Hydrochemical Characteristics and Genesis Analysis of Phreatic Water in the Ulungur River Basin: Postprint

Authors: Tian Hua, Xin Tuo, Deng Tao, Tian Xue, Zhang Jiali, Li Jinfang, Yang Jiayi

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Abstract

To investigate the spatial distribution characteristics and genesis of phreatic water hydrochemistry in different geomorphological units of the Ulungur River Basin, systematic analysis was conducted on the 2018 phreatic water hydrochemical test data using methods including mathematical statistics, Shchukarev classification, Piper trilinear diagram, Gibbs diagram, and ionic ratio coefficients. The results indicate that hydrochemical components of phreatic water in the Ulungur River Basin are primarily influenced by evaporation-crystallization, rock weathering, and ion exchange processes, with total dissolved solids (TDS) and major ion components gradually increasing from the piedmont bedrock area to the alluvial-proluvial-lacustrine plain, and significant differences in hydrochemical characteristics among different geomorphological units. In the piedmont bedrock low mountain area, the hydrochemical type is predominantly HCO3 · SO4-Ca · Na, while in the low mountain and hilly area it is SO4 · Cl-Na · Ca, where the hydrochemical genesis is mainly controlled by evaporation-crystallization and rock weathering. In the intermountain valley area, the hydrochemical type is primarily HCO3 · SO4-Ca · Na, influenced by rock weathering and ion exchange processes. The alluvial-proluvial-lacustrine plain exhibits horizontal zoning of hydrochemical types: the far-channel area is dominated by SO4-Na · Ca and SO4 · Cl-Na · Ca types, while the near-channel area is dominated by SO4 · HCO3-Ca · Na type, all influenced by the combined effects of rock weathering, evaporation-crystallization, and ion exchange. The cation evolution trend follows Ca2+, Na+ → Na+, Ca2+ → Na+ (Ca2+, Mg2+), and the anion evolution trend follows HCO-3(SO2-4) → SO2-4 (HCO-3) → SO2-4 → SO2-4(Cl-) → SO2-4, Cl-.

Full Text

Hydrochemical Characteristics and Formation Mechanism of Phreatic Water in the Ulungur River Watershed

TIAN Hua[1], XIN Tuo[1], DENG Tao[2], TIAN Xue[1], ZHANG Jia-li[1], LI Jin-fang[1], YANG Jia-yi[1] [1]College of Geology and Environment, Xi' an University of Science and Technology, Xi' an 710054, Shaanxi, China [2]China Geo-Engineering Corporation, Beijing 100080, China

Abstract: To investigate the spatial distribution characteristics and formation mechanisms of phreatic water chemistry across different geomorphological units in the Ulungur River watershed, hydrochemical data from 2018 were systematically analyzed using mathematical statistics, the Schakerev classification, Piper diagrams, Gibbs plots, and ion ratio coefficients. The results demonstrate that the hydrochemical composition of phreatic water is primarily influenced by evaporation crystallization, rock weathering, and ion exchange processes. Both total dissolved solids and major ion concentrations increase progressively from the piedmont bedrock area to the alluvial-proluvial and lacustrine plain zones, with significant hydrochemical variations observed among different geomorphological units. In the piedmont bedrock low-mountain area, the hydrochemical type is predominantly $HCO_3 \cdot SO_4$-$Ca \cdot Na$, controlled mainly by evaporation crystallization and rock weathering. The intermontane valley area exhibits $SO_4 \cdot Cl$-$Na \cdot Ca$ type water, influenced by rock weathering and ion exchange. The alluvial-proluvial lacustrine plain displays clear horizontal zoning, with $SO_4 \cdot Cl$-$Na \cdot Ca$ type dominating near the river channel and $SO_4 \cdot HCO_3$-$Ca \cdot Na$ type in distal areas, reflecting combined effects of rock weathering, evaporation crystallization, and ion exchange. The cation evolution trend follows $Ca^{2+} \rightarrow Ca^{2+} \cdot Na^+ \rightarrow Na^+ \cdot Ca^{2+} \rightarrow Na^+ \cdot Ca^{2+} \cdot Mg^{2+}$, while the anion evolution follows $HCO_3^- \rightarrow HCO_3^- \cdot SO_4^{2-} \rightarrow SO_4^{2-} \cdot HCO_3^- \rightarrow SO_4^{2-} \rightarrow SO_4^{2-} \cdot Cl^-$.

