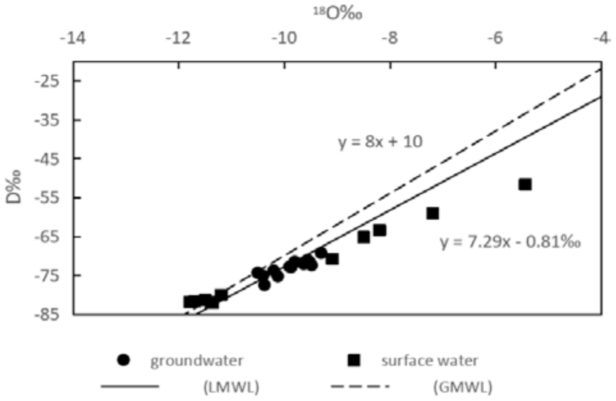

Fig. 6. Line of regression between oxygen-18 and deuterium for the LMWL, GWML, surface water, and groundwater in the study area. The data of LMWL was from the paper written by WEI Wen, CHEN Zongyu, in 2017 [28].

From the plot (Fig. 6), the isotopic content of the groundwater in the study area is distributed on the atmospheric precipitation line, indicating that the groundwater is recharged by atmospheric precipitation, and the isotopic content of the surface water is distributed between the local atmospheric precipitation line and the global atmospheric precipitation line. Compared with the groundwater point deviation, the isotope content of some surface waters is enriched due to evaporation, but most of them are depleted because of the recharge of groundwater. From the distribution of surface water and groundwater isotope content, the scope of the surface water is larger than that of groundwater, and the isotope content of the groundwater is more concentrated and stable. This shows that the recharge source of the groundwater is relatively stable, which is atmospheric precipitation infiltration and surface water. The exposed surface also has stronger evaporation than the groundwater. As a result, the isotopic content of surface water is less concentrated and less stable than that of groundwater [27-28].

In this study, however, stable isotopes were adapted to aid in the identification and the origin of dissolved ions in the rivers and hand-dug wells of the study area. The calculation results of the multisource mass balance model showed that the contribution of the groundwater to surface water recharge is 44.78% and the contribution of precipitation to groundwater recharge is 43.87%.

In Fig. 7 we observed that the nitrate concentration for the surface water and groundwater in areas II and III of the groundwater were elevated, indicating anthropogenic sources in the middle watershed of the region.

Additionally, from the plot it was observed that the recharge zone and runoff zone of the groundwater are located downstream of surface water, and the discharge zone is located upstream of surface water. The oxygen-18 isotope distribution in the downstream area is more dispersed, and in the upstream area is more concentrated, suggesting that the water supply sources in the groundwater recharge and runoff areas are more complex and diverse, while the water source in the excretory area is simpler and more stable.

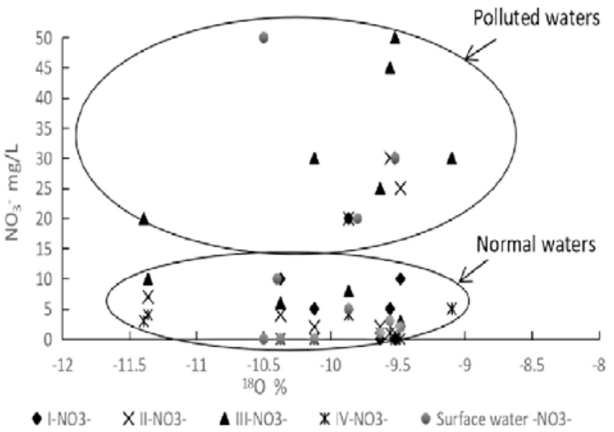

Fig. 7. Scatter plot of oxygen-18 and nitrate concentration of the surface water and groundwater in the region. Groundwater I controls the area between the Linjiang Bridge and Songhuajiang Village section, Groundwater II controls the area between the South Hill Section and Songhuajiang Village section, Groundwater III controls the area between the South Hill Section and Zhenjiangkou section, and Groundwater IV controls the area below Zhenjiangkou section. The site of each section is illustrated in Fig. 1.

CA and PCA Analysis

Factor analysis statistical methods can help identify regional water quality problems caused by natural and human activities [28-30]. This study used two methods in combination. The Varimax rotated factor loading for the surface water is presented in Fig. 8 and Table 10. Extract five principal components with eigenvalues greater than 1. For Factor 1, the information includes 43.836% of all variables, including Ca^{2+}, K, Na, Cl, SO_4^{2-}, HCO_3^-, F, SiO_2, Cu, As, and I, and a total of 12 parameters, between K, Na, HCO_3^-, and SiO_2. High loading implies silicate weathering, high scores for Ca^{2+}, K, Na, SO_4^{2-}, and HCO_3^- means carbonate mineral dissolution, and high loading between Ca^{2+}, K, and Na implies an ion exchange process. F, Cu, As, and I also belong to Factor 1, which contains indicators that do not reflect the impact of human activities, suggesting that they have a common source, the largest possible geochemical role, and symbiotic or simultaneous dissolution with silicate minerals.

Factor 2 controls 27.278% of the water chemistry parameters, including NO_2^-, SiO_2, Mn, Zn, Pb, Cr tot, Al, and Fe. Excluding the loading of SiO_2, which is negative, all other values are positive, suggesting that Mn, Zn, Pb, Cr tot, Al and Fe do not originate from the dissolution of silicate minerals. The high NO_2^- content indicates that the water body has been contaminated. The surface water points in the study area are located

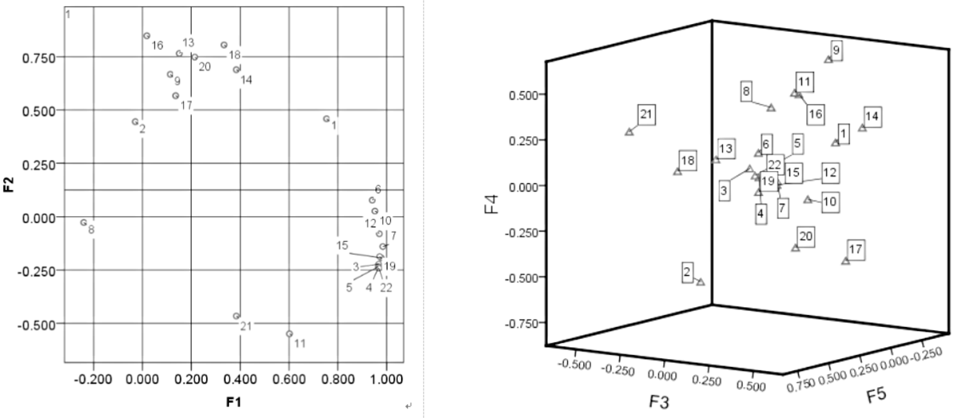

Fig. 8. PCA plot of the surface water (Rectangular, 2D, and 3D diagrams of factors; the numbers are shown in Table 5).

in the agricultural irrigation area, where discharge and withdrawal of irrigation water occurs. The surface water in the area has been affected by the application of agricultural fertilizers and pesticides, and it has begun to show signs of being contaminated. Factor 3 has a variance of about 9.091%, including Cr tot; Factor 4 has a variance of about 7.470%, including Mg, Cr tot, NO_3^-, and NO_2^-; and Factor 5 has a variance of about 7.470%, including NO_3^- and DBS. Factors 3, 4, and 5 together explain the area surface water contamination by agrochemical fertilizers, and also the effect of domestic sewage.

