Assessment of hydrochemical characteristics and heavy metal pollution index in groundwater in the Gorkhi-Terelj of Nalaikh District, Mongolia

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Abstract. The study described in this article aimed to assess the hydrochemical characteristics and heavy metal pollution index of groundwater in the Gorkhi Terelj of Nalaikh district, located in the northeast part of Ulaanbaatar, Mongolia. In this study, we have used 91 groundwater samples, which were collected in 2020. In recent years, tourism has been developing rapidly in this region of Gorkhi Terelj National Park and the tour companies and enterprises in this area are using groundwater for all purposes. Thus, by conducting a research on the quality and composition of groundwater of the region will be significant importance on providing fresh and safe drinking water supply to foreign and domestic tourists. We determined physicochemical and microelement parameters in the selected wells and the results were compared to the Mongolian drinking water standard MNS0900:2018 and WHO 2011. According to our studies the predominant hydrochemical type of groundwater was Ca-HCO_3 (97.8%). In the case of mineralization, about 67% of groundwater wells showed very fresh, and 32.9% was fresh. However, in the case of hardness, 47.2% was very soft, 35.1% was soft, and 17.5% was medium-hard. The most of the microelements were found below the standard levels. But some heavy metals were very high. The uranium concentration varied from 0.073 to 642 μg/L; it surpassed the WHO drinking water standard (30 μg/L) at 30.7% of sampling sites. The concentration of arsenic (As 0.19-49.5 μg/L) in 6 water samples was 1.45-4.95 times higher than the WHO level and MNS0900:2018 standard level, molybdenum (Mo 0.2-77.5 μg/L) was 1.1 times higher in 1 sample, and manganese (Mn 6.0-1599 mg/l) was 1.1-15.9 times higher in 6 water samples. The groundwater quality was calculated with a heavy metal pollution index (HPI). Calculation of the heavy metal pollution index (HPI) showed that 62.6% of the samples showed “very good”, “good” (19.7%; HPI 26.67-50.72), “poor” (7.69 %; HPI 52.19-74.81), “very poor” (1.09%; HPI 88.21), and 8.79% of the samples showed unsuitable for drinking purpose (HPI 110.4-304.9).

Keywords: Hydrochemistry, mineralization, drinking water, fluoride, heavy metals, arsenic, and uranium.

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1 Introduction

Water is an essential element for life. Groundwater is an important resource that uses the drinking, agricultural, and industrial needs of the human population [1]. Water resources in Mongolia are scarce and stressed due to human activity, natural conditions, cold winters, hot summers, and low rainfall. In recent years, due to the declining amount and declining quality of surface water bodies have substantially increased the burden on Mongolia's groundwater. Increasing water demand driven by rapid population growth, fast industrial development, and unplanned urbanization has resulted in severe groundwater degradation [2].

Groundwater conservation, especially in arid and semi-arid regions, has particular economic importance. Water resources are especially important in terms of quantity and quality. Water quality has been a growing environmental problem worldwide, necessitating ongoing monitoring of physicochemical parameters and heavy metals issues. Especially, heavy metals are important to monitor due to their toxicity. Heavy metals in water occur in trace amounts, however, are very toxic to the human organism.

Sources of arsenic (As) and fluoride (F^-) in groundwater are mainly geogenic. Heavy metals and arsenic contamination in drinking water pose a serious threat to human life because of their toxicity, bio accumulative nature, and persistence in the environment [3]. Arsenic contamination of groundwater also influences its quality and brings risks to the people who drink the groundwater for a long time [4].

Uranium naturally occurs in groundwater, and its concentration is mostly influenced by an area's geology [5]. Elevated quantities of uranium in groundwater are frequently caused by the uranium content of igneous rocks [5]. Total dissolved uranium high concentrations are found in groundwater hosted in both granites and black shale rich in uranium [6]. The main objective of this research is to describe drinking water quality and components, as well as pollution of heavy metals in drinking water. To evaluate the overall pollution status in the study area, and heavy metal index was calculated.

2 Materials and methods

2.1 Study area

The Gorkhi Terelj National Park tourist zone is formally in Nalaikh District part of Ulaanbaatar municipality. The Gorkhi Terelj National Park is located 70 km northeast of Ulaanbaatar and 40 km from the Nalaikh District center. The study was conducted in Gorkhi Terelj, Nalaikh district, Mongolia, which lies between the latitudes (48°09′0.73’′N and 107° 34′ 33.62′E) with a total area of 2920 km^2 (Fig. 1).