Keywords: Ulungur River watershed; phreatic water; hydrochemical characteristics; formation mechanism

Groundwater chemistry is intrinsically linked to its ambient environment, with hydrochemical signatures revealing the origin and historical evolution of ionic constituents. Under the combined influences of climate change and human activities, both water quality and quantity in northwest China' s inland basins have undergone significant spatiotemporal transformations in recent years. Investigating groundwater hydrochemical characteristics and evolution mechanisms thus provides crucial insights into the interaction processes between groundwater and its hosting media. Previous studies have demonstrated that groundwater chemistry in arid regions is predominantly controlled by evaporation concentration, leaching, and rock weathering, with hydrochemical compositions becoming progressively complex from recharge to discharge areas and exhibiting pronounced spatial-temporal variability. Ion ratio relationships and hydrogeodynamic parameters serve as important indicators for deciphering hydrochemical signatures and formation mechanisms. Meanwhile, the fragile ecological resources and complex environmental evolution processes in northwest China, coupled with regional urbanization pressures, have created new challenges concerning population, resources, and environmental sustainability. The Ulungur River watershed, located in an arid region of northwest China, relies heavily on groundwater to support agricultural and pastoral activities. However, previous research has primarily focused on lake hydrology, river-ecosystem relationships, and regional water resource assessments, with limited investigation of phreatic water hydrochemistry and evolution. This study systematically examines the hydrochemical characteristics of phreatic water in the Ulungur River watershed, integrating statistical analysis, ion ratios, and hydrogeodynamic parameters to elucidate the hydrochemical signatures and formation mechanisms across different geomorphological units, thereby providing a theoretical basis for understanding water resource formation, circulation, and evolution in the basin.

1. Study Area Overview

The Ulungur River watershed is situated on the northwestern margin of the Junggar Basin, covering a total area of 38,426 km^2. The Ulungur River, the largest in the region, originates from the southern foothills of the Altai Mountains in Qinghe County, Altay Prefecture, flowing through Qinghe, Fuyun, and Fuhai before terminating in Ulungur Lake. The watershed experiences a continental arid climate with an average annual temperature of 4.1°C, mean annual precipitation of 130.9 mm, and mean annual evaporation of 1,580.2 mm. The topography slopes from northeast to southwest, comprising three distinct geomorphological units from east to west: the piedmont bedrock area, intermontane valley area, and alluvial-proluvial lacustrine plain [Figure 1: see original paper]. The piedmont bedrock area includes low mountains and hilly terrain with thin Quaternary cover, poor water storage capacity, and bedrock-dominated substrate, locally exposed, consisting primarily of sandy gravel and argillaceous sandstone. The intermontane valley area features thicker Quaternary deposits, outcropping Devonian, Carboniferous, and Quaternary strata with highly variable topography and steep slopes. The alluvial-proluvial lacustrine plain trends east-west as a Mesozoic-Cenozoic depression, deeper in the west and shallow in the east, with a north-south shallow and central deep configuration. The near-river zone centers on the Ulungur River channel, extending southward to the second terrace margin and northward covering approximately [Figure 1: see original paper] of Quaternary deposits. The distal-river zone, representing the largest portion of the alluvial-proluvial lacustrine plain, comprises phreatic water areas north of the near-river zone and along the eastern lake shores. Quaternary lithology throughout the watershed consists primarily of sandstone, sandy conglomerate, and cohesive soils with well-developed porosity. South of the Ulungur River, the second terrace and the central-northern denudation hills and gently inclined plain areas exhibit undulating topography with significant slope variations, mostly covered by Quaternary residual slope deposits and proluvial materials composed of mud, sand, and sandy gravel with poor water storage capacity, forming a permeable but water-bearing layer. Phreatic water originates in the piedmont bedrock area, flows through the intermontane valley and plain, and ultimately discharges into Ulungur Lake and Jili Lake.

2. Materials and Methods

2.1 Sampling and Testing

Based on the watershed' s geological, geomorphological, and hydrogeological conditions, phreatic water samples were collected and tested in 2018 from the piedmont bedrock, intermontane valley, and alluvial-proluvial lacustrine plain zones [Figure 1: see original paper]. Sampling utilized cleaned 500 mL polyethylene bottles with a minimum pumping time of 15 minutes prior to collection to evacuate air bubbles before sealing. Hydrochemical analyses included simple analysis, comprehensive analysis, and trace elements, all performed by the Xinjiang Physical and Chemical Analysis and Testing Center of the Nuclear Industry. Cations were measured using atomic absorption spectrophotometry, anions by ion chromatography, with detection limits of [specific values] for Ca^{2+} and Mg^{2+}, [specific values] for K^+ and Na^+, [specific values] for Cl^- and ${SO_4}^{2-}$, and [specific values] for ${HCO_3}^-$. Charge balance errors for all samples ranged between -0.5% and -0.3%, meeting the accuracy standard for comprehensive analysis.

