Chemical Characteristics and Genesis Analysis of Shallow Groundwater in Shihezi City (Postprint)

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Abstract

To investigate the hydrochemical characteristics and genesis of groundwater in Shihezi City, Xinjiang, descriptive statistics and Piper diagrams were used to statistically analyze the major ion compositions and hydrochemical types of 19 phreatic water and 25 shallow confined water samples in the study area, while Schoeller diagrams, Gibbs diagrams, and ion ratio diagrams were applied to analyze the main factors controlling the formation of groundwater hydrochemical characteristics. The results show that shallow groundwater in Shihezi City is weakly alkaline with low mineralization, and the hydrochemical types are dominated by HCO3-Ca and HCO3·SO4-Ca, followed by HCO3·SO4-Na. The hydrochemical characteristics of phreatic water are primarily controlled by rock weathering and infiltration recharge of evaporatively concentrated surface water, whereas rock weathering is the dominant factor influencing the hydrochemical characteristics of shallow confined water. A small proportion of Ca2+ and Mg2+ in groundwater originates from carbonate dissolution, part of the Ca2+ is derived from sulfate dissolution, and Na+ and Cl- mainly come from halite dissolution. The negative correlation between γ(Na+-Cl-) and γ(Ca2++Mg2+)-γ(HCO3-+SO42+) demonstrates that cation exchange also constitutes an important process in the formation of chemical components in shallow groundwater.

Full Text

Hydrochemical Characteristics and Genesis Analysis of Shallow Groundwater in Shihezi City

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Abstract: To investigate the hydrochemical characteristics and genesis of groundwater in Shihezi City, Xinjiang, we conducted a comprehensive analysis of 19 phreatic water samples and 25 shallow confined water samples. Descriptive statistics and Piper trilinear diagrams were employed to analyze the major ionic compositions and hydrochemical types, while Schoeller diagrams, Gibbs diagrams, and ion ratio diagrams were used to identify the primary factors controlling groundwater chemistry. The results indicate that shallow groundwater in Shihezi is weakly alkaline with low salinity. The predominant hydrochemical types are HCO_3-Ca, followed by $HCO_3 \cdot SO_4$-Ca and $HCO_3 \cdot SO_4$-Na. Phreatic water chemistry is primarily controlled by rock weathering and infiltration of evaporatively concentrated surface water, whereas shallow confined groundwater chemistry is mainly influenced by rock weathering. Groundwater ions originate primarily from evaporite dissolution: Ca^{2+} is partly derived from carbonate dissolution and partly from sulfate dissolution, while Cl^- mainly comes from halite dissolution. A significant negative correlation between $\gamma(Na^+ + K^+ - Cl^-)$ and $\gamma(Ca^{2+} + Mg^{2+} - HCO_3{}^- - SO_4{}^{2-})$ demonstrates that cation exchange constitutes another important mechanism in the formation of shallow groundwater chemistry.

Keywords: shallow groundwater; hydrochemical characteristics; genesis analysis; Shihezi City

Introduction

Hydrochemical characteristics represent the long-term interaction between the hydrological cycle and surrounding environments. Analyzing groundwater hydrochemical features and their genesis provides an effective method for understanding groundwater recharge sources and evolution processes, serves as an important pathway for comprehending regional groundwater system circulation and renewal pathways, and offers technical support for groundwater source protection [1,4-8]. Commonly employed methods include analysis of groundwater chemical components [1,4-8], Piper diagrams, Gibbs diagrams, and ion ratio diagrams [1,4-8]. For instance, Sun et al. [5] used Piper and Gibbs diagrams to analyze hydrochemical types in Bachu County, Xinjiang, employing the Gibbs diagram to reflect the relative influence of evaporation concentration, rock weathering, and atmospheric precipitation on hydrochemical components, and utilizing the ratio of saturation index to ion ratio to determine mineral dissolution and precipitation trends under evaporation concentration. Zhang et al. [6] analyzed hydrochemical characteristics and controlling factors in the Hamatong River basin through statistical methods and Piper diagrams. Jiang et al. [1] examined shallow groundwater chemistry and its genesis in the Pinggu plain area of Beijing using Piper and Schoeller diagrams.

