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Physicochemical characterization of drinking water from borehole wells in Ulaanbaatar city, Mongolia

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Abstract: Groundwater is the most important natural source for supplying of drinking water around the world, especially in rural areas. The 14th khoroo (sub-district) of Khan-Uul district of Ulaanbaatar is only one khoroo where its inhabitants engage in animal husbandry and agriculture, which play an important role in the district's economic growth, faces an increasing shortage of groundwater due to population and economic growth in the agriculture sector in the sub-district. In this study, we present the hydro-chemical characteristics and spatial distribution of aquifer using GIS and multivariate statistical approaches. During the sampling periods, a total of 51 groundwater samples were collected from 46 deep wells and 5 shallow wells in the area between October and November 2019. Samples included parameters of anions and cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^- , HCO_3^-) and EC. Data from all the samples were subject to cluster and component analysis. As a result, three clusters were defined and it was established that the dominant groundwater type is $\text{HCO}_3^- \text{Ca}^{2+} \text{Na}^+$. The parameter of Mg^{2+} and Ca^{2+} were not set in the permissible limits of the second and third clusters. Principal component analysis (PCA) illustrated that the northern part of the study area is greater affected to anthropogenic activities and aquifer mineralogy. Moreover, it found that Ca^{2+} and Mg^{2+} correlated with each other, which could be helpful in site specific monitoring of groundwater quality. The results of the study will contribute to management and quality control of the groundwater in the city.

Keywords: Hydrochemical process; Ulziit; Multivariate statistical analysis;

INTRODUCTION

Water quality analysis is one of the most important aspects in groundwater studies. Determination of physicochemical characteristics of water is essential for assessing

the suitability of water for domestic, industrial and agriculture [1] use. Groundwater is a valuable source both in Ulaanbaatar, the capital city of Mongolia and throughout the rural areas.

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Almost 46 per cent (1.4 million out of a total 3.2 million people) of Mongolia's population live and work in Ulaanbaatar. In the city, underground water is the source of drinking water for the entire population of the capital city, nearly the entire rural population obtain their water from underground water sources. Water supply for Ulaanbaatar residents is provided by underground fresh water from a depth of 35-40 m in the deep pit of Tuul River [12]. The intensive and rapid pace of ongoing urbanization pose risks for the quality and composition of underground water, which is increasingly failing to meet the hygiene requirements due to environment and soil pollution caused by household waste holes (toilets and dumping of household liquid and solid wastes and without centralized sewage system) in the sprawling ger districts of Ulaanbaatar that have existed for many years. In particular, natural properties of groundwater, especially its nutritional value, exchange, location, movement, and regime, as well as its quality and composition, are beginning to change as a impact of human activities, such as construction work. On the other hand, the quality of natural water that has changed as a result of these man-made impacts, in turn, negative affects our lives and economies [8]. There are reports about Ulaanbaatar's main water source, the Tuul River, being polluted. Water quality in the downstream area of the Tuul River has deteriorated due to the disposal of domestic wastewater from the capital city and communities [9] that have sprung up along the stretch of the river. The city is expected to continue to be over concentrated as the population continues to increase, as a

consequence of which the city could encounter many serious environmental challenges. According to a recent study, groundwater of Ulaanbaatar is contaminated by concentration of NO_3 through atmospheric deposition, fertilizers, industrial waste effluent, and improperly maintained septic systems. There are high levels of aluminum and iron in groundwater originating from inadequate storage of drinking water in the ger districts, the effect of corroded iron pipes and given the soil composition of the geographic areas [10]. However, the evaluation of groundwater resources requires an understanding of hydrogeochemical properties of the aquifer [16]. In order to evaluate the characteristics of groundwater, physicochemical parameters, as well as, hydrochemistry were studied by many researchers nationwide. A large number of groundwater studies have also focused on assessing the suitability of ground water for drinking purposes [14, 15].

Ulziit sub-district, which is our study area, is one of the remote and newly developed urban areas of Ulaanbaatar and its water supply system is not connected to the centralized system. Households, business entities, organizations, and herder families in this urban area have been using only groundwater for drinking and domestic use. Therefore, understanding of the geochemical processes of the aquifers is necessary, but it a time-demanding process important for groundwater quality monitoring and from the perspective of sustainable water resource management. The study's objective was to examine the present status of drinking water quality in the 14th khoroo of Khan-Uul district in Ulaanbaatar.

