

Seasonal variation in groundwater quality along the Kherlen river valley

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ABSTRACT

In this study, 176 groundwater samples were collected along the floodplain of the Kherlen River to assess seasonal variations in groundwater quality. Sampling was conducted three times: twice during the spring and once during the autumn. The analysis included the use of a Piper diagram, a Gibbs diagram, and correlation analysis to evaluate temporal and spatial variations in groundwater hydrochemistry. The results revealed significant seasonal fluctuations in the concentrations of HCO_3^- , Ca^{2+} , Na^+ , Fe , F^- , and NO_3^- , with more pronounced spatial variations during the spring due to the dilution effect of precipitation. In both seasons, the majority of groundwater samples were classified under the Ca-HCO_3 hydrochemical type, while a few samples were identified as Na-HCO_3 and Mixed-HCO_3 types. The findings indicated that the groundwater in the study area mainly originated from rock-water interactions, with only a few samples linked to evaporation mechanisms. High $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ratios and low $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ ratios suggest that groundwater chemistry is primarily influenced by the weathering of carbonate and silicate minerals. Additionally, cation exchange processes, specifically the replacement of Ca^{2+} by Na^+ , were found to actively contribute to the hydrogeochemical evolution of the aquifer system. Correlation analysis further demonstrated that groundwater salinity is predominantly controlled by dissolved ions, as evidenced by strong positive correlations between EC and TDS. Significant associations among major ions, including Ca^{2+} , Mg^{2+} , Na^+ , and HCO_3^- , highlight the influence of geochemical processes such as dolomite dissolution and the weathering of sodium-rich minerals. The positive correlation between nitrate and $\text{Ca}^{2+}/\text{Mg}^{2+}$, along with its negative correlation with HCO_3^- , points to anthropogenic impacts-particularly from agricultural inputs-as significant contributors to groundwater contamination. These findings underscore the need for improved land and water management practices to safeguard groundwater quality in the region.

KEYWORDS

Water quality, Hydrochemistry, Water-rock Interaction

1. INTRODUCTION

Groundwater is a vital resource that plays a significant role in addressing water scarcity challenges worldwide, particularly in semi-arid and arid regions. Its widespread availability and consistent quality make it a reliable source of water supply [1]. Moreover, groundwater is a renewable natural resource and represents a valuable source of freshwater, sustained by the functions of the hydro-ecosystem [2].

Compared to surface water, groundwater is more widely utilized for drinking water supply due to its lower exposure to external environmental influences [3]. However, groundwater remains vulnerable to the impacts of both natural processes and human activities. In particular, groundwater quality is affected by a range of factors, including geochemical characteristics (such as petrographic composition and rock weathering), climatic conditions (such as precipitation and evaporation), and human activities (such as agricultural irrigation and the discharge of industrial and domestic wastewater). In recent decades, the degradation of groundwater quality has become increasingly evident in many countries and regions, drawing greater attention to its serious environmental and public health consequences [4]. The urbanization, excessive pollutant emissions, and overexploitation of groundwater have accelerated changes in the hydrochemical properties of groundwater [5]. The distribution and quality of water resources across our country vary significantly, with groundwater being used as the primary source of water supply in urban areas. Groundwater is also considered a reliable source of drinking water in terms of quality. Approximately 95% of the population uses groundwater for drinking and domestic purposes, while 5% relies on surface water. The Kherlen River Basin includes 42 soums from six provinces Gobi-Sumber, Dornod, Dornogovi, Khentii, Tuv, and Sukhbaatar along with two districts of Ulaanbaatar city [6].

These concentrated soums and settlements are situated in the valleys of the Kherlen River and its tributaries, where limited groundwater resources along the riverbanks are utilized for drinking, domestic, and industrial water supply [7]. Consuming water that does not meet quality standards regularly poses significant health risks to humans.