The Varimax rotated factor loading for the groundwater has been presented in Fig. 9 and Table 11. The extraction of eight principal components with a feature root value greater than 1. Factor 1 contains 18.948% of all variables, including Na, HCO_3^-, F, and I, suggesting the weathering and dissolution of silicate minerals in the regional groundwater. At the same time, the two indicators F and I have a common source, suggesting the symbiosis of minerals. Factor 2 controls 14.662% of the water chemistry parameters, including K, Mn, and Fe. However, there was no evidence to show that they originated from human activities. It is speculated that Mn and Fe are the influence of the region's primary geological environment. According to previous studies [31], regional water quality is affected by these two indicators. Overall, Factor 3, with a variance of about 0.919%, includes Mg, Na, and SO_4^{2+}, suggesting that Mg is from the dissolution of carbonate minerals, as well as ion exchange between Mg and Na. Factor 4, with a variance of about 8.013%, includes Pb, TCr, and Al. Factor 5, with a variance of about 6.674%, includes Ca, Cl, and NO_3^-. Factor 6, with a variance of about 5.530%, includes NO_2^- and COD_{Mn}. Factors 5 and 6 imply that the groundwater is also contaminated by agrochemical fertilizers, and its scores are relatively higher than that of the surface water, suggesting that the irrigation leakage of agricultural irrigation water is responsible for the pollution of the surface irrigation water. Factor 7, with a variance of about 4.897%, includes Cu and DBS and is relatively serious, suggesting that the groundwater is also affected by domestic sewage. We can also speculate that the Cu may be derived from human activities, in addition to natural factors.

Hydrogeology Process of the Surface Water and Groundwater

The surface water Gibbs plot [32-34] (Fig. 10a, b) for the study area indicated that the ion composition

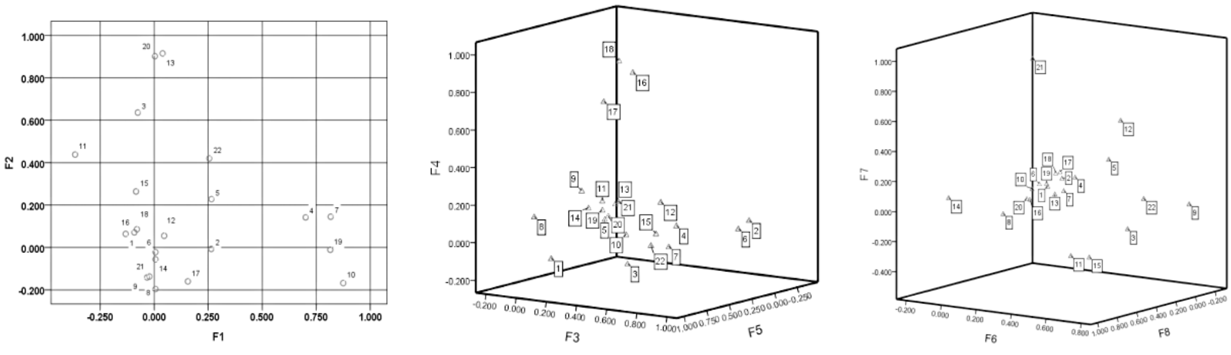

Fig. 9. PCA plot of the groundwater (Rectangular, 2D, and 3D diagrams of factors; the numbers are shown in Table 6).

for the surface water was controlled by evaporation crystallization. The groundwater Gibbs plot (Fig. 10 c, d) also revealed evaporation crystallization as the dominant process controlling the major ion composition for 96% of the groundwater samples. Only 4% were controlled by rock dominance weathering. This conclusion confirms that there is a relationship between the surface water and groundwater.

The calculated negative CAI-1 value indicates that the Cl content in the water is lower than the Na content (Na+K), and the partial Na content in the water is ion exchanged with Ca. Mg in the rock along the water flow, on the contrary, belongs to a type of anion-cation exchange reaction.

In this study, for the 11 surface water samples, the values of CAI-1 calculated at points 1, 3, 5, 6, and 8 were negative, and the rest were positive. The CAI-1 calculation results of the groundwater show that 37.5% of the groundwater points in the I zone are negative, 100% of the groundwater points in the II zone are negative, 76.9% of the groundwater points in the III zone are negative, and 94.1% of the groundwater points in the IV zone are negative. The negative CAI-1 values show that the exchange of Na+K in the water with the Ca+Mg in the rock of the water flow environment from the upper Songhuajiang village section to the downstream Zhenjiangkou section is gradually enhanced. The cation exchange effect of the tributary of the Yinma River and the downstream is particularly strong, and the cation-anion exchange type of reaction in the upper Songhuajiang village area is relatively strong.

In summary, the water chemical composition of the Second Songhua River Basin is mainly derived from evaporation crystallization, rock weathering, and ion exchange.