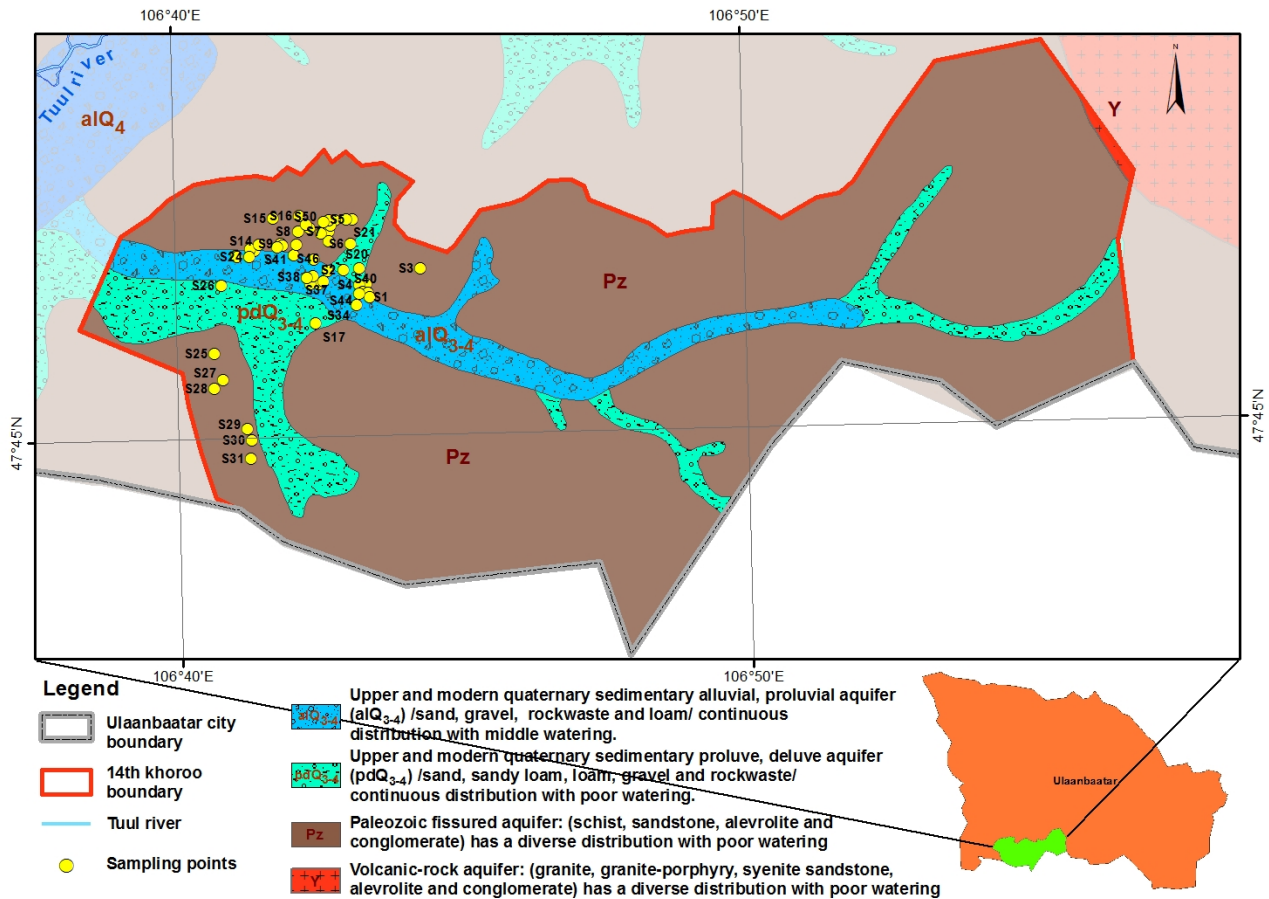


Figure 1. Location map of the study area and groundwater wells

MATERIALS AND METHODS

Description of the study area

The study area, which was randomly selected, was the Ulziit sub-district at 14th khoroo in Khan-Uul district, in the southwest of Ulaanbaatar and 28 km from the centre of the capital city. Ulziit sub-district has a population of approximately 5,500, where water samples for this study were collected. The sub-district, which covers a land area of 7200 hectares and, where 218 herder families live who own 11,600 heads of livestock adjacent to the Special Protected Area (SPA). Ulziit is located in Turgen valley of Bogd Khan SPA. The region consists of several aquifers, which are primarily Modern quaternary and Paleozoic fissured aquifers. The sediment consists of mainly sand, gravel, sandstone, alevrolite and conglomerate.