Studies by other researchers on the groundwater in the region indicate that the groundwater in the Kherlen River Basin is generally fresh, with low mineralization and hardness. However, instances of the water exceeding drinking water standards, particularly due

to elevated levels of nitrogen and iron ions, are relatively common [6, 7, 8, 9]. Additionally, there is a lack of sufficient data on the temporal and spatial variations of the groundwater's hydrochemical characteristics in the region. The study of seasonal changes in groundwater quality is important to understand what time of year pollution occurs [9]. Therefore, studying the spatial and temporal variations in the hydrochemical characteristics of groundwater provides essential information for understanding changes in water quality, which is crucial for the protection and sustainable use of water resources [4].

Urban areas, livestock farms, agriculture, and large mines are located along the Kherlen River valley. Their water supply is mainly provided by groundwater. In the future, there is a need to conduct detailed groundwater quality studies to protect water resources and prevent pollution. Therefore, this study aimed to show the seasonal changes in groundwater quality and pollution along the Kherlen River.

2. MATERIALS AND METHODS

2.1. Study area

The Kherlen River Basin is located in the eastern part of Mongolia, in the Central and Eastern economic regions, and spans several provinces, including Dornod, Dornogovi, Khentii, Tuv, and Sukhbaatar. The basin is one of the largest river basins in our country, covering 6.9% of Mongolia's land area. The upper part of the Kherlen River basin has a dry, cool climate, while the middle and lower parts of the basin have a dry, warm climate.

The average annual air temperature in the Kherlen River basin is 0.1°C, with an average winter temperature of -20.4°C and an average summer temperature of 18.0°C. The total annual precipitation in the basin is 250 mm. In winter, precipitation is less than 10 mm, whereas in summer (June to August), it reaches 180 mm, accounting for more than 70% of the total annual precipitation [7].

2.2. Geological and Hydrogeological condition

The geological structure of the Kherlen River basin consists of a complex assemblage of sedimentary and metamorphic basement rocks dating back to the Cambrian, Devonian, and Carboniferous periods. These are intruded by deep-seated granitic plutons formed during the Jurassic and Triassic periods. The basement is unconformably overlain by Cretaceous deposits composed of light gray sandstones and

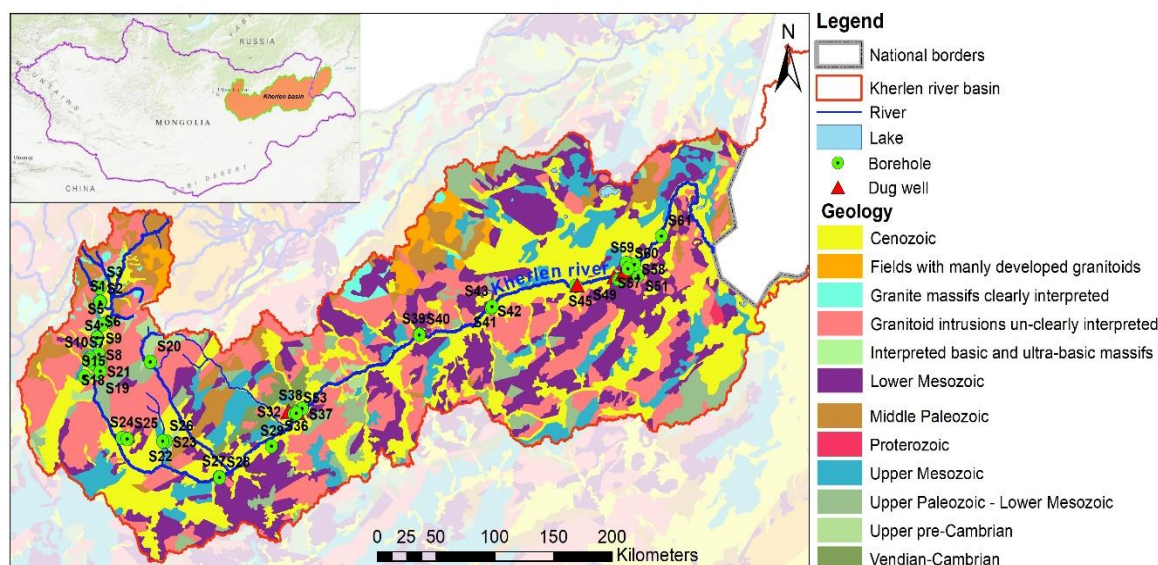


Figure 1. Sampling location of groundwater in the Kherlen River Basin

siltstones. These in turn are overlain by Tertiary continental sediments, including reddish to yellowish-brown gravelly sands, sandy loams, and clayey layers, and capped by Quaternary alluvial and colluvial deposits of sands, gravels, clays, and conglomerates [6, 11].

