Hydrochemical Characteristics and Genesis of Groundwater in the Daihai Basin (Postprint)

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Abstract

The shrinking area and deteriorating water quality of Daihai Lake have severely impacted regional ecological and environmental security. Through hydrogeological investigation, water sampling, and hydrochemical analysis methods including statistical analysis, Shukarev classification, mineral saturation index, ion ratio analysis, and chlor-alkali index, this study investigates the hydrochemical characteristics and genesis of groundwater in the Daihai Basin to reveal the primary factors influencing the evolution of the regional groundwater environment. The results demonstrate: (1) Groundwater in the Daihai Basin is weakly alkaline, predominantly featuring HCO3-Ca·Mg type water; from the basin margin to Daihai Lake, the hydrochemical type transitions from HCO3-Ca to Cl-Na, while the controlling processes shift from leaching to evaporation concentration. (2) Groundwater hydrochemical composition is primarily controlled by leaching, ion exchange, desulfurization, and anthropogenic activities, wherein dissolution and precipitation of carbonate minerals, silicate minerals, gypsum, and rock salt exert significant influences on groundwater chemistry. (3) NO-3 -N content is affected by anthropogenic activities such as nitrogen fertilizer application and livestock and human manure discharge; groundwater occurrence characteristics significantly influence the vertical distribution of NO-3 -N concentration.

Full Text

Preamble

Hydrochemical Characteristics and Genesis of Groundwater in the Daihai Basin

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Abstract: The Daihai Lake area is shrinking daily and its water quality is deteriorating, posing a serious threat to regional ecological and environmental security. Through hydrogeological surveys and water sample collection, combined with hydrochemical analysis methods including statistical analysis, Shukarev classification, mineral saturation indices, ion ratio analysis, and chlor-alkali indices, this study investigates the hydrochemical characteristics and genesis of groundwater in the Daihai Basin to reveal the main factors controlling the evolution of the regional groundwater environment. The results show that: (1) Groundwater in the Daihai Basin is weakly alkaline, with HCO_3-Ca · Mg type as the dominant hydrochemical type; from the basin margin to Daihai Lake, the hydrochemical type transitions from HCO_3-Ca to Cl-Na, with the controlling process shifting from leaching to evaporation concentration. (2) Groundwater chemical composition is primarily controlled by leaching, ion exchange, desulfurization, and anthropogenic activities, among which the dissolution and precipitation of carbonate minerals, silicate minerals, gypsum, and rock salt have significant impacts on groundwater chemistry. (3) Nitrogen content is influenced by human activities such as nitrogen fertilizer application and livestock manure discharge; groundwater occurrence characteristics significantly affect the vertical distribution of NO_3^--N concentrations.

Keywords: Groundwater; Hydrochemical characteristics; Water-rock interaction; Daihai Basin

Introduction

Groundwater, characterized by its wide distribution, easy accessibility, and good water quality, often serves as a crucial water supply source in arid and semi-arid regions. Investigating groundwater hydrochemical characteristics not only reveals regional groundwater evolution patterns but also provides important guidance for sustainable water resource utilization. Inland lakes in arid regions are typically closed systems, receiving recharge primarily from precipitation, surface runoff, and subsurface flow, with evaporation as the main discharge mechanism. Due to water scarcity and surface water interception, groundwater quantity and quality significantly influence lake water balance through hydraulic exchange, consequently affecting lake water level, area, and quality.

Groundwater hydrochemical features are influenced by multiple factors including climate, topography, aquifer lithology, water-rock interactions, and human activities. In mountainous basins of arid regions, groundwater chemical types generally transition from low-salinity HCO_3-Ca type water in piedmont alluvial-pluvial fan areas with rapid flow and strong leaching, to Cl-Na type water in central plain areas where fine-grained media, shallow water tables, and evaporation concentration dominate. In flat plain areas with shallow water tables, groundwater quality is vulnerable to human impacts, such as elevated nitrogen concentrations from agricultural activities, increased downward leakage from confined water exploitation, and contamination from municipal waste and wastewater. Clarifying groundwater evolution under combined natural and anthropogenic influences, particularly the role of human activities, is essential for regional water resource protection and development.

Daihai Lake, the third largest inland lake in Inner Mongolia, covers an area of 56.7 km^2 and plays a vital role in maintaining regional ecological stability. In recent years, due to combined natural and anthropogenic disturbances, the lake area has been shrinking continuously while water quality deteriorates. As a closed lake, Daihai receives recharge from precipitation, seasonal mountain floods, and groundwater, with evaporation as the primary discharge pathway. Since evaporation far exceeds precipitation and reservoir construction has minimized surface water recharge, groundwater's influence on Daihai's water quantity and chemistry has become increasingly significant.