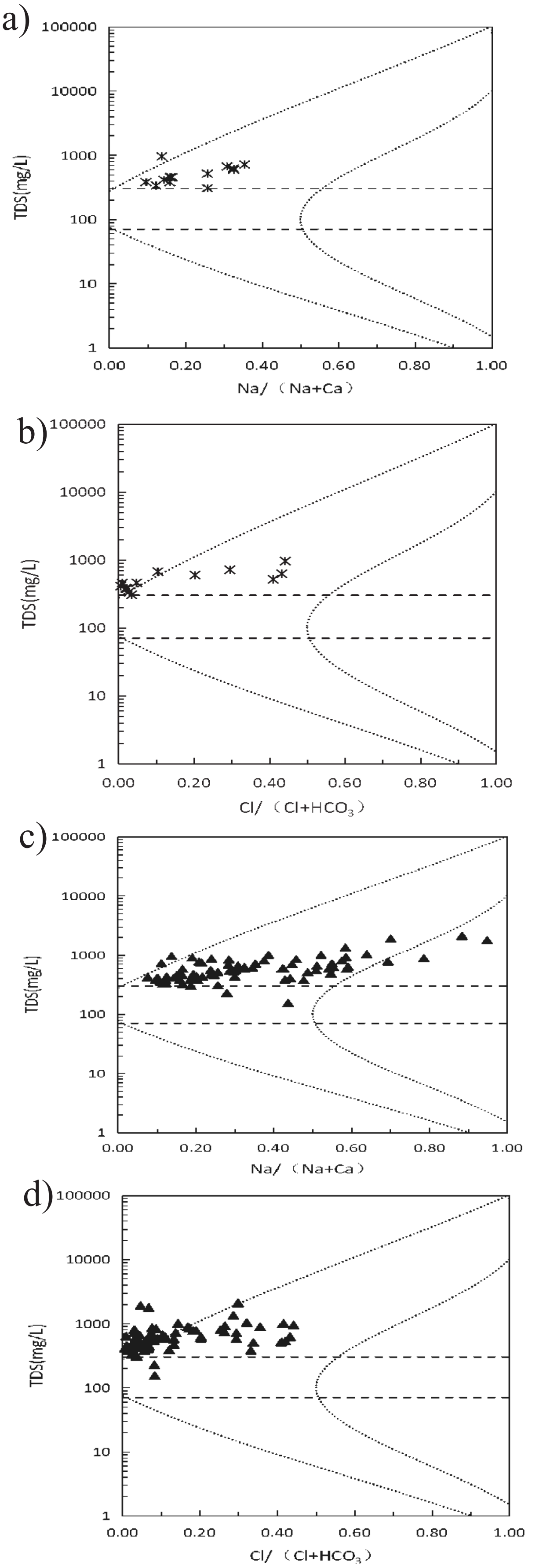

Fig. 10. Gibbs plot of the surface water (a, b) and groundwater (c, d) in the study area, showing similarities of the water sample distribution between the surface water and groundwater.

Water Quality for Irrigation

The research area has carried out a river-lake connectivity project since 2015, aiming to conduct regional surface water connectivity projects to improve the state of environment. The Songyuan Irrigation District, which is one of the more important subprojects of the project, and the project mainly uses the Second Songhua River and the surface lakes in the area for irrigation of crops. Up until now, there was also a large proportion of groundwater irrigation crops being grown to help the growth of the agricultural area in the region. Determining whether the surface and groundwater in the study area are suitable for irrigation is a major issue concerning the national economy and the people's livelihoods. However, irrigation can cause deterioration of soil permeability, soil compaction, and salinization.

The concentration of sodium is an important indicator for evaluating the suitability of water for irrigation, because sodium in the water reacts with calcium and magnesium in the soil, causing clogging of soil particles – reducing the permeability of the soil, and changing the structure of the soil. The

Table 3. Rating of water samples based on the EC and percentage of sodium, by Wilcox.

Category	Surface water n=11	%	Groundwater n=76	%
Excellent to good	11	100%	30	39%
Good to permissible	0	0%	38	50%
Permissible to doubtful	0	0%	0	0%
Doubtful to unsuitable	0	0%	8	11%
Unsuitable	0	0%	0	0%

reduced ability of the soil to maintain stability makes it compact and tightly impermeable to water, which is very detrimental to crop production. In addition, sodium combines with CO_3^{2-} to accelerate the formation of alkaline soils, and combines with Cl^- to form saline soil, neither of which are helpful for crop growth. In order to evaluate the applicability of agricultural irrigation to water bodies in the region, calculations of sodium-related parameters such as SSP, SAR, RSC, MAR, and KR were performed.

Wilcox [33] planned a method for rating waters for irrigation based on the percentage of sodium and electrical conductivity. The calculated Na% in the samples was plotted against electrical conductivity (Fig. 11). According to Wilcox, 100% of the surface water samples are allowed for agriculture purposes; 39% of the groundwater samples are "excellent to good" for agriculture purposes, 50% of the groundwater samples are "good to permissible" for agriculture purposes, and 11% of the groundwater samples are "doubtful to unsuitable" for agriculture purposes (Table 3).

SAR is an estimate of the extent to which sodium ions present in the water would be absorbed in the soil. The higher the SAR value, the greater the risk of the sodium posing a hazard to plant growth (Fig. 12)

The US Salinity Laboratory's (USSL) diagram proposed by Richards (1954) is used to investigate the sampled water, which shows that 60% of the groundwater samples are in the high salinity hazard category (C3), and 91% of the surface water samples are in the low sodium hazard category and the medium salinity hazard category.

According to Table 4, in terms of the MAR and KR indicators of surface water and groundwater in the study area, more than 90% of the surface water points and more than 86% of the groundwater points are suitable as irrigation water. In terms of the RSC indicator, more than 81% of the surface water and groundwater are good for irrigation. The SSP index calculation results show that 90.91% of the surface water points are good for irrigation, and 100% of the groundwater points are excellent for irrigation.

The SSP and KR indicators were all evaluated from the perspective of the proportion of Na^+ in the water of the study area. The MAR indicators were analyzed from the perspective of the proportion of Mg^{2+} in the water. The ratio of Na^+ content in the water was accounted for by the greater possibility of exchanging Ca^{2+} and Mg^{2+} in the soil. If such a water body is used as irrigation, the soil is more likely to form saline soil. The SAR

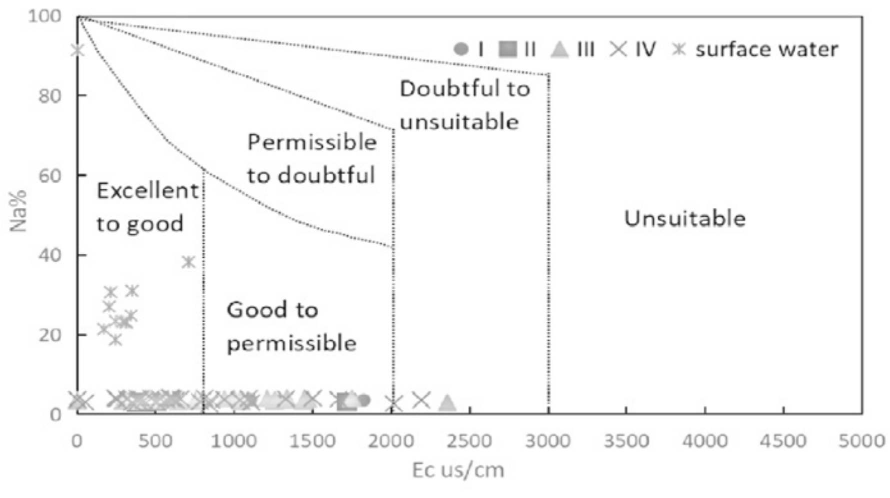

Fig. 11. Rating of surface water and groundwater samples on the basis of EC and percentage of sodium. According to EC and Na, percentage suitability can be divided into five regions, and the water samples falling in each region represent their different evaluation levels for suitability as irrigation water.