Sampling and analytical procedure

A total of 51 groundwater samples were collected from deep wells in the ger districts (n=46), and shallow wells (n=5) between October and November 2019. The depths of the

wells varied from 22 to 102 m. Prior to sampling the wells were pumped for 10 min until steady state chemical conditions were obtained. The samples were collected in 1-liter polyethylene (PET) bottles at 6 different locations in the 14th khoroo of Khan-Uul district. These sample bottles were stored in an ice box, and tested at the Water Analysis Laboratory of the Institute of Geography and Geocology, Mongolian Academy of Sciences. In order to assess the quality of ground water, we used the current Mongolian drinking water standard MNS 0900:2018, as well as relevant WHO standards. The physicochemical parameters of temperature, turbidity, pH, electrical conductivity (EC) and total dissolved solids (TDS) were measured on the spot with calibrated portable instruments.

Multivariate statistical analysis

Multivariate statistics are useful tools to attaining significant information from hydrochemical data set in the groundwater

system. To evaluate the analytical data, multivariate statistical techniques, i.e., correlation analysis, principal component analysis (PCA), and cluster analysis (CA) were used in this study, by using SPSS (version 26.0) software, for windows. Parametric statistical methods were also used for calculating the normal statistical and normal quality

parameters, i.e., the range, mean and standard deviation. Pearson's correlation matrix was used to identify the relationship among the pairs of parameters. When more than two variables were considered simultaneously, multiple linear regression analyses were used to evaluate their interdependency.

RESULTS AND DISCUSSION

Hydrochemistry and water quality

The results of measured parameters of groundwater samples of the study area are summarized in Table 1. The groundwater at most of the sites were predominantly slightly alkaline, the value of which ranged from 7.20 to 7.79, with a mean value of 7.48. This indicates that all well water samples are within the limit of 6.5-8.5 as per the National standard and WHO standard for drinking purpose. TDS has an average value of 268.7 mg/l that ranges from 152 to 691 mg/l. According to WHO (2011) recommendation, TDS up to 500 mg/l is the highest desirable level, and except for the four samples (S17, S23, S45, S48) all other samples fall within the permissible limit. Subsequently, EC of the water samples ranges from 306 to 1258 $\mu\text{S}/\text{cm}$ with a mean of 515.5 $\mu\text{S}/\text{cm}$. The values indicate that all the samples fall within the permissible limit except two samples (S45 and S48), which exceeded the maximum allowed concentration recommended in groundwater of 1000 $\mu\text{S}/\text{cm}$, as determined by the Mongolian standard MNS 0900:2018 and EC up to 1500 $\mu\text{S}/\text{cm}$ WHO (2011) recommendation. Usually, drinking water which has an EC value less than 400 $\mu\text{S}/\text{cm}$ is considered a high quality water. According to standards, the turbidity should not exceed 5 NTU. As showed in Table 1, the obtained values indicate that all water samples, except only from one sampling site (S39), had a turbidity value greater than the maximum permissible level.

Calcium concentration ranged from 29.1 to 117.2 mg/L, with an average value of 57.7 mg/L. The maximum permissible level of Ca^{2+} in groundwater is 100 mg/L as per MNS 0900:2018 and WHO (2011), all the samples fall within the permissible limit except three

samples (S2, S45, S48). Magnesium concentration varied from 8.5 to 51.4 mg/L, with an average value of 19.6 mg/L. The maximum allowable limit of Mg^{2+} in groundwater is 30 mg/L (MNS 0900:2018) and WHO (2011), and all the samples fall within the permissible limit except for four samples (S2, S23, S45, S48). Sodium (Na^+) concentration ranged from 9.03 to 54.3 mg/L. the maximum permissible limit of Na^+ concentration in groundwater is 200 mg/L, as set by MNS 0900:2018 and WHO (2011), and all the samples fall within the permissible limit. Potassium (K^+) concentration was present in very low concentrations for groundwater, varying from 0.48 to 7.20 mg/L, with an average value of 1.33 mg/L.

The mean value of Chloride (Cl^-) is 23.99 mg/L with ranges from 5.30 to 113.60 mg/L. Maximum allowable limit of Cl^- concentration in groundwater is 350 mg/L, as set by MNS 0900:2018 and up to 250 mg/L as determined by WHO (2011). According to the National standard, all the samples fall within the permissible limit. The average concentration of TH , SO_4^{2-} , HCO_3^- are 13.80, 46.59, 223.63 mg/L respectively, where all the samples fall within the permissible limits. But, in the case of NO_3^- one sampling site (S45) had nitrate (NO_3^-) value greater than 50 mg/L MNS 0900:2018 and WHO (2011) recommendation. NO_3^- derived from agricultural and industrial areas were primarily due to leaching from plant nutrients, nitrate fertilizers and domestic and industrial waste. In the case of major anions, HCO_3^- is predominant in groundwater samples, the average value of bicarbonate (HCO_3^-) is 223.63 mg/L and ranged from 158.60 to 332.50 mg/L.