Current research on the Daihai Basin has focused on ecological restoration, climate change, and surface water quantity and chemistry, with limited studies on regional groundwater hydrochemistry. Existing research indicates close connections between regional groundwater and river water, with river composition primarily controlled by silicate weathering and dissolution. This study focuses on groundwater hydrochemical characteristics and genesis to reveal the main controlling factors and evolution patterns, providing a scientific basis for water resource protection and rational utilization in the Daihai Basin.

1.1 Study Area Overview

The Daihai Basin (112°21 -112°54 E, 40°11 -40°50 N) is located in Liangcheng County, Ulanqab City. The region has a mid-temperate continental monsoon climate with an average annual temperature of 5.6°C. Mean annual precipitation and evaporation are 395 mm and 1820 mm, respectively, with precipitation concentrated in June–August, accounting for 70% of the annual total. Major rivers include Tiancheng, Buliang, Wuhao, and Gongba, which produce floods during rainy seasons.

The basin is surrounded by mountains with alluvial-pluvial and lacustrine plains in the center, where Daihai Lake occupies the lowest elevation. In the northern low mountain-hill area, aquifers consist primarily of Archean gneiss and Jurassic volcanic clastic rocks, with mineral composition dominated by feldspar, quartz, and minor mica, yielding single-well discharge of 100–500 m^3/d. The phreatic aquifer north of Daihai Lake consists of Cretaceous and Neogene sandstone, conglomerate, and sandy conglomerate, dominated by feldspar and quartz, with burial depth of 30–40 m and single-well yield of 50–60 m^3/d. The central alluvial-pluvial and lacustrine plain phreatic aquifer comprises Quaternary sandy soil with feldspar, calcite, gypsum, and rock salt, yielding less than 100 m^3/d near Daihai. The eastern phreatic aquifer is dominated by sand with feldspar, quartz, aragonite, and minor chrysotile and sepiolite, yielding 100–300 m^3/d. The southern basalt platform area has aquifers of porous, fractured basalt interbedded with massive basalt, yielding less than 1000 m^3/d. Groundwater recharge occurs through precipitation infiltration, mountain-front lateral inflow, and valley recharge during wet seasons, while discharge occurs via evaporation and artificial extraction.

1.2 Sample Collection and Measurement

In July 2019, 34 sampling sites were established in the Daihai Basin, including 17 unconfined water sites, 16 confined water sites, and 1 lake water site. Groundwater sampling points were domestic wells or centralized water supply wells, with depths ranging from 5-80 m. All sites were located using GPS, and well depth information was obtained from owners. Field measurements of pH, temperature, and total dissolved solids (TDS) were conducted using portable meters after continuous pumping until stable readings were achieved.

In the laboratory, soluble Na^+ and K^+ were analyzed by flame photometry; Ca^{2+} and Mg^{2+} by EDTA titration; Cl^- by argentometric titration; ${SO_4}^{2-}$ by barium titration; ${HCO_3}^-$ by acid-base titration; Fe^{3+} by thiocyanate spectrophotometry; ${NO_3}^-$ by phenoldisulfonic acid spectrophotometry; fluoride by alizarin complexone colorimetry; Fe^{2+}, Mn, and Zn by flame atomic absorption spectrometry; As and Hg by hydride generation atomic fluorescence spectrometry; Cr^{6+} by diphenylcarbazide spectrophotometry; and chemical oxygen demand by acidic permanganate oxidation. Anion-cation balance verification showed relative errors within \$±\$5%, confirming data reliability.

1.3 Data Analysis Methods

SPSS 26.0 software was used for descriptive statistics of ion concentrations. The Shukarev classification method categorized hydrochemical types, while ion concentration ratios, chlor-alkali indices, and mineral saturation indices analyzed controlling factors under different mechanisms. Surfer 8 generated contour maps for spatial distribution analysis. The coefficient of variation (Cv), calculated as the ratio of standard deviation to mean, measured data dispersion. Nitrate concentrations were evaluated against Class III water standards (20 $mg \cdot L^{-1}$ ${NO_3}^-$-N) specified in GB/T 14848-2017.

2.1 Statistical Analysis of Hydrochemical Characteristics

Monitoring results (Table) show Daihai Lake has a mean TDS concentration of 11,683.1 $mg \cdot L^{-1}$ and is alkaline. As a closed lake under long-term evaporation concentration, Daihai has become a saline lake.