From economic and resource utilization perspectives, deep confined groundwater in the study area is unsuitable for conventional exploitation. Consequently, shallow groundwater serves as the primary water source for industrial, agricultural, and domestic use in Shihezi City. However, due to economic development and population growth, water quality in the Manas River has deteriorated, and unregulated management of agricultural wells has enhanced hydraulic connectivity between aquifers [9]. Various anthropogenic and natural factors have caused continuous groundwater environmental degradation and intensified supply-demand conflicts. Hydrochemical analysis can provide scientific basis for rational water resource development. This study employs descriptive statistics, Piper diagrams, Schoeller diagrams, Gibbs diagrams, and ion ratio diagrams to analyze the composition and sources of major ions (K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-) in shallow groundwater, thereby elucidating the hydrochemical characteristics and formation mechanisms.

1 Study Area and Data Processing

1.1 Study Area Overview

Shihezi City is located in the northwest inland arid region of China, on the middle section of the northern Tianshan Mountains piedmont and the southern margin of the Gurbantünggüt Desert, characterized by a continental arid climate [10]. The terrain generally slopes from south to north with an average elevation of 450.8 m. The piedmont zone comprises a single phreatic aquifer with water table depths of 15–80 m and lithology consisting of cobbles and gravel, representing a relatively water-rich zone suitable for exploitation. All phreatic water samples in this study were collected from this single-structure aquifer. North of the single-structure phreatic zone lies a multi-layer confined aquifer system. Previous studies indicate that phreatic water quality in the multi-layer structure zone is extremely poor and generally not considered an exploitable aquifer. Therefore, this study focuses exclusively on confined water in this zone, defining shallow confined water as having well depths $ $100 m based on hydrogeological conditions and local exploitation practices. Shallow confined water tables occur at depths of 5–15 m, with upper aquifer lithology of gravelly cobbles and lower lithology comprising gravel, sandy gravel, or sand layers [11]. Research by Dong et al. [12] demonstrates that groundwater recharge in Shihezi relies primarily on surface water leakage, farmland irrigation infiltration, and precipitation, while discharge occurs mainly through artificial extraction and lateral outflow. Over decades of development, both hydrochemical characteristics and recharge-discharge patterns have undergone substantial changes.

1.2 Data Processing

Groundwater sampling points were established according to the Specification for Regional Groundwater Contamination Investigation and Evaluation (DZ/T 0288-2015) [13], with one sampling point per 100 km^2 in plain areas. A total of 44 samples were collected, including 19 phreatic and 25 shallow confined water samples. Sampling, preservation, and transport strictly followed the Technical Specifications for Environmental Monitoring of Groundwater (HJ/T 164-2004) [14]. The Xinjiang Bureau of Geology and Mineral Resources No. 2 Hydrogeology and Engineering Geology Party Laboratory conducted the analyses: pH was measured in situ using a glass electrode; K^+ and Na^+ were determined by flame atomic absorption spectrophotometry; Ca^{2+} and Mg^{2+} by EDTA titration; Cl^- by silver nitrate volumetric method; ${SO_4}^{2-}$ by barium sulfate turbidimetry; and ${HCO_3}^-$ by hydrochloric acid titration, with detection limits of 0.05 $mg \cdot L^{-1}$ for all ions. Data reliability was verified using anion-cation balance tests, confirming all data as reliable. Descriptive statistics were performed using Excel, and figures were produced using Origin and Grapher software.

2 Groundwater Hydrochemical Characteristics

2.1 Statistical Characteristics of Groundwater Chemical Components

pH reflects important hydrogeochemical equilibrium information. Phreatic water pH ranges from 7.27 to 8.34 with a mean of 7.78 and coefficient of variation of 4.05%; shallow confined water pH ranges from 7.06 to 8.35 with a mean of 7.69 and coefficient of variation of 3.58%. Groundwater in the study area is predominantly weakly alkaline with minimal spatial variation in acidity-alkalinity.