From a regional hydrogeological perspective, the aquifers within the basin can be classified based on their genesis, lithological composition, and groundwater transmissivity. The most significant aquifers are found within the Holocene and Pleistocene alluvial and lacustrine sediments, which are highly permeable and serve as the principal sources of groundwater. In contrast, aquifer complexes within Neogene and Mesozoic lacustrine deposits are typically located at greater depths and exhibit variable transmissivity, often under semi-confined or confined conditions. Additionally, fractured zones within older sedimentary, metamorphic, igneous, and carbonate rocks—ranging in age from the Paleozoic to the Precambrian—form secondary aquifers with limited storage and low permeability, where groundwater occurrence is primarily controlled by the degree of fracturing and faulting (Figure 1).

2.3. Sampling and Analysis

Sample collection and preservation were carried out in accordance with the MNS ISO5667-3:2018 standard. Several physicochemical parameters such as temperature (T), electrical conductivity (EC), total dissolved solids (TDS), and pH were measured in the field by using portable equipment (HANNA HI98195). Turbidity was measured using by HANNA

HI 93703 portable turbidity meter. General chemical analysis was performed in the Water Analysis Laboratory of the Institute of Geoecology and Geography using titration methods. This included the determination of major ions such as Ca^{2+} , Mg^{2+} , Cl^- , HCO_3^- and CO_3^{2-} . In addition, NO_2^- , NO_3^- , NH_4^+ , Fe^{3+} , SO_4^{2-} concentrations were analyzed using a DR1900 spectrophotometer. Microelement concentrations were determined using the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) at the SGS Mongolia laboratory. The ionic balance error between total cations (Ca^{2+} , Mg^{2+} , Na^+ , Fe^{2+} , and Fe^{3+}) and anions (SO_4^{2-} , NO_3^- , NO_2^- , HCO_3^- , CO_3^{2-} , and Cl^-) was calculated for each sample in milliequivalents per liter (meq/L) using the following formula:

$$\text{ionic balance error} = \frac{\sum(\text{cations}) - \sum(\text{anions})}{\sum(\text{cations}) + \sum(\text{anions})} * 100 \quad (1)$$

The ionic balance error for all samples was within the acceptable limit of $\pm 5\%$. To assess groundwater quality, we used guidelines provided by the Mongolian Agency for Standard and Metrology, Environment, Health protection, Safety, Drinking water. Hygienic requirements, assessment of the quality and safety, Standard MNS 0900:2018 (MNS, 2018) [14]. SPSS software-26 was used to show the minimum, maximum, average and standard deviation values of main physico-chemical parameters, Aqua chem-14 to explain the chemical composition of water, and Origin software-26 to determine water-rock interactions.

3. RESULT

In this study, the minimum, maximum, mean, and standard deviation of the main physico-chemical

parameters of groundwater in the Kherlen River Basin were calculated, with seasonal variation trends (Figure 2). According to Figure 2, all measured parameters exhibited noticeable seasonal variations. The pH values ranged from 5.36 to 7.93 in spring and 5.76 to 7.98 in autumn, with average values of 7.14 and 7.32, respectively, indicating slightly acidic to slightly alkaline conditions. A small percentage of samples (3.3% in spring and 5% in autumn) exceeded the Mongolian national standard (MNS, 2018) range of 6.6–8.5.

Electrical conductivity (EC) values displayed the highest variation, ranging from 128 to 2852.5 $\mu\text{S}/\text{cm}$ in spring and 128 to 2782 $\mu\text{S}/\text{cm}$ in autumn, with average values of 722.2 $\mu\text{S}/\text{cm}$ and 726.03 $\mu\text{S}/\text{cm}$, respectively. The MNS 2018 standard limits EC to 1500 $\mu\text{S}/\text{cm}$ for drinking water; 1.2% and 1.8% of samples exceeded this limit in spring and autumn, respectively. Total Dissolved Solids (TDS) varied from 64 to 1711.5 ppm in spring and 64 to 1669 ppm in autumn, with average values of 416.3 ppm and 417.3 ppm. According to WHO guidelines, TDS levels should not exceed 500 mg/L in drinking water, but 26.7% of spring samples and 31.7% of autumn samples exceeded this threshold (Figure 2).