Regional groundwater is generally weakly alkaline. Unconfined water has an average TDS of 383.7 $mg \cdot L^{-1}$ (range: 157.5–1168.0 $mg \cdot L^{-1}$), while confined water averages 386.0 $mg \cdot L^{-1}$ (range: 229.0–950.0 $mg \cdot L^{-1}$). The dominant cation in both unconfined and confined water is Ca^{2+}, and the dominant anion is HCO_3^-. The Cv values for NO_3^--N in unconfined and confined water are 1.83 and 1.42, respectively, indicating substantial spatial variation. With developed agriculture and animal husbandry, fertilizer application, animal manure, and domestic sewage constitute major nitrate sources. Among collected samples, 58.8% of unconfined water and 29.4% of confined water exceeded the Class III standard for nitrate. While groundwater nitrate concentrations are elevated, lake water nitrate is low, likely because Daihai is in a strongly reducing environment with intense denitrification where nitrate cannot persist stably.

2.2 Regional Groundwater Chemical Types and Zoning

Shukarev classification reveals that HCO_3-Ca · Mg type water dominates both unconfined and confined groundwater (Table). Among unconfined water samples, 7 are HCO_3-Ca · Mg type, 4 are HCO_3-Ca type, 2 are HCO_3 · Cl-Ca · Na type, 2 are HCO_3 · Cl-Ca · Mg type, 1 is HCO_3 · SO_4-Mg · Ca type, and 1 is HCO_3-Na · Ca type. Among confined water samples, 9 are HCO_3-Ca · Mg type, 4 are HCO_3-Ca type, 2 are HCO_3-Ca · Na type, and 1 is HCO_3 · Cl-Na type. Daihai Lake water is Cl-Na type.

Due to variations in topography, aquifer lithology, and groundwater flow conditions, groundwater chemical types show distinct formation and spatial distribution patterns. Along the flow direction, hydrochemical components change systematically. Both unconfined and confined water exhibit clear zonation from the piedmont alluvial fan to the basin center (Figure [Figure 2: see original paper]). At the fan apex (elevation 1300–1400 m, water table depth 10–30 m), HCO_3-Ca type water prevails with leaching as the dominant process. In the middle fan (elevation 1250–1300 m, depth 5–10 m), HCO_3-Ca · Mg type dominates, with TDS of 270–350 $mg \cdot L^{-1}$. At the fan margin and central basin (elevation 1200–1250 m, depth <5 m), fine-grained silt layers facilitate concentration processes, increasing Cl^- and Na^+ content. As the ultimate discharge area, groundwater converges at Daihai Lake where intense evaporation forms Cl-Na type water with TDS reaching 11,683 $mg \cdot L^{-1}$. Based on similarities in hydrochemical types and major ion concentrations between unconfined and confined water, these aquifers likely have close hydraulic connections.

2.3.1 Dissolution-Filtration Action

Mineral saturation indices (SI) indicate dissolution-precipitation states. Most groundwater samples show chrysotile and sepiolite dissolution (SI < 0). For calcite and aragonite, 76.5% and 47.1% of samples show precipitation trends (SI > 0.5), though precipitation amounts are minimal (SI < 1). For dolomite, 67.6% of samples show precipitation (SI > 0.5). All samples show gypsum and rock salt in undersaturated states (SI < 0), indicating active dissolution. The SI calculations involve uncertainties; values between -0.5 and 0.5 generally represent dissolution equilibrium.

The $\gamma(SO_4^{2-} + HCO_3^-)/\gamma(Na^+ + K^+ + Ca^{2+} + Mg^{2+})$ ratio indicates silicate dissolution dominance when « 1. Most samples show ratios far « 1, suggesting silicate weathering as the primary water-rock interaction. Correlation analysis (Table) shows $\gamma(Na^+)/\gamma(Cl^-)$ and $\gamma(SiO_2)$ are highly correlated (r = 0.83 and 0.82, respectively), indicating Na^+ sources include both rock salt dissolution and albite weathering. The reaction is: $(Na/Mg/Ca/K)_2SiO_4 + H_2CO_3 \rightarrow H_4SiO_4 + 2Na^+ + {CO_3}^{2-}$.

Comprehensive analysis of mineral saturation indices, correlations, and ion ratios reveals that carbonate minerals (calcite, dolomite, aragonite), silicate minerals (chrysotile, sepiolite, albite), gypsum, and rock salt dissolution-precipitation significantly influence groundwater chemistry. Dissolution of silicate minerals, rock salt, and gypsum constitutes the dominant water-rock interactions.