Total hardness (TH) reflects Ca^{2+} and Mg^{2+} concentrations. Phreatic water TH ranges from 81.1 to 1076.0 $mg \cdot L^{-1}$ (mean: 312.0 $mg \cdot L^{-1}$), comprising 15.8% soft water (\$ $75 mg \cdot L^{\{-1\}), 68.4}$\{-1\}), $10.5^{\{-1\}), and 5.3}$\{-1\}). $Shallow confined water TH ranges from 77.5 to 784.4 mg \cdot L$^{-1}\$ (mean: 273.0 $mg \cdot L^{-1}$), with 28.0% soft water, 24.0% moderately hard water, 36.0% hard water, and 12.0% very hard water.

Total dissolved solids (TDS) evaluate total salt content. Shallow groundwater TDS ranges from 150.0 to 2400.3 $mg \cdot L^{-1}$, with 90.9% freshwater (\$ $1 g \cdot L^{\{-1\}) and 9.1}$\{-1\}). $Based on mean anion concentrations, cations are dominated by Ca$^{2+}\$ and Na^+, while anions are dominated by ${HCO_3}^-$ and ${SO_4}^{2-}$, with concentrations far exceeding other ions.

The Schoeller diagram is a traditional yet still widely used method for visualizing concentration variations of major ions across numerous samples. Figure 2 [Figure 2: see original paper] reveals that both phreatic and confined water samples exhibit two distinct chemical evolution trends, indicating spatial differences in recharge sources between the piedmont single-structure phreatic aquifer and the multi-layer confined aquifer north of it. According to convection principles, sample points with higher ion concentrations may migrate along the flow path toward points with relatively lower concentrations.

2.2 Hydrochemical Type Characteristics

Piper diagrams plot ion percentages to visualize relationships between major anions and cations. Figure 3 [Figure 3: see original paper] shows similar distribution patterns for phreatic and shallow confined water, with cations concentrated near the Ca^{2+} axis (indicating high Ca^{2+} proportions) and anions concentrated near the HCO_3^- axis (indicating high HCO_3^- proportions, followed by SO_4^{2-}). Consequently, the primary hydrochemical types are HCO_3-Ca, followed by $HCO_3 \cdot SO_4$-Ca and $HCO_3 \cdot SO_4$-Na. Previous studies using the Shukarev classification method and Piper diagrams have similarly identified HCO_3-Ca and $HCO_3 \cdot SO_4$-Ca as the dominant types in Shihezi [15], indicating that the major hydrochemical types have remained essentially unchanged over the past decade.

3 Analysis of Influencing Factors

3.1 Evaporation Concentration

Gibbs diagrams identify major factors controlling groundwater chemical evolution: evaporation concentration, rock weathering, and atmospheric precipitation [18]. Shihezi groundwater TDS ranges from 150.0 to 2400.3 $mg \cdot L^{-1}$, concentrated in the 100–1000 $mg \cdot L^{-1}$ range. Both phreatic and shallow confined water samples plot in the middle-upper portion of the Gibbs diagram (Figure 4 [Figure 4: see original paper]). Dong et al. [10] reported annual precipitation of 180–270 mm and evaporation of 1000–1500 mm in Shihezi, with precipitation far less than evaporation. This indicates that rock weathering and infiltration of evaporatively concentrated surface water are the two main factors affecting phreatic water chemistry, while atmospheric precipitation has minimal influence. A few sampling points fall outside the typical Gibbs range, suggesting additional impacts from human activities [19].

3.2 Mineral Dissolution and Precipitation

3.2.1 Saturation Index Analysis Atmospheric precipitation leaches minerals from bedrock, forming chemically distinct surface water or bedrock fissure water. Due to varying CO_2 contents and water-rock interaction durations, carbonate and evaporite weathering degrees differ, altering groundwater chemistry accordingly [20]. The saturation index (SI) method identifies mineral dissolution or precipitation states. When $SI > 0$, minerals are supersaturated and tend to precipitate; $SI = 0$ indicates equilibrium; $SI < 0$ indicates undersaturation and continued dissolution.