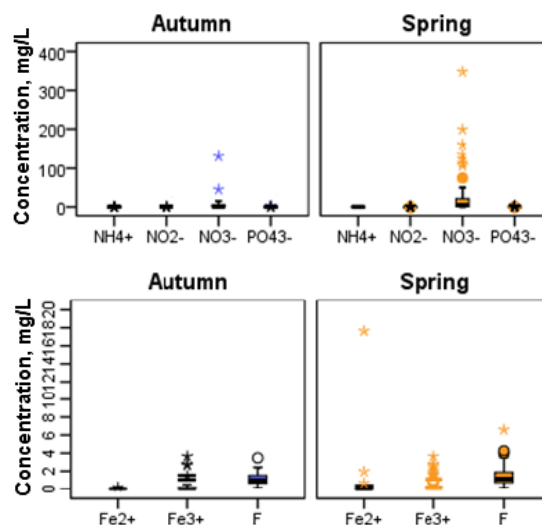
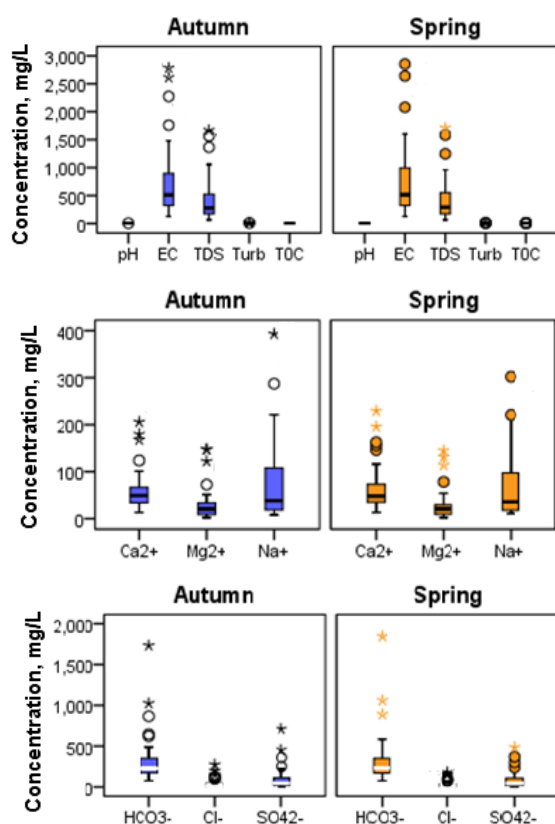


Figure 2. The trend of seasonal variation of water quality parameters in the study area

For cations, the concentration of calcium ions (Ca^{2+}) ranged from 13.0 to 229.3 mg/L in spring and 13.0 to 205.6 mg/L in autumn, with average values of 60.8 mg/L and 57.5 mg/L. According to the MNS 2018 standard, the permissible limit is 100 mg/L; 11.7% of spring samples and 8.33% of autumn samples exceeded this limit. Magnesium ions (Mg^{2+}) varied from 2.4 to 145 mg/L in spring and 2.4 to 148 mg/L in autumn, with average values of 26.7 mg/L and 26.9 mg/L. Elevated Mg^{2+} levels were observed in 23.3% of spring samples and 25% of autumn samples. Sodium (Na^{+}) concentrations ranged from 10.9 to 302.2 mg/L in spring and 8.1 to 393.1 mg/L in autumn, with mean values of 65.74 mg/L and 69.7 mg/L, respectively. In both seasons, 6.7% of the samples exceeded the MNS 2018 limit of 200 mg/L.

