Hydrochemical Characteristics and Genesis of Groundwater in the Northwestern Ili River Valley (Postprint)

Authors: Alim Aklam

Date: 2021-04-23T00:00:00+00:00

Abstract

To investigate the hydrochemical characteristics and genesis of groundwater in the northwestern Ili River Valley, Xinjiang, mathematical statistics, Piper trilinear diagram, Gibbs diagram, and ion ratio plots were employed to analyze the sampling and monitoring data of groundwater from the northwestern Ili River Valley in 2018. The results show that: (1) Groundwater in the study area is weakly alkaline water with relatively high total hardness, the overall variability of groundwater chemical component concentrations is not significant, the main cation is Ca2+, and the main anion is HCO3-. (2) The hydrochemical types of groundwater are predominantly HCO3-Ca, HCO3·SO4-Ca, HCO3·SO4-Ca·Mg, HCO3·SO4-Ca·Na, and HCO3-Ca·Mg types. (3) The chemical components of groundwater in the study area are primarily controlled by rock dissolution, while evaporation-concentration and cation exchange processes also contribute to the chemical components of groundwater to a certain extent, and individual groundwater sampling points may be affected by anthropogenic activities. (4) Na+, Cl-, and SO42- in groundwater mainly originate from the dissolution of evaporite rocks such as rock salt and gypsum, while Ca2+ and Mg2+ mainly originate from the dissolution of minerals such as calcite, dolomite, and gypsum.

Full Text

Chemical Characteristics and Genesis Analysis of Groundwater in the Northwest Yili River Valley

Ailihamu Aikelamu[1,2,3], ZHOU Jinlong[1,2,3], ZHANG Jie[1,2,3], WEI Xing[1,2,3], YU Dong[1,2,3], CHEN Jinsong[1,2,3]

[1]College of Water Conservancy and Civil Engineering, Xinjiang Agricultural University, Urumqi 830052, Xinjiang, China
[2]Xinjiang Hydrology and Water Resources Engineering Center, Urumqi 830052,

Xinjiang, China
[3]Xinjiang Key Laboratory of Hydraulic Engineering Security and Water Disasters Prevention, Urumqi 830052, Xinjiang, China

Abstract

To investigate the hydrochemical characteristics and genesis of groundwater in the northwest Yili River Valley, Xinjiang, we systematically analyzed 35 groundwater samples collected from June to October 2018 using descriptive statistical methods, Piper trilinear diagrams, Gibbs diagrams, ion ratio diagrams, and saturation index calculations. The results indicate that groundwater in the study area is weakly alkaline with elevated total hardness. Chemical components exhibit low overall variability, with calcium (Ca^{2+}) as the dominant cation and bicarbonate (HCO_3^-) as the dominant anion. The hydrochemical characteristics can be classified into five primary water types: HCO_3-Ca, $HCO_3 \cdot SO_4$-Ca, $HCO_3 \cdot SO_4$-Ca · Mg, $HCO_3 \cdot SO_4$-Ca · Na, and HCO_3-Ca · Mg. Rock weathering constitutes the primary control on groundwater chemistry, though evaporation-concentration and cation exchange processes also contribute significantly. Some sampling points may be influenced by anthropogenic activities. Sodium (Na^+), chloride (Cl^-), and sulfate (SO_4^{2-}) originate primarily from the dissolution of evaporite minerals such as rock salt and gypsum, while calcium and magnesium derive from the dissolution of calcite, dolomite, and gypsum.

Keywords: northwest Yili River Valley; groundwater; hydrochemical characteristics; Gibbs diagram; ion ratio; Xinjiang

Introduction

Groundwater represents a critical component of water resources, driving socioeconomic development, shaping ecological environments, and maintaining regional environmental stability. In arid and semi-arid regions, groundwater serves as the primary water source, supplying over half of industrial water demand and one-third of agricultural water consumption. Groundwater chemistry is influenced by multiple factors including climate, atmospheric precipitation, geological structure, mining activities, and human interventions, while also being controlled by stratigraphic lithology and leaching processes. As research on groundwater chemical components has advanced, numerous scholars have integrated regional hydrogeological and lithological conditions to classify hydrochemical types using the Alekin, Piper, and Durov diagrams, thereby investigating the sources and controlling factors of major chemical components in different regions.