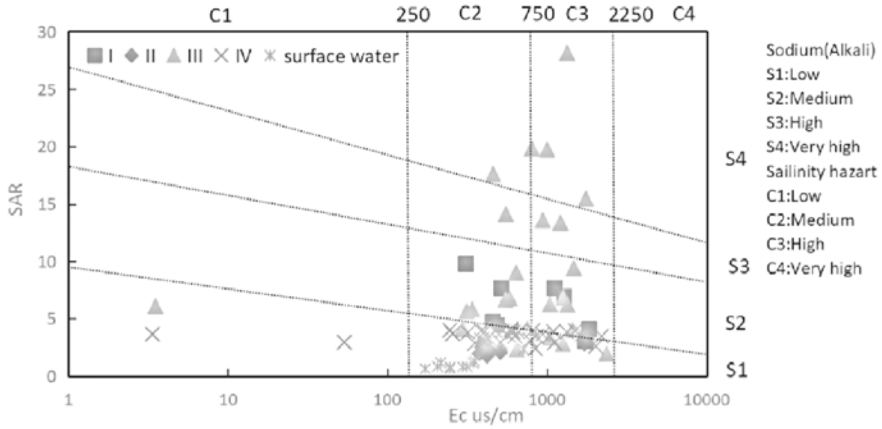

Fig. 12. US Salinity Laboratory (USSL) diagram representing the salinity and sodium hazard. According to EC and SAR, it is divided into 16 regions, and the water samples falling in each region represent different evaluation levels of the plant growth hazard for irrigation water.

Table 4. Geochemical classification of surface water and groundwater in the region. Irrigation water quality evaluation results for the surface water and groundwater using the SSP, RSC, MAR, and KR indices.

Category		Grade	n = 11/76	%	Category	Grade	n = 11/76	%
Surface water	SSP				RSC			
	Excellent	0–20	0	0.00	Good	<1.25	9	81.82
	Good	20–40	10	90.91	Medium	1.25–2.5	1	9.09
	Permissible	40–60	0	0.00	Bad	>2.5	1	9.09
	Doubtful	60–80	0	0.00	MAR			
	Unsuitable	>80	1	9.09	Suitable	<50	11	100.00
	EC (us/cm)				Unsuitable	>50	0	0.00
	Excellent	<250	6	54.55	KR			
	Good	250–750	5	45.45	Suitable	<1	10	90.91
	Permissible	750–2250	0	0.00	Unsuitable	>1	1	9.09
	Doubtful	2250–5000	0	0.00				
	Unsuitable	>5000	0	0.00				
Groundwater	SSP				RSC			
	Excellent	0–20	76	100.00	Good	<1.25	64	84.21
	Good	20–40	0	0.00	Medium	1.25–2.5	8	10.53
	Permissible	40–60	0	0.00	Bad	>2.5	4	5.26
	Doubtful	60–80	0	0.00	MAR			
	Unsuitable	>80	0	0.00	Suitable	<50	66	86.84
	EC (us/cm)				Unsuitable	>50	10	13.16
	Excellent	<250	4	5.26	KR			
	Good	250–750	39	51.32	Suitable	<1	72	94.74
	Permissible	750–2250	32	42.11	Unsuitable	>1	4	5.26
	Doubtful	2250–5000	1	1.32				
	Unsuitable	>5000	0	0.00				

Table 5. Part of chemical compositions of surface water samples.

ID	Sample ID	Water temper (ºC)	PH	Turbidity/NTU	EC us/cm	Eh/mv	DO/mg/L	TH/mg/L	TDS/mg/L
1	2012101705	8.5	8.44	125.6	205.8	115.1	10.49	79.26	168
2	2012101805	8.9	8.94	20.5	247	132.8	11.92	114.93	204
3	2012102006	8.1	8.41	117.5	215.7	125.2	17.25	103.04	261
4	2013080908	30.6	8.4	17.6	4.23	-27.6	0.21	184.11	2979
5	2013103004	7	8.15	17.2	345	-19.5	5.3	149.06	312
6	2013103103	9	8.24	46.2	246	71	6.15	109.6	221
7	2014070113	20	8.44	195	314	82.5	9.26	124.27	242
8	2014070601	18.8	7.97	40.5	172.4	152	8.29	89.32	227
9	2014071301	24.4	7.57	16.2	352	86.1	8.5	120.39	282
10	2014071305	25.4	8.59	10.6	295	183.3	9.35	112.62	230
11	2014071704	17	7.54	34.5	712	97.9	4.44	201.94	528

Table 6. Part of chemical compositions of groundwater samples.

Subarea	ID	Sample ID	Water temper (ºC)	PH	Turbidity/ NTU	EC us/cm	Eh/mv	DO/mg/L	TH/mg/L	TDS/mg/L
I	1	2014070401	11.8	6.8	2.3	1826	90.5	9.02	135.92	306
I	2	2014070402	11.2	7.39	2	1728	204.5	7.75	233.01	457
I	3	2014070406	8.5	7	0.4	1105	190	4.08	361.16	666
I	4	2014070503	12.6	7.22	1.5	1268	34	7.42	388.35	716
I	5	2014070511	10.9	6.81	2.7	515	165.6	6.77	279.61	593
I	6	2014070602	11.4	7.39	1.9	457	96.8	3.6	306.8	515
I	7	2014070608	11	7.16	2.6	309	-36.5	3.99	310.68	625
I	8	2014070611	10.8	7.2	2.2	481	130.6	4.56	563.11	957
II	9	2012091508	8	7.07	1.9	1715	162.3	2.99	222.38	454
II	10	2012091509	8.3	7.58	13.1	432	13.8	4.6	218.96	412
II	11	2012091510	8	7.63	8.5	420	121.6	2.79	205.27	379
II	12	2012091511	6.9	8.1	3.1	426	11.6	2.15	212.11	379
II	13	2012091610	7.5	7.12	10.3	509	185.1	21.7	174.48	334
II	14	2012091612	8.3	7.1	7.8	377	159.2	13.98	215.53	410
II	15	2012101704	8.2	8.07	7.6	404	127.5	5.35	126.82	299
II	16	2012101707	8.3	7.73	5	392	151.2	41.85	214.01	429
III	17	2014070108	8.5	6.6	0.2	1337	100.5	3.3	388.35	1032
III	18	2014070201	11.6	6.68	3.1	459	172.9	5.94	520.39	1004
III	19	2014070204	8.7	7.12	2.7	3.51	1116	8.54	419.42	775
III	20	2014070206	9	7.44	0.5	549	-35	4.01	310.68	531
III	21	2014070207	8.5	6.66	5.4	1212	185.3	7.73	221.36	509
III	22	2014070306	10.1	7.24	3	940	-21.3	3.98	427.18	1004
III	23	2014070312	9.5	7.54	1.8	1443	614.5	9.88	213.59	379
III	24	2014071105	11.3	7.24	2.1	1043	161.2	7.17	58.25	155
III	25	2014071106	8.5	6.9	10.8	1471	250.3	6.82	194.17	386