2.3.2 Ion Exchange Action

The $\gamma((Na^+ + K^+) - Cl^-)/\gamma({SO_4}^{2-} + {HCO_3}^-)$ ratio verifies cation exchange occurrence. Most samples plot near the 1:1 line (Figure [Figure 4: see original paper]), indicating significant cation exchange. Chlor-alkali indices ($CAI\text{-}1 = (Cl^- - (Na^+ + K^+))/Cl^-$; $CAI\text{-}2 = (Cl^- - (Na^+ + K^+))/({SO_4}^{2-} + {HCO_3}^- + {CO_3}^{2-} + {NO_3}^-)$) determine exchange direction. Negative values indicate forward cation exchange (groundwater $Ca^{2+} + Mg^{2+}$ replace aquifer Na^+), while positive values indicate reverse exchange. Most samples show negative CAI-1 and CAI-2, confirming forward cation exchange, though sites DQ-07, DQ-09, and DQ-15 show positive values, indicating localized reverse exchange. Thus, Na^+ content is primarily controlled by feldspar dissolution and cation exchange, while Ca^{2+} and Mg^{2+} are influenced by carbonate and gypsum dissolution and ion exchange.

2.3.3 Desulfurization Action

The $\gamma({SO_4}^{2-})/\gamma(Cl^-)$ ratio indicates desulfurization intensity; lower ratios signify stronger desulfurization that reduces ${SO_4}^{2-}$ and increases ${HCO_3}^-$. Half the samples show $\gamma({SO_4}^{2-})/\gamma(Cl^-) < 0.5$ (Figure [Figure 4: see original paper]), indicating strong desulfurization, particularly at sites DQ-07, DQ-09, DQ-15, DS-08, and DS-16 with deep water tables.

2.3.4 Anthropogenic Activities

While regional groundwater chemistry is controlled by hydrogeological processes, severe nitrogen pollution occurs locally in unconfined water due to human activities. Hydraulic connections between unconfined and confined water cause water quality deterioration in confined aquifers as well.

Spatial distribution maps (Figure [Figure 5: see original paper]) show nitrate concentration exceedances in both unconfined and confined water concentrated around Daihai Town in the southern lake area. This region features extensive flat terrain, widespread farmland, and high population density, resulting in stronger anthropogenic impacts. Excessive nitrogen fertilizer application, domestic sewage discharge, and livestock manure are nitrate pollution sources. The shallow Quaternary unconfined aquifer with permeable vadose zone and oxidizing conditions facilitates nitrate accumulation. Due to discontinuous and thin aquitards, close hydraulic connections exist between unconfined and confined water, causing downward nitrate migration. The relatively isolated confined water environment with lower redox potential enables denitrification, resulting in significantly lower nitrate concentrations than in unconfined water. Thus, groundwater occurrence characteristics markedly influence the vertical distribution of NO_3^--N concentrations.

3 Conclusions

(1) Daihai Lake is a slightly saline alkaline lake with mean TDS of 11,683.1 $mg \cdot L^{-1}$. Lake water originates from atmospheric precipitation, seasonal mountain floods, and groundwater. As lake area shrinks and reservoirs intercept surface water, groundwater' s contribution to lake recharge is increasing.

(2) Basin groundwater is generally weakly alkaline. Both unconfined and confined water have Ca^{2+} as the dominant cation and HCO_3^- as the dominant anion, with average TDS of 383.7 $mg \cdot L^{-1}$ and 386.0 $mg \cdot L^{-1}$, respectively.

(3) The dominant hydrochemical type is HCO_3-Ca · Mg, transitioning from HCO_3-Ca at the basin margin to Cl-Na toward Daihai Lake, with controlling processes shifting from leaching to evaporation concentration. Similarities in hydrochemical types and major ion concentrations between unconfined and confined water suggest close hydraulic connections.

(4) Groundwater chemistry is primarily controlled by leaching, ion exchange, and desulfurization. Carbonate minerals (calcite, dolomite, aragonite), silicate minerals (chrysotile, sepiolite, albite), gypsum, and rock salt dissolution-precipitation significantly influence groundwater composition. Silicate, rock salt, and gypsum dissolution are the dominant water-rock interactions. Na^+ is also affected by feldspar dissolution and cation exchange; SO_4^{2-} is influenced by gypsum dissolution and desulfurization; NO_3^--N is impacted by agricultural nitrogen fertilizers and livestock manure.

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