Previous studies have examined groundwater in the Yili River Valley from various perspectives. Duan Dongwei established that phreatic and confined waters share similar origins and maintain hydraulic connectivity based on regional groundwater system theory. Shao Jie analyzed hydrochemical characteristics and variations along different profiles in the Yili River Basin, elucidating groundwater flow circulation patterns. Qiu Yubo investigated the paleo-groundwater hydrodynamic system of the Xishanyao Formation to reconstruct the planar migration of interlayer oxidation fluids. While these studies demonstrated that natural factors and aquifer minerals predominantly influence regional groundwater chemistry, the specific mineral sources of chemical components require further investigation. This research systematically classifies groundwater types across the entire study area and analyzes the origins of hydrochemical components to identify the primary mineral phases controlling groundwater characteristics. The findings provide a theoretical foundation for understanding groundwater origin and evolution patterns, supporting rational development, utilization, and protection of regional water resources.

1.1 Study Area Overview

The Yili River Valley is situated within the Tianshan Mountains in northern Xinjiang, bounded by the Keguqin and Boluokelu Mountains to the north and the Ha' erketawu and Nalati Mountains to the south. Major rivers include the Yili, Kunes, Tekes, and Kashi Rivers, with an average annual surface runoff of 165.5$×10^{8}$ m^3, accounting for 20.7% of Xinjiang' s total surface water resources. Annual precipitation reaches 52.45$×10^{8}$ m^3, with total groundwater recharge of 3$×10^{8}$ m^3, making this a water-rich region in Xinjiang. The northwest Yili River Valley lies in the western Tianshan Mountains of China' s border region, surrounded by mountains on four sides with topography sloping downward from east to west, and characterized by a semi-humid continental temperate climate.

Quaternary strata are well-developed within the study area [Figure 1: see original paper], comprising accumulations of various ages and origins. Along the east-west trending Yili River, Quaternary thickness gradually increases to a maximum of one kilometer, with alternating monolayer and multilayer structures containing coarse and fine-grained rock layers. Fine-grained multilayer lithology predominates on both sides of the Yili River. The geomorphology transitions from north to south into inclined gravelly fine soil plains and alluvial-proluvial fine soil plains, with the central plain area along the Yili River exhibiting primarily alluvial-proluvial fine soil plain characteristics [Figure 2: see original paper].

Groundwater types include unconsolidated rock pore water, Mesozoic-Cenozoic clastic rock fissure-pore water, and bedrock fissure water. In the plain area, most groundwater is shallow with depths $ $10 m, symmetrically distributed about the Yili River, gradually deepening toward the mountainous region to maximum depths $ $100 m. Groundwater receives recharge through rainfall infiltration, river leakage, reservoir seepage, floodwater infiltration, and lateral groundwater inflow, and discharges via artificial extraction, spring outflow, phreatic evapotranspiration, and downstream lateral outflow.

1.2 Water Sample Collection and Testing

A total of 35 groundwater samples were collected from June to October 2018, including 17 phreatic water and 18 confined water samples from depths ranging 15–200 m. Samples were stored in polyethylene bottles rinsed three times with the target water before collection, then sealed and labeled. Field parameters including pH, total dissolved solids (TDS), and electrical conductivity (EC) were measured on-site using a German HI9829 high-precision portable multi-parameter water quality meter. Laboratory analysis of K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, ${SO_4}^{2-}$, ${HCO_3}^-$, and ${NO_3}^-$ concentrations was conducted by the Second Hydrogeological and Engineering Geological Brigade of the Xinjiang Geology and Mineral Bureau. Analytical methods included ethylenediaminetetraacetic acid (EDTA) titration for Ca^{2+} and Mg^{2+}, flame atomic absorption spectrophotometry for K^+ and Na^+, silver nitrate volumetric method for Cl^-, barium sulfate turbidimetry for ${SO_4}^{2-}$, acid-base titration for ${HCO_3}^-$, and UV spectrophotometry for ${NO_3}^-$. All ion detection limits were $0.05\ mg \cdot L^{-1}$, with cation-anion charge balance errors maintained below 5%.

1.3 Research Methods

Hydrochemical data were processed using SPSS 22.0 for descriptive statistics. Piper trilinear diagrams were employed to classify regional groundwater types, while Gibbs diagrams, ion concentration ratios, and PHREEQC software were utilized to analyze hydrochemical characteristics and genesis under various controlling factors.

2.1 Hydrochemical Characteristics

Statistical analysis reveals that both phreatic and confined waters exhibit low variability in chemical composition, with maximum coefficient of variation of 1.09. Groundwater pH ranges from 6.90 to 8.10 (average 7.58), indicating weakly alkaline conditions. Total dissolved solids (TDS) vary between 111.00 and 2318.92 $mg \cdot L^{-1}$ (average 604.07 $mg \cdot L^{-1}$), with 97.1% of samples containing TDS <1 $g \cdot L^{-1}$, classifying as freshwater. Total hardness ranges from 151.00 to 2920.00 $mg \cdot L^{-1}$ (average 604.07 $mg \cdot L^{-1}$), with 25.7% soft water ($ 300$mg \cdot L^{\{-1\}), 25.7}${-1}), and48.6 450$mg \cdot L^{-1}) according to groundwater quality standards .