Table 6. Continued.

III	26	2014071107	12.1	7.8	1.9	1000	84	8.88	174.76	636
III	27	2014071109	20	8.44	195	314	82.5	9.26	291.26	562
III	28	2014071205	8.6	6.94	2.8	339	183.3	6.75	539.8	895
III	29	2014071207	8.5	6.55	1.2	644	213	7.58	182.52	378
III	30	2014071211	11.6	7.61	2.1	584	68	6.08	240.78	540
III	31	2014071212	8.5	7.22	1.2	1048	208	8.34	256.31	474
III	32	2014071214	8.5	6.78	4.5	1256	132.2	5.64	155.34	320
III	33	2014071307	10.1	7.89	2.4	753	159.2	10.89	322.33	582
III	34	2014071504	13.6	7.82	3.2	1342	134.4	6.7	326.21	682
III	35	2014071509	12.1	7.45	1.7	2360	181.1	10.26	186.41	727
III	36	2014071510	11.3	7.22	2.6	1752	219.3	8.29	143.69	483
III	37	2014071604	25.4	8.59	10.6	295	183.3	9.35	225.24	441
III	38	2014071611	10.9	7.82	2.1	640	158	4.06	388.35	835
III	39	2014071612	9.8	7.9	2.1	435	206	9.6	100.97	227
III	40	2014071613	10.5	7.7	1.7	1262	172.6	10.34	407.77	741
III	41	2014071616	8.5	6.78	1.7	803	-62.2	4.37	978.64	1892
III	42	2014071618	10.5	7.76	2.2	552	163.1	9.36	365.05	844
IV	43	2012091507	11.9	7.44	93.7	784	-111	2.83	201.85	380
IV	44	2012091901	8.2	7.79	9.8	386	-152.8	2.1	253.23	807
IV	45	2012091907	8.3	7.56	11.8	940	149.4	4.01	297.71	610
IV	46	2012092001	9.7	7.53	18.5	1038	-92	2.98	188.21	430
IV	47	2012092003	10.1	7.84	9.9	570	-141.1	2.55	239.54	550
IV	48	2012092401	6.1	8.58	8.5	629	161.2	5.49	287.38	545
IV	49	2012092406	10.5	7.78	43	1331	68	6.47	136.85	374
IV	50	2012092502	9.4	8.19	11.8	660	-72.9	3.43	256.59	585
IV	51	2012092508	7.6	8.79	7	256	177.5	11.09	390.01	808
IV	52	2012092602	7.9	7.52	8.8	473	4.2	10.56	229.22	720
IV	53	2012092606	9.5	7.8	27.9	246	-29.6	4.25	225.79	775
IV	54	2012101009	8.6	8.52	1.9	597	2	6.32	297.24	890
IV	55	2012101115	9	9.07	10.8	404	166.1	10.69	202.12	549
IV	56	2012101204	8	8.22	14.5	596	179.2	6.3	344.8	1785
IV	57	2012102004	8	8.57	3.2	353	184.2	8.59	174.38	327
IV	58	2012102009	6.9	8.26	3.4	319	146.8	12.09	158.53	404
IV	59	2012102011	6.1	7.84	11.6	599	59.2	7.65	269.5	622
IV	60	2012102410	8	8.67	8.1	426	99.5	11.17	229.87	432
IV	61	2012102412	11.7	7.65	9.9	1503	68.9	3.53	356.69	920
IV	62	2012102501	7.5	8.35	10.3	814	129.3	36.5	190.24	592
IV	63	2012102515	8.7	7.99	4.2	2194	132.2	3.84	229.87	468
IV	64	2012102603	8.8	8.21	36.5	1095	35.1	3.83	253.65	657
IV	65	2012102605	8.1	7.78	9.7	53.6	105.3	3.06	253.65	453

Table 6. Continued.

IV	66	2012103103	12	8.18	4.7	2019	116	3.34	231.03	413
IV	67	2012103109	8	8	11.9	390	-91.6	4.33	259.91	474
IV	68	2012103115	8.6	7.29	30.2	1665	31.8	16.62	276.41	580
IV	69	2012110101	8.1	7.94	18.3	854	25.3	13.19	466.18	862
IV	70	2012110103	11	7.96	6.3	844	10.3	4.7	239.28	413
IV	71	2012110115	8.2	7.32	16.3	1111	41.8	6.42	198.02	356
IV	72	2013080504	8.5	7.43	13	529	88.5	30.5	504.18	1337
IV	73	2013080511	8.1	7.26	21.1	615	68.8	11.25	263.05	587
IV	74	2013080604	12.4	8.11	1.3	3.36	-82.3	2.03	341.97	692
IV	75	2013080610	8	7.96	15.3	509	85.1	14.15	263.05	460
IV	76	2013080701	8.1	7.41	9.9	594	94.4	25.9	439.65	2107

Table 7. Statistics of the measured parameters for collected surface water samples