2.2 Analytical Methods

Based on sample testing and data feasibility, SPSS 10.0 was employed for basic statistical analysis of hydrochemical parameters and Schakerev classification of water samples to characterize the spatial distribution of hydrochemical components and types. Piper diagrams were constructed to reveal hydrochemical patterns, while Origin 10.0 was used to plot Gibbs diagrams and analyze ion ratio relationships to identify regional hydrochemical formation processes and controlling factors. Hydrogeological and sampling point distribution maps and hydrochemical evolution schematics were generated using Section 11.0.

3. Results and Discussion

3.1 Hydrochemical Characteristics

3.1.1 Major Ion Composition Statistical summaries indicate that phreatic water in the Ulungur River watershed is generally weakly alkaline. The piedmont bedrock low-mountain area and intermontane valley zone exhibit mineralization values below 1 $g \cdot L^{-1}$, classifying as freshwater. The low hill area and alluvial-proluvial lacustrine plain show brackish water characteristics with mineralization exceeding 1 $g \cdot L^{-1}$, with some samples reaching saline water concentrations above 7 $g \cdot L^{-1}$. Total hardness correlates positively with mineralization across all geomorphological units. Cation dominance follows the pattern $Ca^{2+} > Na^{+} > Mg^{2+}$ in the piedmont bedrock low-mountain area and intermontane valley, transitioning to $Na^{+} > Ca^{2+} > Mg^{2+}$ in the low hill area and alluvial-proluvial lacustrine plain. Anion composition varies spatially: the intermontane valley and near-river plain areas show ${SO_4}^{2-} > {HCO_3}^{-} > Cl^{-}$, while the piedmont bedrock low hill area and distal plain zone exhibit ${SO_4}^{2-} > Cl^{-} > {HCO_3}^{-}$. Significant variation coefficients for major ions across geomorphological units reflect heterogeneous spatial distributions.

3.1.2 Hydrochemical Types Schakerev classification and Piper diagrams [Figure 3: see original paper] were used to classify and map hydrochemical types [Figure 2: see original paper], revealing distribution patterns and evolution trends. The piedmont bedrock low-mountain area is characterized by $HCO_3 \cdot SO_4$-$Ca \cdot Na$ type water with mineralization below 1.0 $g \cdot L^{-1}$. Transitioning to the low hill area, ion concentrations increase, yielding $SO_4 \cdot Cl$-$Na \cdot Ca$ type water with mineralization between 1.0–1.5 $g \cdot L^{-1}$. The intermontane valley zone shows similar hydrochemical types to the piedmont bedrock area but with elevated ion concentrations, predominantly $SO_4 \cdot HCO_3$-$Ca \cdot Na$ type. The alluvial-proluvial lacustrine plain exhibits clear horizontal zoning: near-river areas maintain $HCO_3 \cdot SO_4$-$Ca \cdot Na$ type, while distal-river zones are dominated by $SO_4 \cdot Cl$-$Na \cdot Ca$ type with mineralization exceeding 2.0 $g \cdot L^{-1}$.

3.2 Hydrochemical Formation Mechanisms

Under natural conditions, groundwater undergoes dissolution, adsorption, leaching, exchange, and redox reactions with aquifer media during flow, resulting in continuous elemental cycling between water and its environment. Ion relationships thus provide crucial insights into regional hydrochemical controls.

3.2.1 Evaporation Concentration Gibbs diagrams effectively identify hydrochemical formation mechanisms by classifying inland groundwater evolution into three domains: precipitation dominance, rock weathering dominance, and evaporation crystallization dominance. The Gibbs plot [Figure 4: see original paper] reveals that piedmont bedrock low-mountain samples plot right of the rock weathering domain, indicating additional processes beyond simple weathering. Low hill area samples cluster in the evaporation crystallization zone with ratios between 0.2–0.9, showing clear evaporative control. Intermontane valley samples are distributed across both weathering and evaporation zones, reflecting combined influences. Alluvial-proluvial lacustrine plain samples plot in the intermediate zone with ratios below [specific value], indicating rock weathering dominance with minor evaporation effects, particularly in near-river areas. Distal-river samples show greater dispersion with higher average ratios, suggesting stronger evaporation influence.

3.2.2 Leaching The $\gamma(Na^{+})/\gamma(Cl^{-})$ ratio serves as a hydrochemical genesis indicator, reflecting the enrichment degree of Na^{+} relative to Cl^{-} and revealing continental salinization processes. The relationship plot [Figure 5: see original paper] shows most sample points plotting above the seawater dilution line with $\gamma(\mathrm{Na}^+) > \gamma(\mathrm{Cl}^-)$, indicating non-marine origin and leaching dominance. Piedmont bedrock low-mountain, intermontane valley, and near-river plain samples cluster near the lower left, suggesting minimal halite dissolution. In contrast, low hill area and distal-river plain samples show greater dispersion with higher average $\gamma(\mathrm{Na}^+)/\gamma(\mathrm{Cl}^-)$ ratios, indicating significant halite leaching effects.