Cation concentrations follow the order $Ca^{2+} > Na^+ > Mg^{2+} > K^+$, with Ca^{2+} ranging 26.11–267.01 $mg \cdot L^{-1}$ (average 79.15 $mg \cdot L^{-1}$), Na^+ ranging 3.03–247.01 $mg \cdot L^{-1}$ (average 43.47 $mg \cdot L^{-1}$), Mg^{2+} ranging 2.77–179.35 $mg \cdot L^{-1}$ (average 42.43 $mg \cdot L^{-1}$), and K^+ ranging 0.87–9.01 $mg \cdot L^{-1}$ (average 2.82 $mg \cdot L^{-1}$). Anion concentrations follow ${HCO_3}^- > {SO_4}^{2-} > Cl^- > {NO_3}^-$, with ${HCO_3}^-$ ranging 60.76–523.17 $mg \cdot L^{-1}$ (average 235.32 $mg \cdot L^{-1}$), ${SO_4}^{2-}$ ranging 26.50–1109.24 $mg \cdot L^{-1}$ (average 154.57 $mg \cdot L^{-1}$), Cl^- ranging 6.43–179.35 $mg \cdot L^{-1}$ (average 31.32 $mg \cdot L^{-1}$), and ${NO_3}^-$ ranging 0–26.52 $mg \cdot L^{-1}$ (average 10.19 $mg \cdot L^{-1}$). Among 34 samples, 29 exhibited ${NO_3}^-$ concentrations $ 20$mg \cdot L^{-1}.

2.2 Hydrochemical Type Classification

Piper trilinear diagrams effectively illustrate relationships among major groundwater components and facilitate hydrochemical classification [Figure 3: see original paper]. The primary groundwater types in the study area include HCO_3-Ca, $HCO_3 \cdot SO_4$-Ca, $HCO_3 \cdot SO_4$-Ca · Mg, $HCO_3 \cdot SO_4$-Ca · Na, and HCO_3-Ca · Mg types, with localized occurrences of SO_4-Ca · Mg, SO_4-Na · Mg, and SO_4-Ca types. Groundwater TDS remains generally low, with most samples meeting drinking water standards.

3.1 Main Controlling Factors of Groundwater Chemistry

Gibbs diagrams distinguish hydrochemical evolution under atmospheric precipitation, evaporation-crystallization, and rock weathering influences. Given the long residence time of groundwater in aquifers and pronounced water-rock interactions, the rock weathering domain can be appropriately expanded when applying Gibbs analysis to groundwater systems. The Gibbs diagram for the study area [Figure 4: see original paper] shows that most groundwater samples plot within the "rock weathering" domain, with some distributed in the "evaporation-crystallization" domain. Combined with geomorphological characteristics, both phreatic water from alluvial-proluvial fine soil plains and confined water from inclined gravelly plains are primarily controlled by rock weathering, with partial influence from combined rock weathering and evaporation-crystallization.

The scattered distribution of $\gamma(Na^+)/\gamma(Cl^-)$ ratios indicates that groundwater chemistry may also be affected by cation exchange processes and human activities. Samples show good clustering for $\gamma(Na^+)/\gamma(Na^+ + Ca^{2+})$ but poor clustering for $\gamma(Cl^-)/\gamma(Cl^- + HCO_3^-)$, suggesting additional influences from cation exchange and anthropogenic factors.

3.2 Cation Exchange Processes

Cation exchange involves the replacement of cations in water with cations adsorbed on soil particles under certain conditions. The relationship between $\gamma(Na^+\text{-}Cl^-)$ and $\gamma[(HCO_3^- + SO_4^{2-})\text{-}(Ca^{2+} + Mg^{2+})]$ typically identifies cation exchange; when $\gamma(Na^+\text{-}Cl^-)$ $\gamma[(HCO_3^- + SO_4^{2-})\text{-}(Ca^{2+} + Mg^{2+})]$, cation exchange is confirmed [Figure 5: see original paper]. Most phreatic and confined water samples plot near the 1:1 line, with points concentrated in the region where $\gamma(Na^+\text{-}Cl^-) > \gamma[(HCO_3^- + SO_4^{2-})\text{-}(Ca^{2+} + Mg^{2+})]$, demonstrating significant cation exchange. Given that cation exchange predominantly occurs in sandy and fine-grained strata, and considering the study area' s stratigraphic characteristics, these processes are most active in inclined gravelly fine soil plains and alluvial-proluvial fine soil plains.