For anions, bicarbonate (HCO_3^{-}) concentrations ranged from 76.3 to 1845 mg/L in spring and 76 to 1753 mg/L in autumn. Carbonate (CO_3^{2-}) levels remained low, between 0.0 and 6.0 mg/L. The sulfate (SO_4^{2-}) concentrations varied from 4 to 485 mg/L in spring and 4.2 to 710 mg/L in autumn, remaining within the permissible limit of 500 mg/L.

Nitrate (NO_3^{-}) concentrations were notably high, ranging from 0.0 to 347.8 mg/L in spring and 0 to 196 mg/L in autumn, with average values of 59.9 mg/L and 15.7 mg/L, respectively. According to the MNS 2018 standard, the limit for nitrate is 50 mg/L. In the spring, 15% of the samples exceeded this limit by 1.05 to 7 times, while 8.3% of autumn samples exceeded it by 1.01 to 3.9 times. Study result shows that nitrate concentrations were found to be relatively high in the middle and down of the basin, especially in hand

wells. Nitrate pollution was believed to be mainly due to livestock manure, septic tank.

In the upper part of the basin, some mineral water wells exhibited slightly acidic properties, with distinct taste and detectable levels of carbon dioxide and bivalent iron ions. The permissible concentration of total iron (Fe) is 0.3 mg/L according to MNS and WHO standards. However, 23.3% of spring samples and 20% of autumn samples exceeded this limit.

Fluoride (F^-) concentrations were found to range between 0.13 and 6.6 mg/L in spring and 0.13 and 3.48 mg/L in autumn, with average values of 1.49 mg/L and 1.15 mg/L, respectively. Both the WHO and Mongolian standards recommend fluoride levels between 0.70 and 1.5 mg/L. In spring and autumn, 21.7% and 18.3% of the samples were below this range, while 38.3% of samples exceeded the recommended upper limit, indicating potential health risks (Figure 2).

3.1. Water Quality and chemical composition

Piper diagrams are an important tool for understanding groundwater hydrochemical types, hydrochemical evolution, and hydrochemical properties [2].

The Piper diagram indicates that in the spring season, 56.7% of all samples belong to the $Ca-HCO_3$ type, 20% to the $Na-HCO_3$ type, 8.3% to the Mixed- HCO_3 type, and 15% represent water with a mixed composition and no dominant cation. Regarding the anion triangle, 90% of the samples are dominated by the HCO_3^- anion. In comparison, during the autumn season, 53.3% of the samples belong to the $Ca-HCO_3$ type, 20% to the $Na-HCO_3$ type, 3.33% to the mixed- SO_4 type, and 23.37% represent water with a variety of mixed compositions and no dominant cation. There is a slightly variation between the two seasons in terms of chemical composition (Figure 3).

3.2. Person correlation analyses

Correlation analysis is a crucial method for understanding the chemical processes occurring within groundwater systems [10]. In this study, Pearson's correlation was employed to evaluate the relationships between chemical parameters, with the results illustrated as a correlogram in Figure 4.

During both seasons, EC showed a strong positive correlation with TDS ($r=0.994$ in spring and $r=0.993$ in autumn), reflecting the influence of dissolved ions on groundwater salinity. However, EC and TDS exhibited weak correlations with F^- , Fe, and K ($r=-$