Parameters	Unit	Minimum	Maximum	Mean	Std.Deviation	Coefficient of variation (%)
Water temper (ºC)	(ºC)	7.00	30.60	16.15	8.34	51.63
PH	_	7.54	8.94	8.24	0.42	5.10
Turbidity	NTU	10.60	195.00	58.31	60.48	103.72
EC	us/cm	4.23	712.00	282.65	172.29	60.96
Eh	mv	-27.60	183.30	90.80	65.24	71.85
DO	mg/L	0.21	17.25	8.50	4.58	53.91
TH	mg/L	79.26	201.94	126.23	37.86	30.00
TDS	mg/L	168.00	2979.00	514.00	823.03	160.12
Ca^{2+}	mg/L	20.22	65.32	35.10	14.84	42.28
Mg^{2+}	mg/L	4.81	13.21	9.23	2.14	23.23
K^+	mg/L	1.29	39.83	6.57	11.11	169.16
Na^+	mg/L	9.66	865.50	96.08	255.49	265.91
Cl^-	mg/L	8.86	801.79	91.98	235.84	256.40
SO_4^{2-}	mg/L	4.21	138.37	41.45	37.09	89.49
HCO_3^-	mg/L	63.88	915.70	200.24	242.24	120.98
NO_3^-	mg/L	0.00	50.00	11.00	16.15	146.81
NO_2^-	mg/L	0.00	0.70	0.09	0.20	225.86
F^-	mg/L	0.24	1.66	0.57	0.41	70.58
SiO_2	mg/L	3.99	30.08	14.79	7.06	47.73
COD_{Mn}	mg/L	1.94	29.66	5.27	8.11	153.83
Cu	ug/L	0.00	48.40	9.37	13.51	144.14
Mn	ug/L	70.00	480.00	200.91	159.90	79.59
Zn	ug/L	1.90	49.30	18.30	14.32	78.26
As	ug/L	0.90	91.60	11.49	26.74	232.75
Pb	ug/L	0.80	11.10	3.89	2.95	75.76
Cd	ug/L	0.00	0.20	0.03	0.06	237.11

Table 7. Continued.

T-Cr	ug/L	0.60	17.90	6.79	6.11	90.02
Al	ug/L	121.20	3430.00	1081.95	1099.45	101.62
I^-	ug/L	0.00	71.00	11.91	19.95	167.54
Fe	ug/L	130.00	2340.00	1120.91	703.38	62.75
DBS	ug/L	14.00	39.00	24.86	8.57	34.46

Table 8. Statistics of the measured parameters for the collected groundwater samples of four aquifer sub-areas, I, II, III, IV.

I-Parameters	Unit	Minimum	Maximum	Mean	Std. Deviation	Coefficient of variation(%)
Water temper (ºC)	(ºC)	8.50	12.60	11.03	1.18	10.67
PH	_	6.80	7.39	7.12	0.23	3.26
Turbidity	NTU	0.40	2.70	1.95	0.73	37.68
EC	us/cm	309.00	1826.00	961.13	604.74	62.92
Eh	mv	-36.50	204.50	109.44	81.62	74.58
DO	mg/L	3.60	9.02	5.90	2.08	35.25
TH	mg/L	135.92	563.11	322.33	124.65	38.67
TDS	mg/L	306.00	957.00	604.38	192.68	31.88
Ca^{2+}	mg/L	41.99	205.29	93.51	49.44	52.87
Mg^{2+}	mg/L	7.55	51.90	21.59	15.36	71.16
K^+	mg/L	0.55	3.14	1.56	0.86	55.48
Na^+	mg/L	14.22	53.27	32.34	13.82	42.75
Cl^-	mg/L	7.09	186.12	98.82	71.47	72.32
SO_4^{2-}	mg/L	0.00	167.42	35.38	55.64	157.29
HCO_3^-	mg/L	191.64	371.66	271.49	68.97	25.41
NO_3^-	mg/L	0.00	110.00	20.00	36.94	184.68
NO_2^-	mg/L	0.00	0.60	0.16	0.20	128.37
F^-	mg/L	0.26	0.57	0.41	0.10	25.52
SiO_2	mg/L	24.70	53.29	34.06	9.65	28.34
CODmn	mg/L	1.30	18.60	4.80	5.73	119.30
Cu	ug/L	0.00	3610.00	1030.00	1148.58	111.51
Mn	ug/L	3.20	33.70	16.44	10.00	60.85
Zn	ug/L	0.70	24.20	8.99	8.73	97.09
As	ug/L	0.00	4.60	1.89	1.59	84.03
Pb	ug/L	1.90	6.70	3.74	1.56	41.87
T-Cr	ug/L	126.40	1111.00	299.54	333.49	111.33
Al	ug/L	2.00	14.00	6.63	3.54	53.48
I^-	ug/L	70.00	3580.00	1478.75	1371.27	92.73
Fe	ug/L	14.30	29.80	22.99	5.67	24.65
DBS	ug/L	0.65	3.31	1.46	0.81	55.32

Table 8. Continued.

II-Parameters	Unit	Minimum	Maximum	Mean	Std.Deviation	coefficient of variation(%)
Water temper (ºC)	(ºC)	6.90	8.30	7.94	0.50	6.28
PH	_	7.07	8.10	7.55	0.42	5.55
Turbidity	NTU	1.90	13.10	7.16	3.71	51.80
EC	us/cm	377.00	1715.00	584.38	458.55	78.47
Eh	mv	11.60	185.10	116.54	67.11	57.59
DO	mg/L	2.15	41.85	11.93	13.89	116.49
TH	mg/L	126.82	222.38	198.70	32.66	16.44
TDS	mg/L	299.00	454.00	387.00	50.83	13.14
Ca2+	mg/L	46.03	79.45	63.44	13.00	20.49
Mg2+	mg/L	2.48	22.43	9.87	7.28	73.75
K+	mg/L	0.58	2.26	1.39	0.69	49.43
Na+	mg/L	7.76	12.66	9.80	1.67	17.08
Cl-	mg/L	1.77	10.55	5.52	2.55	46.26
SO42-	mg/L	0.00	11.41	3.63	4.87	134.19
HCO3-	mg/L	177.88	312.93	245.40	46.48	18.94
NO3-	mg/L	1.00	30.00	11.38	11.73	103.16
NO2-	mg/L	0.00	0.04	0.01	0.01	194.26
F-	mg/L	0.34	0.86	0.58	0.16	26.95
SiO2	mg/L	27.04	63.57	35.85	12.10	33.75
CODmn	mg/L	0.10	6.40	1.11	2.15	192.81
Cu	ug/L	0.00	770.00	305.00	302.18	99.08
Mn	ug/L	0.30	3.90	2.06	1.36	65.76
Zn	ug/L	0.00	47.60	10.00	16.57	165.73
As	ug/L	0.00	0.70	0.33	0.32	96.95
Pb	ug/L	0.00	5.00	1.53	1.96	128.72
T-Cr	ug/L	0.00	14.90	4.86	5.09	104.62
Al	ug/L	0.00	18.00	4.13	6.56	158.94
I-	ug/L	20.00	2130.00	665.00	817.40	122.92
Fe	ug/L	9.00	46.00	20.50	11.55	56.35
DBS	ug/L	0.24	1.06	0.60	0.28	46.93
III-Parameters	Unit	Minimum	Maximum	Mean	Std.Deviation	Coefficient of variation(%)
Water temper (ºC)	(ºC)	8.50	25.40	12.38	3.81	30.79
PH	_	6.55	8.59	7.65	0.55	7.22
Turbidity	NTU	0.20	195.00	3.09	37.75	1222.67
EC	us/cm	3.51	2360.00	1012.38	529.65	52.32
Eh	mv	-62.20	1116.00	152.65	224.35	146.97
DO	mg/L	3.30	10.89	8.20	2.24	27.26
TH	mg/L	58.25	978.64	349.52	184.32	52.74
TDS	mg/L	155.00	1892.00	773.75	347.13	44.86