Table 1. Statistical summary of the measured parameters of collected groundwater samples

Parameters	Values form collected samples (n=51)			
	Minimum	Maximum	Mean	Std. Deviation
pH	7.20	7.79	7.48	0.16
EC (μS/cm)	306.00	1258.00	515.51	228.16
TDS (mg/L)	152.00	691.00	268.67	131.22
Na ⁺ (mg/L)	9.03	54.30	22.21	10.32
K ⁺ (mg/L)	0.48	7.20	1.33	1.02
Ca ²⁺ (mg/L)	29.10	117.20	57.69	21.19
Mg ²⁺ (mg/L)	8.50	54.10	19.59	10.85
Cl ⁻ (mg/L)	5.30	113.60	23.99	22.98
SO ₄ ²⁻ (mg/L)	6.00	280.00	46.59	59.86
NO ₃ ⁻ (mg/L)	0.00	70.00	12.59	11.55
HCO ₃ ⁻ (mg/L)	158.60	332.50	223.63	35.75
T (NTU)	1.60	6.22	3.21	1.06
Total Hardness (TH)	7.37	32.87	13.80	6.04
Na +K	9.51	57.16	23.53	10.87
Ca+ Mg	44.60	171.30	77.27	30.84
Ca + Mg/Na + K	1.09	6.62	3.57	1.14

The variation of major cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) and anions (HCO₃⁻, Cl⁻, SO₄²⁻, NO₃⁻) in groundwater samples is illustrated in the Box and Whisker plot (Fig. 2) where Ca²⁺ and HCO₃⁻ are the dominant cations and anions, respectively. It showed that, the order of relative abundance of major cations in the groundwater is Ca²⁺ > Mg²⁺ > Na⁺+K⁺, while the anions are HCO₃⁻>SO₄²⁻>Cl⁻>NO₃⁻. EC and TDS of the groundwater samples (S17,

S45, S48) showed large percentage of contribution from Ca²⁺, HCO₃⁻ and SO₄²⁻. Sampling sites S45, S48 and S17 in the Paleozoic fissured aquifer and quaternary sedimentary proluvial aquifer increase in minerals concentration was observed, indicating an increase in hardness and mineralization. These aquifers consist of sandstone, alevrolite, conglomerate, sand and rockwaste.

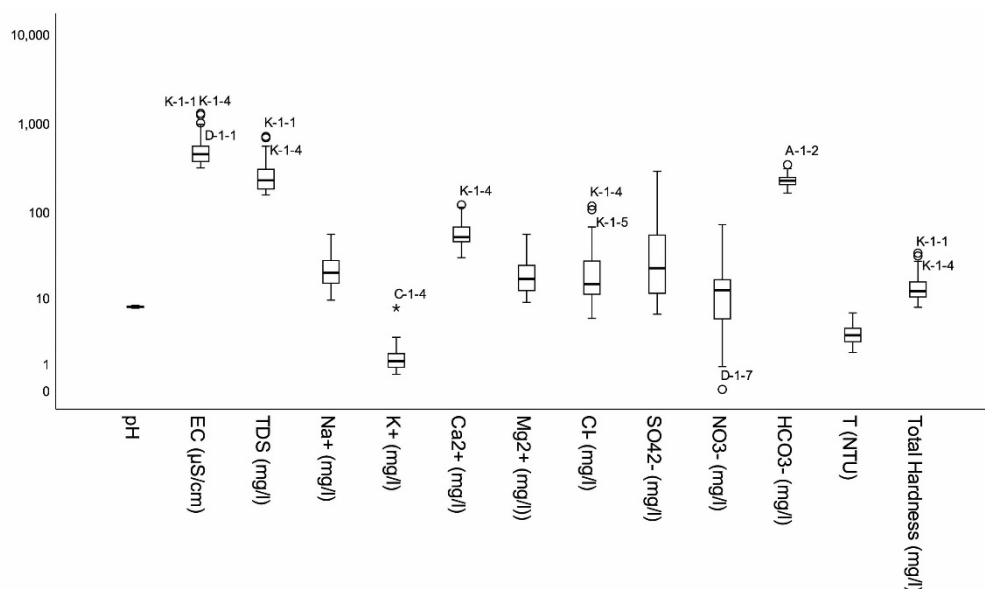


Figure 2. Box and Whisker plot showing the variation of major ion concentration of groundwater