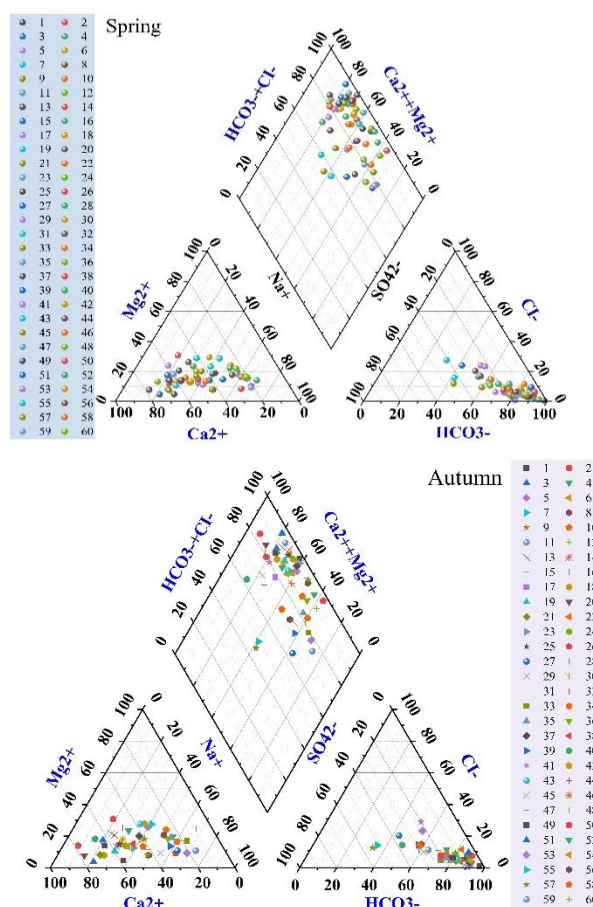


Figure 3. Piper diagram showing the chemical composition of groundwater in the study area

0.017 to 0.384), indicating a less impact of these ions on overall salinity. Conversely, strong positive correlations with other major ions suggest that dissolved ions are the primary contributors to the observed EC and TDS values.

The concentrations of Ca^{2+} and Mg^{2+} displayed either negative or weak correlations with pH (Ca^{2+} : $r=-0.017, -0.227$; Mg^{2+} : $r=0.096, 0.102$), suggesting that lower pH values favor the solubility of these ions. The significant positive correlation between Ca^{2+} and Mg^{2+} further indicates that dolomite dissolution is a probable source, consistent with its widespread presence in shale and Quaternary formations. Furthermore, a strong positive correlation was observed between Mg^{2+} and HCO_3^- ($r=0.648$ to 0.676), reinforcing the hypothesis that dolomite weathering significantly contributes to groundwater mineralization.

The correlation analysis also revealed a strong association between HCO_3^- and Na^+ ($r=0.702, 0.818$), indicating the occurrence of concurrent geochemical processes—specifically, the dissolution of carbonate

minerals and the weathering of sodium-bearing rocks within the groundwater system.

NO_3^- exhibited positive correlations with (Ca^{2+} and Mg^{2+}) ions ($r=0.410$, 0.500 for Ca^{2+} and $r=0.636$, 0.406 for Mg^{2+} during both the spring and autumn seasons. Conversely, weak negative correlations were observed with HCO_3^- ($r=-0.032$, -0.007). The positive correlation between NO_3^- and Ca^{2+} and Mg^{2+} ions during the spring and autumn seasons suggests that these ions may share common sources, such as livestock manure or the mineral composition of the soil. This indicates that these ions may infiltrate into the groundwater simultaneously (Figure 4).

