Hydrogeochemical and isotopic composition of groundwater in the Horgos River Watershed in the North-Western Ili Basin in Sinkiang Province, China

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Abstract. In this study, hydrogeochemical and stable environmental isotopic (oxygen-18 and deuterium) data of groundwater in the Horgos River watershed in the north-western Ili Basin were examined to determine the groundwater chemical characteristics, as well as the origins of the groundwater and surface water. The quaternary aquifer’s structure and spatial distribution is complex. Hydrogeochemical data shows that the groundwater is alkaline due to the presence of bicarbonate as the dominant anion. In the north, the dominant groundwater cation was Ca²⁺ while Mg²⁺ ions were highest in the south. In addition, water types varied from HCO₃⁻-SO₄²⁻-Ca and HCO₃⁻-SO₄²⁻-Mg to HCO₃⁻-SO₄²⁻-Mg-Ca and SO₄²⁻-HCO₃⁻-Mg-Ca. Overall, the groundwater in this study showed high total hardness. The dissolving and evaporation inspissation were considered the main controlling factors. Isotopic data (oxygen-18 and deuterium) indicated that the Horgos River was the main recharge source for the groundwater, which rapidly infiltrated across sandstone macropores. Furthermore, surface water and shallow groundwater were significantly affected by evaporation.

1. Introduction
The climate is relatively dry in northwest China. Annual evaporation exceeds annual precipitation significantly. Moreover, due to surface water scarcity, groundwater is particularly important for water resources.

As an emerging border city (figure 1), Horgos City has become a focus area for economic development and ecological environmental protection to the west of Sinkiang. Water consumption in the city in agriculture, industry, and domestic use has grown rapidly. Because of the complex groundwater environment of the Horgos River watershed and the fragility of its ecological environment, groundwater exploitation, management, and protection is critical from socio-economic and environmental points of view [1].

Studying the geochemistry of groundwater contributes to a better understanding of the main hydrogeochemical processes that control the groundwater environment and its relationship with groundwater migration. A goal of this study was to assess groundwater quality; thus, parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), and major ions (cations and anions) were evaluated. Analyses of environmentally stable isotopes (oxygen-18 and deuterium) were used to define groundwater sources and origins, as well as the main recharge sources feeding the groundwater aquifers [2-5].
In this study, groundwater resources and environment problems of the Ili River Basin were investigated. Also, groundwater distribution characteristics and the process of controlling groundwater geochemistry formation were analyzed using hydrogeochemistry and stable environmental isotope (oxygen-18 and deuterium) data.

2. Studied area

2.1. Physiography and climate of the study area
Horgos River is located in the northwest of the Ili Basin in Sinkiang, at the border of China and Kazakhstan (figure 1). The Horgos River originates in the north Tianshan mountain, flows through the plains from north to south, and then ends in the Ili River. The portion of the Horgos River within

![Figure 1. Location map of studied area.](image)
China’s border is 69 kilometers long, its watershed area is 2,736 square kilometers, and it has a natural drop of 2,500 meters. It covers topographical features of rock mountain, piedmont desert belt, fine soil plain, and then desert [6]. This study focused on the plain portion, which is about 50 kilometers long, where the area is relatively flat and the altitude of the terrain gradually descends from north to south.

The study area is a typical arid or semi-arid climate region of North-West China. According to statistical data from the Huocheng meteorological station, the average yearly temperature is 9.3 °C and the multi-year average precipitation and evaporation are 218.9 mm (mainly between July and August) and 1401.1 mm, respectively.

2.2. Hydrogeologic setting

Aquifers in the plain of the Horgos River watershed are mainly composed of quaternary aquifer. There are three types of aquifer matrices and structural features (figure 2). In the north, gravel is the main aquifer matrix; toward the center of the plain, the aquifer matrix is comprised of gravel, sand, and clay, and the southern end of the plain features a coverage of silt, fine sand, and clay. Therefore, this section is mainly an alluvial aquifer of a fine soil plain in the lower reaches of the Ili River, and lacks high-quality groundwater resources.