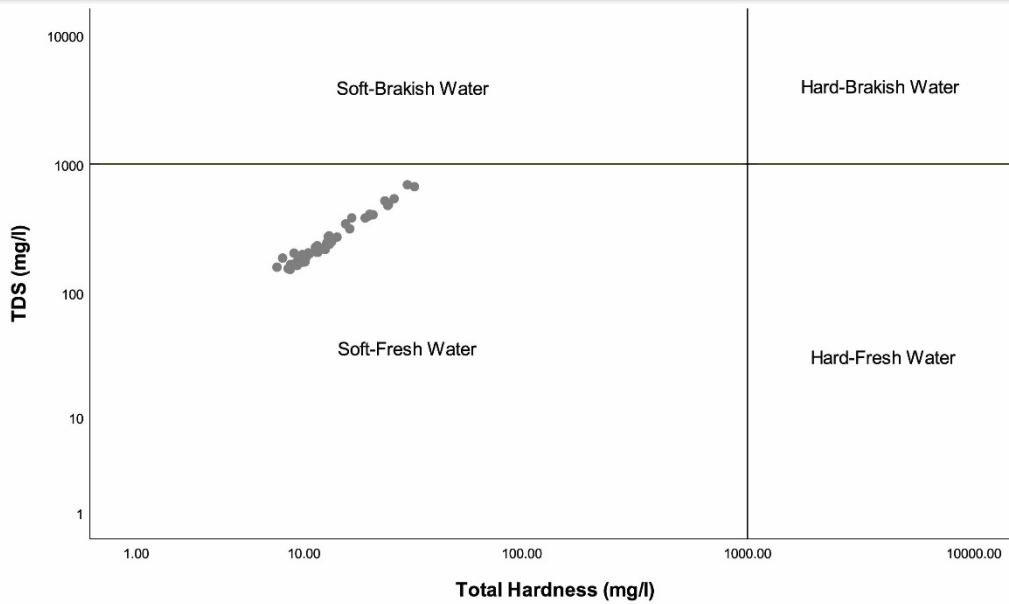


Figure 3. Groundwater quality in the study area based on TDS and TH

Hydrochemical facies

The total hardness (TH) in mg/L was determined by $(2.497 \text{ Ca}^{2+} + 4.115 \text{ Mg}^{2+})$, according to Todd [11]. TH in the groundwater varied from 7.37 to 32.87 mg/L with an average value of 13.80 mg/L (Table 1). Hardness of water is due to the presence of

divalent metallic cations with calcium and magnesium in abundance. A detailed classification of groundwater quality based on TDS and TH (Fig. 4) shows that the majority of groundwater samples were classified under soft-fresh category.

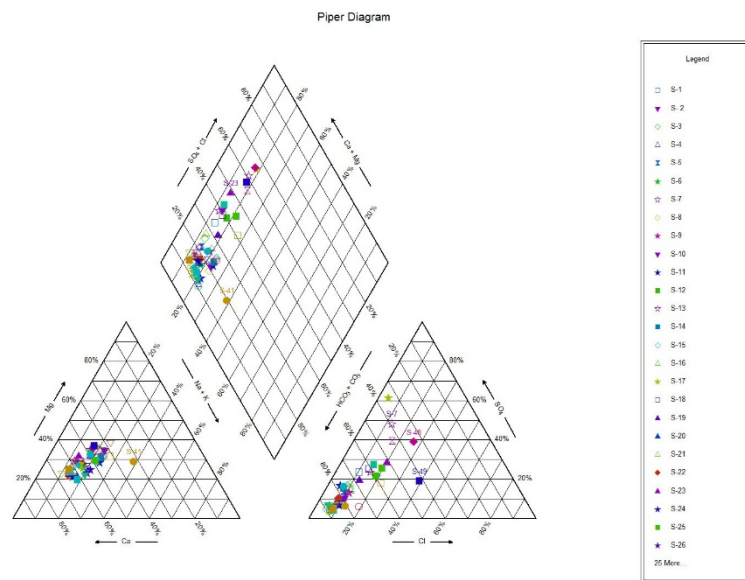


Figure 4. Classification of groundwater types after the ion change

Dispersion of ions is represented using Piper diagram (Fig. 4). The largest anion dispersion is represented by HCO_3^- concentration, and the Ca^{2+} concentration has the largest cation dispersion. Hydrochemical facies are distinct zones that possess cation and

anion concentration, which help to identify the classes of water. According to the diagram, the dominant water types, which is $\text{Ca}^{2+}-\text{HCO}_3^-$ indicates that the hydrochemistry of the groundwater samples is characterized by alkaline earths, which have excessive alkali

metals. Most of the samples in this study belong to $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ type followed by $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-\text{-SO}_4^{2-}$, respectively.

The Durov diagram is used to graphically illustrate cation and anion concentrations, related to pH and TDS values. From the results, ion balance diagram indicated that the most prominent water types

are the Ca-HCO_3 (78%), followed by Mx-HCO_3 (7.8%), in the third level by Ca-[Mg]-HCO_3 (3.9%), the fourth Ca-[Mg]-SO_4 (1.96%), $\text{Ca-[Mg]-HCO}_3\text{-[SO}_4]$ (1.96%) and groundwater was dominated by calcium and bicarbonate belonging to the group of Ca-HCO_3 water type.