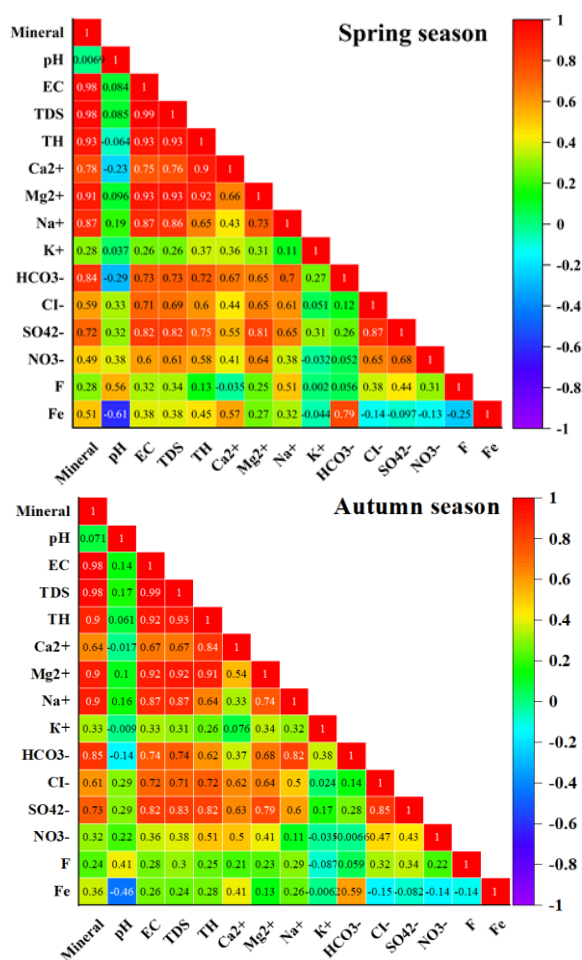


Figure 4. Correlogram of the hydro chemical parameters

3.3. Mechanism controlling the groundwater geochemistry

Groundwater quality is greatly influenced by climatic conditions and human activities. The Gibbs diagram is widely used to assess the relationship between groundwater chemistry and the lithological characteristics of the aquifer. The Gibbs diagram plots

the dominant cations [$\text{Na}/(\text{Na}+\text{Ca})$] and the anions [$\text{Cl}/(\text{Cl}+\text{HCO}_3^-)$] against TDS. The diagram shows 3 dominant mechanisms, from bottom to top: precipitation dominance, rock dominance, and evaporation dominance. These mechanisms indicate that water-rock interactions are the major factors controlling groundwater chemistry [11].

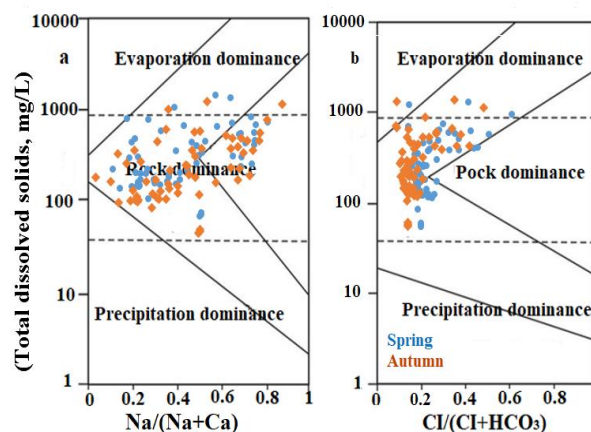


Figure 5. Mechanism controlling the of groundwater

As shown in Figure 5, the majority of the samples collected during the spring and autumn seasons were categorized in the rock mechanism, while only a few samples were classified in the evaporation mechanism. The evaporation mechanism increases TDS due to elevated concentrations of Na^+ and Cl^- ions. In contrast, samples associated with the rock weathering mechanism are primarily influenced by factors such as the region's arid climate, low rainfall, high temperatures, and land residence period in the aquifer. During the spring season, groundwater samples GW16, GW31, GW35, and GW59 were situated within the evaporation-dominant zone, with Gibbs Ratio 1 values ranging from 0.4 to 0.89 and Gibbs Ratio 2 values from 0.01 to 0.47. In the autumn season, samples GW16, GW31, and GW55 also plotted within the evaporation-dominant field, exhibiting Gibbs Ratio 1 values between 0.42 and 0.66 and Gibbs Ratio 2 values between 0.01 and 0.43. In both seasons, the relatively high $\text{Na}^+(\text{Na}^++\text{Ca}^{2+})$ ratios and low $\text{Cl}^-(\text{Cl}^++\text{HCO}_3^-)$ ratios suggest that groundwater chemistry is predominantly influenced by water-rock interactions, particularly the weathering of carbonate and silicate minerals. Additionally, the results indicate that cation exchange processes specifically the replacement of Ca^{2+} by Na^+ are actively contributing to the hydrogeochemical evolution of the aquifer system.

4. DISCUSSION

The groundwater in the upper part of the Kherlen River basin is mostly classified as fresh water with low mineralization and hardness, but in some cases the concentration of nitrogen ions and iron ion exceed the drinking water standard [15]. According to the results of water analysis conducted in previous years, the average mineralization of groundwater in the basin is 950 mg/l and the average hardness is 5.6 mg-eq/L [9].

From the findings of a study by Maki Tsujimura et al. in 2007, the groundwater in the upper part of the basin was predominantly Ca-HCO₃ type water, while the chemical composition of the water in the middle and down parts changed, and the concentration of Na⁺, Mg²⁺, Cl⁻, and HCO₃⁻ ions was significantly higher than that in the upper part of the water [16].