According to the hole structure in this area, the quaternary aquifer is more than 500 meters thick. The groundwater level line on the plane indicates that groundwater migration is from north to south and is eventually emptied into the Ili River.

![Figure 2. Hydrogeologic section of A—B in studied area.](image)

3. Sampling and analysis

This study was carried out on 23 groundwater samples and 5 surface water samples (figure 1). The samples were collected in August 2014 while investigating groundwater resources and environmental geological problems in the Ili River Valley; all sampling sources were picked after long-term mining.

The samples were collected into 500 ml PET plastic bottles that had been washed at least 3 times. No preservatives were added to the samples. After collecting each sample, the bottle was sealed with a membrane. Samples for oxygen-18 and deuterium (δ18O and δD) concentration determinations were collected in 30 ml PET brown plastic bottles that had been washed at least 3 times; these samples were filtered by a 0.02 µm membrane before sampling. Its treatment was the same as the other samples during the complete analysis. Coordinates of the sampling position were determined by a Venture HC handheld GPS. The sample situ parameters (temperature, pH, oxidation-reduction potential, dissolved oxygen, electrical conductivity, and total dissolved solids) were determined in situ using a HACH-CEL900 portable water analyzer. Stable isotope (oxygen-18 and deuterium) concentrations were determined at Chang’an University using an IWA-35EP laser liquid water isotope analyzer via the axis integral cavity absorption spectrum technique with a testing accuracy of ±1‰ to ±2‰. Complete hydrogeochemical analysis samples were measured at the Geological Environment Monitoring...
Institute of Sinkiang by an atomic absorption spectrophotometer (WFX-110 type); its measuring accuracy was ±2%.

4. Results and discussion

4.1. Hydrogeochemical characteristics of groundwater

Table 1 shows the results of the hydrogeochemical characteristics of the water samples. The pH of the groundwater samples varied from 7.12 to 8.28; the pH of surface water varied from 8.34 to 8.91, indicating that it was weakly alkaline. The surface water had significantly higher pH levels than the groundwater; and the pH of shallow groundwater was higher than that of deep groundwater.

Table 1. Hydrogeochemical parameters and major constituents (in mg/L) of the studied water.