Table 8. Continued.

Ca2+	mg/L	18.66	172.63	84.57	38.33	45.33
Mg2+	mg/L	2.83	196.27	33.99	37.91	111.54
K+	mg/L	0.26	2.80	0.82	0.66	79.87
Na+	mg/L	8.15	161.30	54.35	42.33	77.89
Cl-	mg/L	3.55	248.16	39.77	60.48	152.07
SO42-	mg/L	0.00	846.07	143.03	169.68	118.63
HCO3-	mg/L	63.88	569.11	322.66	129.59	40.16
NO3-	mg/L	3.00	100.00	35.63	24.75	69.46
NO2-	mg/L	0.00	0.04	0.00	0.01	227.10
F-	mg/L	0.28	1.56	0.76	0.30	39.97
SiO2	mg/L	15.57	67.99	25.04	12.74	50.87
CODmn	mg/L	0.50	7.70	3.20	2.17	67.73
Cu	ug/L	0.00	2760.00	307.50	675.36	219.63
Mn	ug/L	4.50	1012.00	168.29	196.54	116.79
Zn	ug/L	0.20	39.10	4.45	8.71	195.79
As	ug/L	0.70	13.60	4.48	2.95	65.97
Pb	ug/L	0.90	12.80	3.48	3.00	86.33
T-Cr	ug/L	70.10	1788.00	363.35	326.45	89.85
Al	ug/L	0.00	21.00	5.63	5.52	98.05
I-	ug/L	20.00	12210.00	778.75	3017.30	387.45
Fe	ug/L	14.10	33.70	21.86	5.52	25.25
DBS	ug/L	0.56	2.18	0.81	0.39	48.24
IV-Parameters	Unit	Minimum	Maximum	Mean	Std. Deviation	Coefficient of variation(%)
Water temper (ºC)	(ºC)	6.10	12.40	8.81	1.56	17.75
PH	_	7.26	9.07	7.97	0.46	5.77
Turbidity	NTU	1.30	93.70	15.39	16.73	108.74
EC	us/cm	3.36	2194.00	747.06	509.08	68.14
Eh	mv	-152.80	184.20	48.73	97.65	200.38
DO	mg/L	2.03	36.50	8.88	8.09	91.11
TH	mg/L	136.85	504.18	269.11	84.36	31.35
TDS	mg/L	327.00	2107.00	675.41	385.58	57.09
Ca2+	mg/L	20.63	137.05	65.85	23.89	36.28
Mg2+	mg/L	4.01	71.20	25.31	15.73	62.16
K+	mg/L	0.36	2.80	1.31	0.76	58.08
Na+	mg/L	6.19	508.50	75.01	104.49	139.31
Cl-	mg/L	3.55	319.05	51.87	66.79	128.74
SO42-	mg/L	0.00	378.67	40.16	71.00	176.78
HCO3-	mg/L	204.23	1083.73	384.14	166.88	43.44
NO3-	mg/L	0.00	50.00	9.38	13.68	145.76
NO2-	mg/L	0.00	0.20	0.01	0.04	289.81

Table 8. Continued.

F-	mg/L	0.34	8.49	1.34	1.43	106.02
SiO2	mg/L	10.69	55.28	27.82	12.81	46.05
CODmn	mg/L	0.00	33.40	3.02	7.30	241.39
Cu	ug/L	0.00	7840.00	819.12	1514.42	184.88
Mn	ug/L	0.00	73.80	7.07	13.05	184.63
Zn	ug/L	0.00	78.20	8.83	16.32	184.76
As	ug/L	0.00	5.30	0.68	1.18	172.44
Pb	ug/L	0.00	18.20	1.92	3.56	185.12
T-Cr	ug/L	0.40	401.60	33.48	81.98	244.90
Al	ug/L	0.00	92.00	13.09	22.85	174.60
I-	ug/L	10.00	48930.00	4807.65	12451.21	258.99
Fe	ug/L	10.00	49.90	24.96	9.65	38.66
DBS	ug/L	0.25	3.28	1.18	0.75	63.65

Table 9. Isotopic compositions of water samples collected in the Second Songhua River Basin.

	ID	Sample ID	Processed Delta 2H/‰	Processed Delta 18O/‰
Groundwater samples	1	DX1	-71.57	-9.52
	2	DX2	-75.29	-10.12
	3	DX3	-72.45	-9.48
	4	DX4	-77.5	-10.37
	8	DXJJ	-71.06	-9.56
	9	DXSHJ	-72.92	-9.87
	10	DXQY	-72.14	-9.63
	11	ES16	-74.4	-10.5
	12	ES14	-71.5	-9.8
	13	ES12	-74.4	-10.5
	14	ES10	-75.1	-10.4
	15	ES08	-72.8	-9.9
	16	ES02	-73.8	-10.2
	17	ES05	-69.3	-9.3
Surface water samples	18	DBP3	-81.98	-11.36
	19	DBQY	-70.76	-9.1
	20	DBSHJ	-81.91	-11.39
	21	DBJJ	-51.63	-5.44
	22	ES15	-81.8	-11.8
	23	ES13	-81.6	-11.7
	24	ES11	-81.3	-11.5
	25	ES07	-80	-11.2
	26	ES04	-63.3	-8.2
	27	ES06	-65.1	-8.5
	28	ES03	-59	-7.2

Table 10. Results of factor analysis after varimaxa rotation for surface water.