3.2.3 Cation Exchange Adsorption Cation exchange between aquifer solids and groundwater can be evaluated using the relationship between $\gamma(\mathrm{Na}^+ + \mathrm{K}^+ - \mathrm{Cl}^-)/\gamma(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+})$ and $\gamma(\mathrm{SO_4}^{2-} + \mathrm{HCO_3}^-)$. Stronger cation exchange produces steeper slopes. The plot [Figure 6: see original paper] shows most samples clustering near the theoretical exchange line, confirming cation exchange occurrence. Exchange intensity decreases from the intermontane valley center toward both eastern and western geomorphological units, with western plain areas showing stronger exchange than piedmont bedrock zones. The intermontane valley exhibits a slope of [specific value], indicating the strongest exchange, while the piedmont bedrock low hill area shows the weakest exchange with a slope of [specific value]. Near-river plain areas display slopes of [specific value], greater than distal-river areas, reflecting river water influence on hydrochemical composition.

3.3 Hydrochemical Evolution Characteristics

Natural groundwater flow involves complex spatial hydrochemical transformations controlled by multiple factors. A conceptual evolution model [Figure 7: see original paper] was developed based on hydrochemical signatures and hydrogeological conditions. The piedmont bedrock low-mountain area features steep topography, optimal hydrodynamic conditions, and the lowest hydrodynamic parameters. Easily soluble ions such as $\mathrm{HCO_3}^-$ and $\mathrm{SO_4}^{2-}$ initially enter groundwater, while moderately soluble ions like Ca^{2+} and Na^+ become dominant constituents. Snowmelt and rainfall infiltration further dilute the water, yielding $\mathrm{HCO_3 \cdot SO_4}$ type chemistry. In the low hill area, reduced topographic gradients and increased hydrodynamic parameters deteriorate flow conditions while enhancing evaporation. Extensive phreatic water discharge and spring formation, followed by evaporation and subsequent recharge, elevate mineralization and evolve the water type toward $\mathrm{SO_4 \cdot Cl}$.

From the intermontane valley to the alluvial-proluvial lacustrine plain, Quaternary thickness increases and topographic gradients decrease from east to west. Both near-river and valley zones share similar hydrodynamic parameters, but divergent evaporation intensities drive hydrochemical differentiation. The valley zone, influenced by rock weathering and ion exchange, maintains $\mathrm{HCO_3 \cdot SO_4}$ type water. Near-river areas, affected by ion exchange, rock weathering, and evaporation, develop $\mathrm{SO_4 \cdot HCO_3\text{-}Ca \cdot Na}$ type water. In distal-river and lake discharge zones, maximum hydrodynamic parameters create the poorest flow conditions, where sustained evaporation combined with ion exchange and leaching produces $SO_4 \cdot Cl$ type water, with some areas reaching $SO_4 \cdot Cl$-$Na \cdot Ca$ composition.

These findings indicate that ion exchange, rock weathering, and variable-intensity evaporation crystallization collectively control the hydrochemical zonation in the alluvial-proluvial lacustrine plain. Recent global warming has altered atmospheric water cycling in northwest China' s arid regions, modifying rainfall patterns and frequencies. Increased precipitation events enhance groundwater recharge, reorganizing hydrochemical compositions. Additionally, land use differs markedly between near-river and distal-river zones: near-river areas are predominantly forested with high vegetation coverage, while distal-river zones feature extensive cultivated land with well-developed canal systems and flood irrigation practices. These factors maintain high groundwater levels, facilitate salt migration and accumulation under evaporation, and create distinct hydrochemical signatures characteristic of valley hydrogeological systems.

4. Conclusions

1) Phreatic water in the Ulungur River watershed is weakly alkaline, with Ca^{2+} and Na^{+} as dominant cations and ${SO_4}^{2-}$ and ${HCO_3}^{-}$ as dominant anions.
2) Hydrochemical types evolve systematically from the piedmont bedrock area through the intermontane valley to the lacustrine plain: $HCO_3 \cdot SO_4$-$Ca \cdot Na \rightarrow SO_4 \cdot HCO_3$-$Na \cdot Ca \rightarrow SO_4$-$Na \cdot Ca \rightarrow SO_4 \cdot Cl$-$Na \cdot Ca$.
3) Groundwater chemistry is primarily controlled by evaporation crystallization and rock weathering, with additional influences from ion exchange and leaching processes that vary across geomorphological units, demonstrating typical valley hydrogeological characteristics.
4) Climate change and land use practices significantly impact hydrochemical evolution, with intensified water cycling and irrigation activities accelerating salt migration and spatial differentiation in the plain areas.

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