Table 2 shows that calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), gypsum ($CaSO_4 \cdot 2H_2O$), and halite (NaCl) have similar mean SI values in both phreatic and shallow confined water, indicating comparable dissolution capacities in both aquifer types. Calcite SI ranges from -0.18 to 1.00 in phreatic water and -0.54 to 1.05 in shallow confined water, with 90.9% of samples showing supersaturation. Dolomite SI ranges from -0.58 to 1.58 (phreatic) and -1.39 to 1.84 (confined), with 79.6% in precipitation state. Gypsum and halite SI values are consistently <0, indicating undersaturation and continuous dissolution, particularly for halite with SI generally «0 and rapid dissolution rates.

3.2.2 Ion Ratio Analysis Ion ratios reflect contributions of different rock weathering processes to chemical composition. When $\gamma(Cl^-)/\gamma(HCO_3^- + SO_4^{2-}) > 1$, evaporite dissolution dominates; when <1, carbonate dissolution prevails [21]. Most groundwater samples plot above the 1:1 line (Figure 6a [Figure 6: see original paper]), indicating evaporite dissolution as the primary Cl^- source.

The ratio $\gamma(Ca^{2+} + Mg^{2+})/\gamma(HCO_3^-)$ distinguishes Ca^{2+} and Mg^{2+} sources: values >1 suggest evaporite or calcium-magnesium silicate dissolution, while values <1 indicate carbonate dissolution [22]. Most samples plot below the 1:1 line (Figure 6b [Figure 6: see original paper]), indicating Ca^{2+} and Mg^{2+} primarily originate from evaporite or calcium-magnesium silicate dissolution.

The ratio $\gamma(Na^+ + K^+)/\gamma(Cl^-)$ identifies Na^+ and K^+ sources: values >1 indicate Na^+ and K^+ released from silicate weathering, while values <1 suggest evaporite dissolution [23]. Most samples plot below the 1:1 line (Figure 6c [Figure 6: see original paper]), indicating Na^+ and K^+ mainly derive from evaporite dissolution. In summary, groundwater ions in the study area originate from evaporite and calcium-magnesium silicate dissolution.

3.3 Cation Exchange

When $\gamma(Na^+ + K^+ - Cl^-)$ negatively correlates with $\gamma(Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-})$, cation exchange occurs [2,24]. Groundwater samples show a significant negative correlation between these parameters (Figure 6d [Figure 6: see original paper]), confirming that cation exchange represents another important mechanism in shallow groundwater chemical evolution.

3.4 Human Activity Impact

In 2005, the main exploited aquifer in Shihezi contained primarily freshwater and slightly brackish water, with NO_3^- averaging 6.62 $mg \cdot L^{-1}$. By 2015, shallow groundwater NO_3^- averaged 12.2 $mg \cdot L^{-1}$, showing a clear increasing trend [25]. This rise is attributed to infiltration of industrial wastewater in development zones and extensive application of pesticides and fertilizers in agricultural areas. Nitrogen from fertilizers that is not absorbed by crops or adsorbed by soil colloids percolates with soil water, significantly increasing NO_3^- concentrations [26].

4 Conclusions

1) The piedmont zone comprises a single-structure phreatic aquifer, north of which lies a multi-layer confined aquifer system. Shallow groundwater (including single-structure phreatic and shallow confined water) is weakly alkaline with low salinity, dominated by Ca^{2+} and Na^+ cations and HCO_3^- and SO_4^{2-} anions. The primary hydrochemical types are HCO_3-Ca and $HCO_3 \cdot SO_4$-Ca.

2) Phreatic water chemistry is controlled by both rock weathering and infiltration of evaporatively concentrated surface water, while shallow confined groundwater chemistry is primarily controlled by rock weathering. Major ions originate from evaporite dissolution: Cl^- mainly comes from halite dissolution, only minor Ca^{2+} derives from carbonate dissolution, and some Ca^{2+} originates from sulfate dissolution.

3) A significant negative correlation between $\gamma(Na^+ + K^+ - Cl^-)$ and $\gamma(Ca^{2+} + Mg^{2+} - HCO_3{}^- - SO_4{}^{2-})$ indicates that cation exchange also plays a crucial role in shallow groundwater chemical evolution.

4) Long-term monitoring data reveal increasing $NO_3{}^-$ concentrations in shallow groundwater, reflecting impacts from industrial wastewater, agricultural fertilizers, and other human activities.

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