| Samples | Cations mg/L | Anions mg/L | pH | Cond μS/cm | TDS mg/L | Total hardness |
|---------|--------------|-------------|----|------------|----------|----------------|
|         | K⁺ | Na⁺ | Ca²⁺ | Mg²⁺ | Cl⁻ | SO₄²⁻ | HCO₃⁻ |          |          |          |          |
| S01     | 0.5 | 5.5 | 36.1 | 7.3  | 3.5  | 38.4 | 103.7 | 8.51 | 218.8 | 151.3 | 120.1 |
| S02     | 0.3 | 0.0 | 32.1 | 7.3  | 2.1  | 38.4 | 91.5  | 8.34 | 214.1 | 147.8 | 110.1 |
| S03     | 4.1 | 34.9 | 56.1 | 41.3 | 31.9 | 167.1 | 231.9 | 8.41 | 702.0 | 473.1 | 310.2 |
| S04     | 2.0 | 9.4 | 32.1 | 19.4 | 7.0  | 76.8 | 112.3 | 8.9  | 251.0 | 209.4 | 160.1 |
| S05     | 4.6 | 54.1 | 36.1 | 36.4 | 28.4 | 180.6 | 183.1 | 8.91 | 598.0 | 440.0 | 240.2 |
| G01     | 0.6 | 6.2 | 56.1 | 2.4  | 3.5  | 67.2 | 97.6  | 8.28 | 290.0 | 197.7 | 150.1 |
| G02     | 0.7 | 6.6 | 49.7 | 7.8  | 2.8  | 50.0 | 134.2 | 8.09 | 317.0 | 202.8 | 156.1 |
| G03     | 1.8 | 8.8 | 68.1 | 24.3 | 10.6 | 76.8 | 219.7 | 7.83 | 482.0 | 342.6 | 270.2 |
| G04     | 1.0 | 7.2 | 36.1 | 19.4 | 3.5  | 76.8 | 128.1 | 8.25 | 263.0 | 227.2 | 170.1 |
| G05     | 2.5 | 25.3 | 100.2 | 29.2 | 12.8 | 124.9 | 292.9 | 7.59 | 712.0 | 497.7 | 370.3 |
| G06     | 1.9 | 34.3 | 68.1 | 17.0 | 26.9 | 115.3 | 207.5 | 7.97 | 587.0 | 390.8 | 240.2 |
| G07     | 1.9 | 9.9 | 80.2 | 21.9 | 14.2 | 67.2 | 262.4 | 7.8  | 601.0 | 374.9 | 290.2 |
| G08     | 18.1 | 106.5 | 192.4 | 70.5 | 67.4 | 547.5 | 396.6 | 7.28 | 1668.0 | 1308.6 | 770.6 |
| G09     | 2.1 | 27.5 | 60.1 | 21.9 | 21.3 | 103.7 | 207.5 | 7.74 | 579.0 | 372.0 | 240.2 |
| G10     | 1.3 | 9.0 | 32.1 | 19.4 | 7.1  | 38.4 | 158.7 | 7.12 | 296.0 | 214.6 | 160.1 |
| G11     | 2.5 | 49.6 | 60.1 | 34.0 | 42.5 | 192.1 | 195.3 | 8.10 | 703.0 | 504.4 | 290.2 |
| G12     | 9.8 | 41.6 | 92.2 | 41.3 | 24.8 | 201.7 | 292.9 | 7.57 | 849.0 | 585.8 | 400.3 |
| G13     | 1.6 | 20.2 | 101.8 | 25.8 | 16.3 | 98.0 | 353.9 | 7.31 | 676.0 | 478.6 | 360.3 |
| G14     | 2.4 | 19.7 | 80.2 | 24.3 | 14.2 | 86.5 | 278.3 | 7.48 | 574.0 | 399.4 | 300.2 |
| G15     | 1.9 | 26.5 | 70.5 | 25.3 | 10.6 | 76.8 | 288.0 | 7.43 | 553.0 | 379.4 | 280.2 |
| G16     | 4.3 | 139.0 | 222.8 | 79.7 | 156.0 | 551.4 | 476.0 | 7.15 | 1927.0 | 1414.8 | 884.7 |
| G17     | 3.1 | 29.0 | 72.1 | 38.9 | 24.8 | 96.1 | 329.5 | 7.67 | 674.0 | 464.8 | 340.3 |
| G18     | 2.2 | 25.3 | 56.1 | 35.0 | 28.4 | 99.9 | 246.5 | 7.68 | 546.0 | 389.0 | 284.2 |
| G19     | --  | --  | --  | --  | --  | --  | --  | 7.59 | 2910.0 | 0  | 0  |
| G20     | 2.0 | 36.2 | 41.7 | 28.2 | 10.6 | 57.6 | 268.5 | 7.60 | 2350.0 | 332.2 | 220.2 |
| G21     | 4.0 | 29.8 | 41.7 | 26.7 | 17.7 | 109.5 | 195.3 | 8.19 | 622.0 | 349.9 | 214.2 |
Electrical conductivity (EC) is used to characterize groundwater circulation [7]. Electrical conductivity of the collected samples varied from 263 μS/cm in sample G04 up to 2910 μS/cm in sample G19; the surface water samples varied from 214.1 μS/cm to 702 μS/cm. As was the case with pH, the EC of shallow groundwater was significantly higher than that of deep groundwater. This indicated that shallow groundwater was obviously influenced by evaporation and concentration.