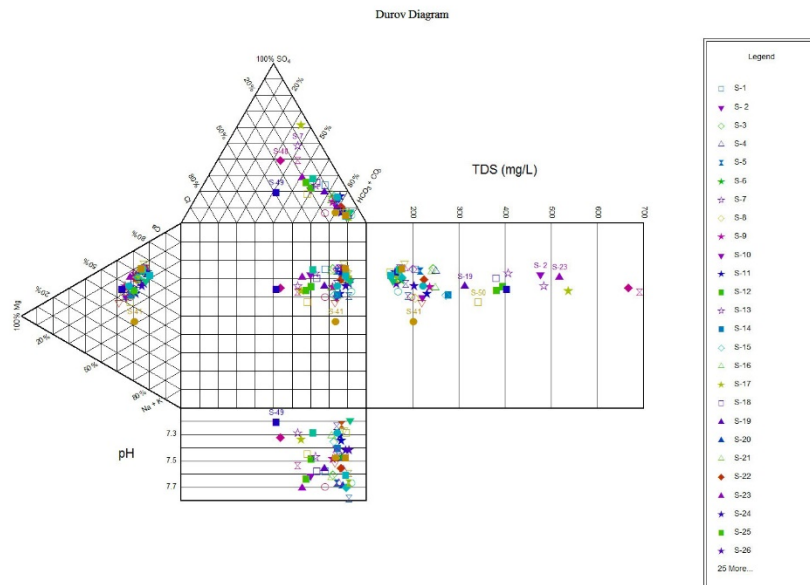


Figure 5. Chemical composition of water samples

Hydrogeochemical processes evaluation Gibbs plot was used to determine the mechanism controlling the groundwater chemistry. The measured parameters of groundwater were plotted in Gibbs diagram and it was found that the majority of samples in the study area are characterized by rock-water interactions, which are an indication of the chemical alteration of rock-forming minerals, influencing the quality of groundwater by rock dissolution, through which the water flows beneath the surface [4]. The cations and anions are derived mainly from rock weathering rather than evaporation and precipitation (Fig. 6). These may have been influenced by chemical weathering of rock forming minerals. The

processes responsible for major solutes of groundwater are most likely controlled by mineral dissolution. The $\text{Cl}/\sum\text{anions}$ ratios of groundwater samples varied from 0.028 to 0.258, with an average value of 0.070 (Table 3). In contrast, the $\text{HCO}_3/\sum\text{anion}$ ratios ranged from 0.411 to 0.913 with an average value of 0.771. These results suggest that rock weathering, mostly silicate weathering, carbonate dissolution and evaporate dissolution are dominant in the aquifers. The rock-water interaction is a broad classification that encompasses all lithogenic influences like silicate weathering, carbonate dissolution and evaporates dissolution.

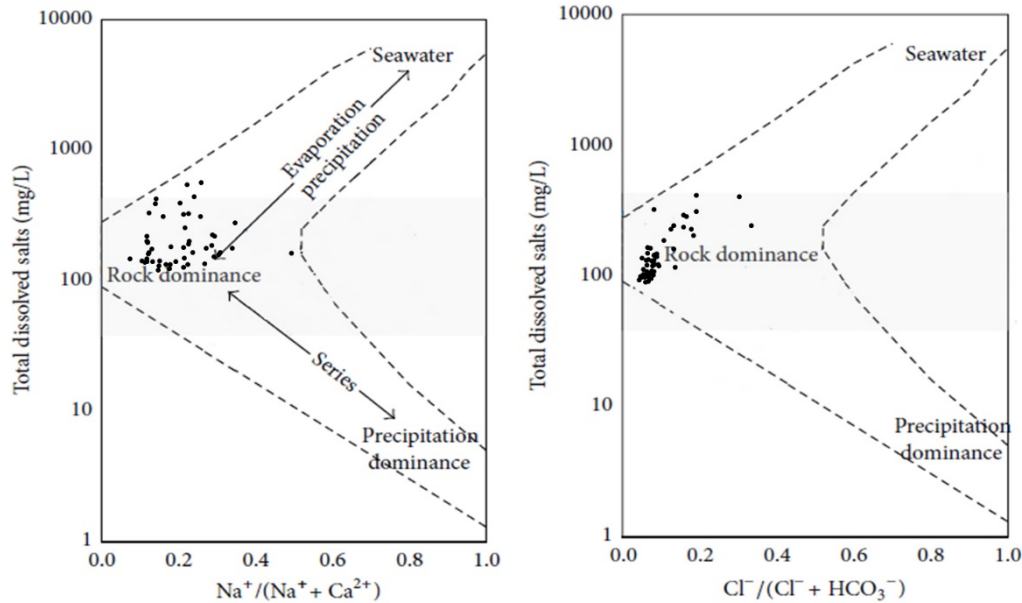


Figure 6. Gibbs plot showing the mechanisms controlling the groundwater chemistry