Indicators	Factors				
	1	2	3	4	5
Ca^{2+}	.754	.459	.085	.107	-.386
Mg^{2+}	-.029	.445	-.368	-.635	.051
K	.967	-.222	-.101	.014	.038
Na	.966	-.240	-.041	-.026	.050
Cl	.966	-.234	-.061	-.017	.052
SO_4^{2-}	.941	.077	-.043	.109	.051
HCO_3^-	.984	-.140	-.012	-.062	-.058
NO_3^-	-.240	-.027	.443	.515	.643
NO_2^-	.114	.667	.053	.561	-.375
F	.952	.026	.117	-.155	-.118
S_iO_2	.602	-.549	.159	.462	.049
Cu	.970	-.080	.031	-.066	.006
Mn	.151	.765	-.288	.043	.043
Zn	.384	.689	.486	.296	-.029
As	.978	-.193	-.040	-.015	.025
Pb	.018	.848	.066	.414	-.119
TCr	.136	.567	.584	-.375	.244
Al	.334	.805	-.364	.003	.243
I	.971	-.187	-.066	-.114	.017
Fe	.214	.748	.306	-.335	.251
DBS	.384	-.466	-.437	.259	.527
CODmn	.968	-.241	-.013	-.012	.042
Eigenvalue	11.397	7.092	2.364	1.942	1.313
% of variance	43.836	27.278	9.091	7.470	5.049
Cumulative %	43.836	71.114	80.205	87.675	92.724

Extraction method: principal component analysis (PCA)
Rotation method: orthogonal rotation method with Kaiser standardization.
a: Rotation converges after the 9 iteration.

Table 11. Results of factor analysis after varimaxa rotation for groundwater.

	Factors							
	1	2	3	4	5	6	7	8
Ca^{2+}	-.132	.064	.098	-.077	.853	.028	.027	.032
Mg^{2+}	.264	-.007	.860	.089	-.062	.068	.075	-.043
K	-.076	.636	.150	-.194	.096	.429	-.212	-.068
Na	.701	.142	.505	.051	.149	.105	.076	-.110
Cl	.265	.228	.312	.124	.619	.228	.191	-.234
SO_4^{2-}	.006	-.022	.929	.080	.171	-.057	.020	-.035
HCO_3	.817	.145	.382	-.088	.028	.122	.014	.036
NO_3^-	.006	-.196	-.080	.113	.744	-.082	-.127	.290
NO_2^-	-.033	-.141	-.169	.159	.071	.716	-.023	-.184
F	.875	-.168	.023	-.076	-.100	.000	.026	.142

Table 11. Continued.

SiO_2	-.366	.438	-.136	.087	-.102	.044	-.468	-.176
Cu	.046	.055	.343	.148	.052	.490	.551	.112
Mn	.039	.915	.014	.101	.004	.050	-.026	-.002
Zn	.006	-.056	-.083	.085	.139	-.088	.073	.836
As	-.084	.264	.101	-.088	-.299	.412	-.340	.293
Pb	-.092	.071	.062	.791	-.108	.027	-.028	.213
TCr	.156	-.160	.105	.689	.284	.009	.093	-.129
Al	-.080	.086	.029	.861	-.012	.048	.111	-.014
I	.815	-.011	-.087	.054	-.021	-.064	.006	-.121
Fe	.003	.902	-.060	.024	-.040	-.115	-.083	-.010
DBS	-.022	-.137	.000	.106	-.051	-.076	.858	.000
COD	.255	.420	.226	-.105	-.035	.575	.028	.028
Eigenvalue	4.169	3.226	2.402	1.763	1.468	1.217	1.077	1.049
% of variance	18.948	14.662	10.919	8.013	6.674	5.530	4.897	4.768
Cumulative %	18.948	33.610	44.529	52.542	59.216	64.746	69.643	74.411

Extraction method: principal component analysis (PCA).
Rotation method: orthogonal rotation method with Kaiser standardization.
a: Rotation converges after the 9 iteration.

and RSC indicators can be used to estimate the amount of Na^+ adsorbed by soil and the amount of HCO_3^- and CO_3^{2-} that can be combined with Na^+ in the water. That is to say, if water with both indicators higher than the standard limit is used as irrigation water, the risk of salt and alkaline soil formation is increased. Based on the above analysis, combined with the SSP, KR, and MAR calculation results, if the Second Songhua River Basin downstream water (including both the surface water and groundwater) is used as irrigation water, the saline soil and saline-alkali soil will easily be produced. That is, the downstream water body is not suitable as irrigation water. Under the background of the connecting project of the West River and lake in Jilin, and the greatly increasing irrigation area, it is necessary to use certain treatment measures for the water before it is used for irrigation. Otherwise, salinization of the soil will occur, which will affect the crop yields and damage the state of the environment.

Conclusions

Based on the above research, the following three conclusions are drawn:

1. The research of isotope content indicated that the groundwater recharge source was relatively stable. The surface water received atmospheric precipitation and groundwater recharge, while groundwater was recharged by atmospheric precipitation. The overall environment of the area was alkaline. A total of 92% of the surface water and groundwater TDS was less than 1 g per liter, making it weak mineralized water. The dominant water types of the surface and groundwater were Ca-HCO_3 and Ca-Mg-HCO_3.
2. The Gibbs plot, CAI-1 index, and Varimax rotated factor loading for the water showed that silicate weathering, carbonate mineral dissolution, and the ion exchange process controlled the hydro-chemistry compositions. The high NO_2^- score and the middle DBS score showed that the water body has begun to be contaminated by agriculture, and was also affected by domestic sewage.
3. The indicator calculation results of the SSP, MAR and KR showed that the surface water and groundwater in the study area could be used for irrigation, while the water downstream of the basin may accelerate the formation of alkaline and saline soil if used for irrigation. Under the background of the connecting project of the West River and lake in Jilin, and the greatly increasing irrigation area, it is necessary to use certain treatment measures for the downstream water before it is used for irrigation. Otherwise, salinization of the soil will be caused, which will affect crop yields and damage the state of the environment.

Acknowledgements

This research was funded by the National Key R&D Program lof China, grant number 2018YFC1800400.

Supported by National Natural Science Foundation of China (41072255, 41807155) and Natural Science Foundation of Jilin Province (20150101116JC). The authors acknowledge the laboratory of the Heilongjiang Province Hydrogeology and Environmental Geology Investigation Institute and the Laboratory of Geographical Resources Institute of Geographic Sciences and Natural Resources Research, CAS for element analysis of the water samples. Supported by the 111 project, No. B16020. We also appreciate valuable suggestions from the editor and anonymous reviewers for improving the manuscript.

Conflict of Interest

The authors declare no conflict of interest.

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