The total dissolved solids (TDS) of the studied groundwater samples ranged from 197.7 mg/L to 585.8 mg/L, except for samples G08 (1308.6 mg/L) and G16 (1414.8 mg/L). For surface water samples, the total dissolved solids ranged from 147.8 to 473.1 mg/L. In the horizontal direction, the total dissolved solids of the groundwater samples increased from north to south, and the same changing trend was demonstrated as the groundwater depth increased. This phenomenon indicated that groundwater of the Horgos River watershed traveled from north to the south, which was consistent with the research results of Yin X X, et al. on the zoning of groundwater chemical types and the hydrochemistry action in the same area [8].

The total hardness (TH) was mainly determined by the concentration of calcium and magnesium ions [9]. The ground water samples of the Horgos River watershed plain ranged from 150.1 mg/L in sample G01 up to 884.7 mg/L in sample G16 for total hardness. Accordingly, 65% of the groundwater samples (13 samples) were considered hard, and the remaining samples (7 samples) were considered very hard. Samples G19, G22, and G23 were not detected. Samples S01 and S02 were considered moderately hard at levels of 120.1 mg/L and 110.1 mg/L, respectively. The TH of 2 of the 5 surface water samples (S04 and S05) were considered hard (160.1 mg/L and 240.2 mg/L) and sample G03 was considered very hard at 310.2 mg/L.

Table 1 provides concentrations of the major constituents (cations and anions). The Na+ concentrations ranged from 6.2 to 49.6 mg/L, except for samples G08 and G16, which were more than 100 mg/L. The Na+ ion concentrations were 5.5 mg/L in the upper reaches of the Horgos River. K+ concentrations were quite low, varying from 0.6 to 18.1 mg/L in the groundwater samples, and was detected at about 0.5 mg/L in sample S01. Groundwater Ca2+ concentrations ranged from 32.1 mg/L in sample G10 to 222.8 mg/L in sample G16, and the water of Horgos River was 36.1 mg/L. The Mg2+ ion concentrations ranged from 2.4 mg/L to 79.7 mg/L in groundwater samples, and 7.3 mg/L in sample S01. The Cl- ion concentrations in the groundwater samples were high, up to 156 mg/L; however, it was only 3.5 mg/L in sample S01. The bicarbonate HCO3- content varied from 97.6 mg/L to 396.6 mg/L in the groundwater samples; it was 103.7 mg/L in sample S01. The sulfate ion SO42- concentrations in the groundwater samples ranged from 50 mg/L to 201.7 mg/L, except for samples G08 and G16, which recorded the highest values at 547.5 mg/L and 551.4 mg/L, respectively. Sample S01 was recorded at 38.4 mg/L. Higher Ca2+ and bicarbonate concentrations were observed in samples G08 and G16 because of the abundance of clay minerals and sulfates (such as gypsum) in the aquifer. The Ca2+ concentrations were greater than those of Mg2+ in all samples. The ion concentrations in sample S01 were very low, but very high in samples G08 and G16. The ion concentrations of other samples decreased as the depth increased; they also gradually reduced from the north to the south.

From the calculation results, it can be seen that bicarbonate was the dominant anion in 84% of the samples. Sulfate ions SO42- were the dominant anion in only 4 samples (G08, G11, G16, and S05). Ca2+ was the dominant cation in the groundwater in the northern portion of the plain, while Mg2+ ions were dominant in the southern portion. In this change process, ion concentration order varied from Ca2+ > Mg2+ to Mg2+ > Ca2+ or Mg2+ > Na+ > Ca2+. Water types varied from HCO3-SO4-Ca or HCO3-SO4-Ca-Mg to HCO3-SO4-Mg-Ca or even SO4-HCO3-Mg-Ca.

4.2. Environmental isotopes
Some evidence indicates that the stable environment isotopes of oxygen-18 (δ18O) and hydrogen (δ2H/δD) are excellent tracers for determining groundwater origins [10]. Table 2 gives the environmental isotopic composition results. The studied groundwater samples ranged from -12.47%
to -3.07‰ for δ¹⁸O, and from -86.92‰ to -40.69‰ for δD, and -11.79‰ for δ¹⁸O and -78.20‰ for δD in sample S01.