3.3 Rock Weathering and Dissolution

Rock dissolution through weathering and water-rock interactions introduces chemical components into groundwater. Ion ratio diagrams can identify mineral sources of these components [Figure 6: see original paper]. The $\gamma(Na^+)/\gamma(Cl^-)$ ratio indicates silicate mineral dissolution; most samples plot above the $\gamma(Na^+)/\gamma(Cl^-) = 1$ line, suggesting that in addition to rock salt dissolution, groundwater chemistry is influenced by sodium-bearing silicate minerals such as albite.

The $\gamma(Ca^{2+}+Mg^{2+})/\gamma(HCO_3^-)$ ratio reflects carbonate dissolution. Most samples plot above the 1:1 line, and the majority fall below the $\gamma(Ca^{2+}+Mg^{2+})/\gamma(HCO_3^-) = 1$ line, indicating that Ca^{2+} and Mg^{2+} originate from both carbonate and evaporite mineral dissolution. The $\gamma(SO_4^{2-})/\gamma(Ca^{2+}+Mg^{2+})$ ratio further demonstrates that gypsum weathering contributes to Ca^{2+} and Mg^{2+} formation.

The $\gamma(SO_4^{2-})/\gamma(HCO_3^-)$ ratio reveals combined effects of evaporite and carbonate dissolution. Most sampling points are distributed between the $\gamma(SO_4^{2-})/\gamma(HCO_3^-) = 1$ line and the 1:1 line, with 51.4% plotting above the line and 48.6% below, indicating that both evaporite and carbonate dissolution influence groundwater chemistry. Saturation index analysis shows that halite and gypsum are undersaturated (SI < 0) and actively dissolving, while most carbonate minerals (aragonite, calcite, dolomite) are at or near saturation (SI ≥ 0), suggesting precipitation under evaporation-concentration effects.

The $\gamma(Ca^{2+})/\gamma(Mg^{2+})$ ratio ranges from 0.29 to 6.06 (average 1.78), with 26 of 35 samples plotting between 1 and 2, indicating dual effects of carbonate and gypsum weathering. Both phreatic and confined waters receive recharge from atmospheric precipitation, with groundwater flow directed from mountainous areas toward plains. Stable isotope studies demonstrate that phreatic and confined waters in the Yili River Valley plain share atmospheric precipitation origins and exhibit strong hydraulic connectivity between different hydrogeological units. The relationship between SO_4^{2-} and HCO_3^- concentrations can identify SO_4^{2-} mineral sources; when SO_4^{2-} $Ca^{2+} + HCO_3^-$, all SO_4^{2-} originates from gypsum dissolution. All study area samples plot near the y = x line, indicating that SO_4^{2-} primarily derives from gypsum and mirabilite dissolution.

3.4 Evaporation-Concentration Effects

Under evaporation-concentration, highly soluble salts accumulate while less soluble salts precipitate. Saturation index (SI) analysis reveals mineral saturation states: SI < 0 indicates undersaturation and dissolution, SI $= 0$ represents equilibrium, and SI > 0 signifies oversaturation and precipitation . Halite and gypsum saturation indices are negative, indicating active dissolution. Most carbonate minerals show SI ≥ 0, suggesting saturation and potential precipitation. Evaporation-concentration drives dissolution of Cl^- and SO_4^{2-} while causing precipitation of Ca^{2+} and Mg^{22+}, collectively influencing groundwater chemistry.

4 Conclusions

(1) Groundwater in the northwest Yili River Valley is weakly alkaline with high total hardness. Chemical components show low variability, with Ca^{2+} as the dominant cation and ${HCO_3}^-$ as the dominant anion.

(2) The primary hydrochemical types are HCO_3-Ca, $HCO_3 \cdot SO_4$-Ca, $HCO_3 \cdot SO_4$-Ca · Mg, $HCO_3 \cdot SO_4$-Ca · Na, and HCO_3-Ca · Mg.

(3) Rock weathering predominantly controls groundwater chemistry, with evaporation-concentration and cation exchange contributing significantly. Some areas exhibit notable cation exchange effects. Ion ratio analysis demonstrates that Na^+, Cl^-, and ${SO_4}^{2-}$ originate from evaporite dissolution (rock salt, gypsum), while Ca^{2+} and Mg^{2+} derive from carbonate and gypsum mineral dissolution. Evaporation-concentration processes drive accumulation of Cl^- and ${SO_4}^{2-}$ while promoting precipitation of Ca^{2+} and Mg^{2+}, collectively influencing groundwater chemistry.

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Note: Figure translations are in progress. See original paper for figures.