Table 2. Statistical summary of saturation indices (SI) of some mineral phases and ratios of some chemical constituents in the groundwater

Parameters	Minimum	Maximum	Mean	Std. Deviation
Total Cations	59.970	223.510	100.808	39.296
Total Anions	187.100	634.600	306.796	108.914
Cl/∑Anions	0.028	0.258	0.070	0.042
HCO ₃ /∑Anions	0.411	0.913	0.771	0.132
Na/(Na+Cl)	0.234	0.750	0.529	0.120
(Na+K)/Cl	0.322	3.157	1.354	0.686

Correlation analysis

Correlation coefficients are generally used to establish the relationship between two variables. This is an approach to demonstrate how well one variable predicts the others [4]. The Pearson's correlation matrix for the analyzed parameters of the groundwater samples is presented in Table 3. It has been observed that the correlation between EC and TDS was significantly positive ($r=0.996$). The significantly positive correlation between EC and Ca, SO₄, TDS and Mg are indications that these ions are derived from the same source of water. Calcium is positively correlated with magnesium ($r=0.836$) and the presence of magnesium in these waters might be due to silicate weathering.

Principal component analysis (PCA)

A total of 13 water quality parameters, i.e., pH, EC, TDS, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, NO₃⁻, HCO₃⁻, T (NTU) and Total Hardness were analyzed by PCA for differentiating the various processes acting on the hydrogeochemistry. These parameters were grouped into 2 major PCs explaining 77% of the total variance in the data set (Table 4). The selection of variables was solely based on the eigen values (>1). The performed Kaiser–Meyer–Olkin (KMO) test yielded a value 0.616, which suggests that the data is eligible for performing principal component analysis. Varimax rotation was used to maximize the sum of the variance of the factor coefficients, which better explained the possible sources that influenced the water systems.

Positive scores in PCA indicate that water samples are affected by the parameters that significantly loaded on a specific component, where as negative scores suggest that water quality is essentially unaffected by those

parameters. The variances explained by the PCs are 67.031%, and 10.287% for PC1, and PC4, respectively. PC1 is heavily loaded with EC, TDS, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, NO₃⁻, HCO₃⁻ and Total Hardness.

Table 4. Varimax rotated principal component analysis of water quality parameters (significant values (> 0.5) are in bold type face)

Parameters	PC1	PC2
pH	-0.008	0.774
EC (μS/cm)	0.989	-0.048
TDS (mg/l)	0.988	-0.055
Na ⁺ (mg/l)	0.857	-0.159
K ⁺	0.439	-0.238
Ca ²⁺ (mg/l)	0.906	0.054
Mg ²⁺ (mg/l)	0.974	-0.118
Cl ⁻ (mg/l)	0.831	-0.056
SO ₄ ²⁻ (mg/l)	0.878	-0.241
NO ₃ ⁻ (mg/l)	0.701	0.233
HCO ₃ ⁻ (mg/l)	0.799	0.278
T (NTU)	-0.028	0.600
Total Hardness (mg/l)	0.985	-0.048
Eigen value	8.232	1.242
% of Variance	63.187	9.687
Cumulative %	63.187	72.875

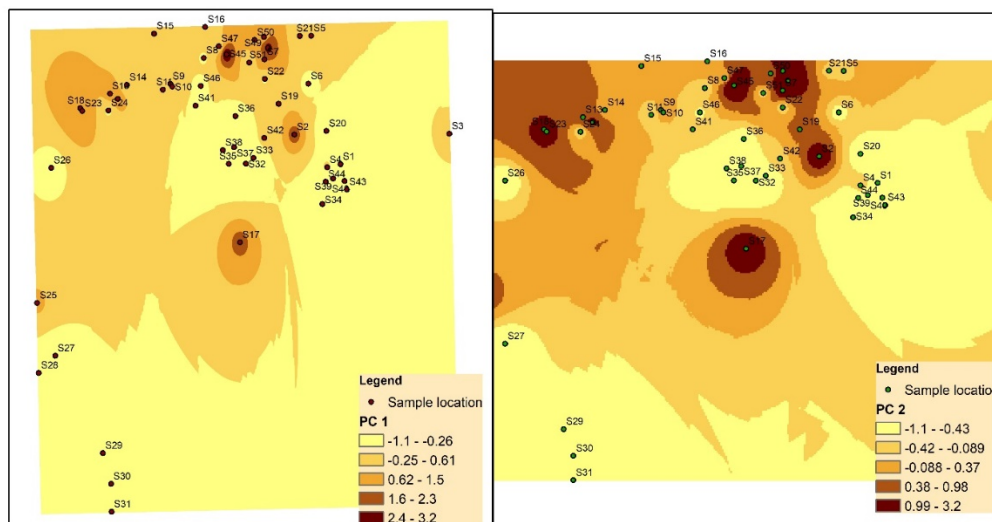


Figure 7. Spatial distribution of factor scores (PCs) (a) PC1 and (b) PC2 in the study area