Table 2. Isotopic composition of water samples.

| Samples | δD ‰  | δ¹⁸O ‰  | Samples | δD ‰  | δ¹⁸O ‰  | Samples | δD ‰  | δ¹⁸O ‰  |
|---------|-------|---------|---------|-------|---------|---------|-------|---------|
| S01     | -78.02| -11.79  | G060    | -76.92| -11.67  | G16     | -79.73| -11.68  |
| S02     | -79.15| -11.45  | G07     | -83.05| -12.20  | G17     | -83.37| -11.98  |
| S03     | -66.57| -8.14   | G08     | -86.92| -12.23  | G18     | -81.42| -11.60  |
| S04     | -73.23| -9.70   | G09     | -84.91| -11.86  | G19     | -79.66| -11.28  |
| S05     | -40.69| -3.07   | G10     | -84.82| -12.47  | G20     | -77.79| -11.54  |
| G01     | -81.02| -11.60  | G11     | -81.37| -11.84  | G21     | -49.00| -5.42   |
| G02     | -81.87| -12.34  | G12     | -84.08| -12.41  | G22     | -82.15| -12.15  |
| G03     | -83.81| -11.84  | G13     | -81.08| -11.69  | G23     | -83.77| -12.15  |
| G04     | -83.17| -12.42  | G14     | -78.45| -11.30  |
| G05     | -79.34| -11.56  | G15     | -81.55| -11.63  |

It is important to study the isotope characteristics of the water in the study area, especially with respect to the local meteoric water line (LMWL). A given year’s average concentration of environmental isotopes of atmospheric precipitation in Urumqi are -86.25‰ for δD and -12.42‰ for δ¹⁸O; this was used as the background value of precipitation in the study area. The δ¹⁸O and δD of the majority of the samples were higher than the background value. Furthermore, both the maximum δ¹⁸O and δD occurred in the plain area of the surface water, which indicated that significant evaporation occurred when precipitation translated into groundwater. Evaporation was more intense in the plain compared to the mountain area.

According to IAEA data from 1986-2002, the equation of the local meteoric water line of Urumqi is as follows:

δD=7.21δ¹⁸O+4.50  \hspace{1cm} (1)

This diagram shows that some surface water and groundwater samples fell between the LMWL of Urumqi (Figure 3). Additionally, most groundwater samples were characterized by relatively depleted oxygen-18 and deuterium contents, indicating that they were not significantly affected by evaporated open water or soil water, which implied rapid infiltration of Horgos River waters across sandstone macropores. As a result, the environmental isotope concentrations of groundwater were diluted, while surface samples were characterized by a relative enrichment of oxygen-18 and deuterium contents. This indicated that they were significantly affected by evaporation and could not be quickly replenished by fresh water.

Figure 3. Relationship between δ¹⁸O and δD for the studied groundwater samples.
In the vertical direction, oxygen-18 and deuterium concentrations in groundwater presented an obvious depletion tendency as depth increased.

5. Conclusions
The studied groundwater hydrogeochemical compositions were strongly influenced by dissolving and evaporation inspissation. The groundwater in the study area originated from atmospheric precipitation, which is mainly replenished by the Horgos River. This was evident from the following results:

- The pH measurements revealed an alkaline chemical environment of the groundwater in the Horgos River watershed plain because bicarbonate was the dominant anion for the majority of groundwater samples.
- The pH and EC of shallow groundwater was higher than groundwater occurrence in deep water; total dissolved solids and total hardness of groundwater samples presented a changing trend of increasing with an increase of depth and the same from north to south;
- Except for samples G19, G22, and G23, 65% of groundwater samples were considered hard; the remaining samples were considered very hard.
- As depth increased and the plain moved from north to south, oxygen-18 and deuterium depletion became more apparent.

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