According to a 2020 study by researchers from the Institute of Geography and Geoecology found that well water in the upper part of the basin, in the Mungunmort soum and Baganuur areas of Tuv province, was mostly Ca-HCO₃ in terms of chemical composition. The mineralization of groundwater in these wells ranged from 96.1 to 797.3 mg/L and the hardness was 0.8 to 4.8 mg-eq/L. However, the average mineralization of well water with mineral springs was 2626.6 mg/L and the hardness was 15.4 mg-eq/L [17].

Furthermore, the Institute's 2022 study indicated that the chemical composition of groundwater varied significantly depending on geographical location. Mineralization levels ranged from 141 to 1221 mg/L, hardness from 1.08 to 11.33 mg-eq/L, iron ion concentrations from 0.86 to 3.65 mg/L, fluoride ion from 0.15 to 2.81 mg/L, and nitrate concentrations ranged between 0.0 and 131 mg/L [7].

Similarly, a 2022 study by researchers at the Institute of Chemistry and Chemical Technology also found that the mineralization of groundwater ranged from 256.3–2083 mg/L, hardness from 1.8–7.8 mg-eq/l, iron ion from 0.86–3.65 mg/L, and fluoride ion from 0.04–3.74 mg/L [18].

Our study results indicated that the mineralization and hardness levels of some well water do not meet the requirements for drinking and domestic use. The total mineralization ranged from 116 to 2554 mg/L in the spring season and from 116 to 2502 mg/L in the autumn season, with average values of 602 mg/L and 598 mg/L, respectively. Moreover, the total hardness (TH) varies from 42.3 to 1026 mg/L and 42 to 961 mg/L, with average values of 254 mg/L and 261 mg/L, respectively.

The results of the aforementioned researchers are consistent with the findings of our study, demonstrating similar outcomes.

5. CONCLUSION

1. In both spring and autumn, the hydrochemical composition of groundwater was predominantly characterized by Ca-HCO₃ and Na-HCO₃ water types. In the upper reaches of the basin, Ca-HCO₃-type water was dominant, reflecting limited anthropogenic influences. In the middle part of the basin, a transition was observed with the coexistence of both Ca-HCO₃ and Na-HCO₃ types, suggesting ongoing ion exchange processes and increasing interaction with geological formations. In the lower reaches, a more diverse hydrochemical signature was identified, including Ca-HCO₃, Na-HCO₃, and Mixed-SO₄ types. This variation is attributed to the geological formations, hydrogeological characteristics, and human activities influencing the groundwater composition in these areas.
2. The findings of the study indicate that nitrate contamination is more prominent in the middle and lower reaches of the basin, particularly in shallow wells (4–8 m) located in the Khentii and Dornod provinces. These wells are widely used by households for agricultural purposes, such as growing vegetables and watering livestock. In spring seasons, the increased nitrate concentrations in the water are likely associated with factors such as wastewater, leakage from septic tanks, livestock waste, and excessive use of fertilizers.
3. The positive correlations between EC and TDS indicate that dissolved ions are the primary factors influencing groundwater salinity. Additionally, the relationships between major ions, such as calcium, magnesium, bicarbonate, and sodium, along with weak correlations with other ions, suggest that geochemical processes like the dissolution of dolomite and the weathering of sodium-bearing rocks play a significant role in shaping the chemical composition of groundwater. Furthermore, the positive correlation of nitrate with Ca²⁺ and Mg²⁺, and its negative correlation with HCO₃⁻, indicate that anthropogenic influences-particularly agricultural practices such as manure application, agricultural runoff, and soil thawing during spring-are significantly affecting groundwater chemistry.
4. Based on the results of the study, it is evident that the hydrochemical composition of groundwater under both seasonal conditions is primarily

controlled by rock weathering and cation exchange processes. Although evaporative influence is observed at some points, water–rock interactions are the predominant factor governing the overall groundwater chemistry.

The quality and contamination of groundwater along the floodplain of the Kherlen River are influenced by natural factors and human activities, particularly agriculture and livestock activities. Therefore, it is essential to implement proper groundwater management and take effective protective measures to preserve its quality and prevent further changes.

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