CA has been used to evaluate the spatial similarities and site groupings among the sampling sites, where sampling sites belonging to a particular cluster exhibit similar

characteristics with respect to the analyzed parameters. 3 major clusters were recognized from all analyzed parameters for the 51 sampling sites.

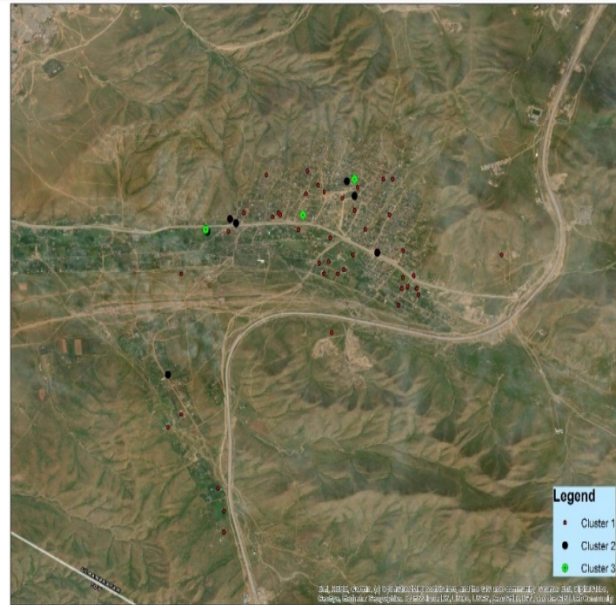


Figure 8. Cluster members of K-Means Cluster Analysis

Table 5. Mean values of chemical parameters for each cluster

Parameters	Cluster 1	Cluster 2	Cluster 3
pH	7.48	7.50	7.40
EC ($\mu\text{S}/\text{cm}$)	404.13	787.44	1147.67
TDS (mg/l)	205.46	421.44	632.00
Na^+ (mg/l)	18.13	31.01	48.73
K^+ (mg/l)	1.16	1.64	2.56
Ca^{2+} (mg/l)	48.07	83.39	105.53
Mg^{2+} (mg/l)	14.59	31.14	49.87
Cl^- (mg/l)	13.89	54.06	65.10
SO_4^{2-} (mg/l)	21.18	94.44	233.33
NO_3^- (mg/l)	9.16	19.72	35.67
HCO_3^- (mg/l)	211.02	264.70	264.33
T (NTU)	3.26	3.17	2.70
Total Hardness (mg/l)	10.92	20.90	29.98

CONCLUSIONS

In the present study, an attempt was made to evaluate groundwater quality of Ulziit sub-district of 14th khoroo, Khan-Uul district deep aquifer. Study samples included water samples from deep and shallow wells that supply water to the residents of the 14th khoroo.

Our results indicate that both water pH values and EC of groundwater in studied area was within the standard values, indicating minimal, if any pollution. The TDS value of all the samples fall within the permissible limit except for four samples. Calcium and magnesium concentration show that the

majority of samples are within the maximum permissible limit, except for three and four samples. NO_3^- in one sample (S45) exceeded the permissible limit of (MNS 0900:2018) and WHO value (50 mg/l). The highest levels of NO_3^- were found in a sample from one household.

The predominant cation trend in 14th khoroo aquifer is $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ + \text{K}^+$. The abundance of major anions in the 14th khoroo deep aquifer is in the following order: $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$.

In our study, all samples of groundwater quality, based on TDS and TH, were classified as soft fresh water.

As a result, three clusters were defined and the predominating groundwater types are HCO_3^- , Ca^{2+} - Na^+ . Parameter of Mg^{2+} and Ca^{2+} were not set in the permissible limits of the second and third clusters. PCA analysis illustrated that the northern part of the study area is more affected to anthropogenic activities

and aquifer mineralogy. Moreover, it found that Ca^{2+} and Mg^{2+} correlated with each other, which could be helpful for site specific monitoring of groundwater quality. In addition, multivariate statistical analysis is one of the proper techniques to reveal hydro-chemical process and water quality.

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