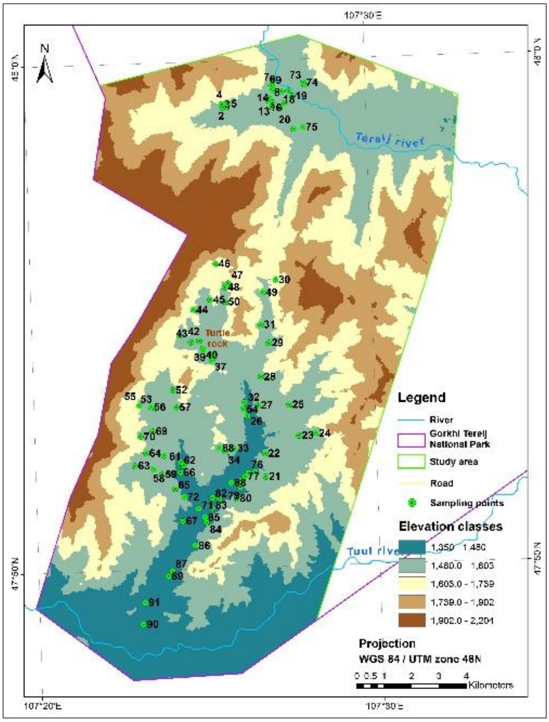

Fig.1. The study area

The study area has high granite stone mountains with forest-covered northern slopes, multitudes of wildflower meadows along with the spectacular shape rocks formed by wind and it is a favorite scenery for the visitors.

2.2 Hydrogeology and Geology

Aquifers of Tuul and Terelj Rivers are sands, gravels, and clays with scattered Quaternary friable sediments. For hydrogeological conditions, in the Tuul River basin, there are two kinds of aquifers: granular (unconsolidated) and fissured aquifers (consolidated). The geological structure of Gorkhi Terelj National Park covers granite rock penetrated the sedimentary, magic rocks of Devonian, sandstone, siltstone, and upper Triassic to lower Jurassic Granite plutons of Mesozoic and Paleozoic age region is distributed on the study area [7].

2.3 Sampling and analytical methods

A total of 91 samples were collected from groundwater around the study area in 2020 (Fig.1). In the research work, samples were taken from wells produced mainly from

Quaternary sedimentary, and from some wells located in relatively elevated areas, water samples were taken from fissured aquifers.

The physicochemical parameters were measured in situ such as electrical conductivity (EC), total dissolved solids (TDS), temperature (T°C), and pH using a HI98195 multi-parameter. Turbidity was measured using HANNA (HI93703) turbidity meter. Total alkalinity was determined by the hydrochloric acid titrimetric method (methyl orange), total chloride was determined by the silver nitrate titrimetric method (potassium chromate), and total hardness was measured using EDTA titration (Tuvaanjav, 2006). Nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), and sulphate (SO_4^{2-}) were determined by HI 83399 photometer and UV spectrophotometric method.

General chemical analyses and pollution parameters were determined by the following methods and analyzed in the Water analysis laboratory of the Institute of Geography and Geoecology. The concentrations of the heavy metals (i.e., Al, As, Ba, Be, Cd, Mn, Mo, Ni, Pb, Sb, Se, Sr, Zn, and U) in groundwater samples were measured by inductively coupled plasma-optical emission spectrometry in SGS laboratory of “SGS IMME Mongolia” LLC.

2.4 Statistical and graphical analysis

Statistical analyses and graphical analysis were performed using ArcGIS, Aquachem software, and Statistical Software for Social Sciences (SPSS) 21.

To assess the quality of groundwater, we used the Guidelines for World Health Organization and the Mongolian Drinking Water Standard MNS0900:2018 [8, 9].

2.5 Evaluation of Groundwater Quality by HPI Indexing Approach

The Heavy metal pollution index (HPI) method was used to calculate the overall heavy metal contamination in groundwater. The HPI is based on the weighted arithmetic quality mean method and developed in two steps [10]. First by establishing a rating scale for each selected parameter giving weightage and second by selecting the pollution parameter on which the index is to be based (Table 1).

The HPI evaluates the composite influence of individual heavy metals on water quality, as a ranting technique [11]. HPI was calculated for 14 trace metals.

Table 1. The relative weight of heavy metals

Heavy metals (μg/L)	WHO standard & MNS 0900:2018 (μg/L)	Weight (w_i)	Relative Weight (W_i)
Al	500.0	1	0.022
As	10.0	5	0.111
Ba	700.0	1	0.022
Be	0.20	2	0.044
Cd	3.00	4	0.089
Mn	70.0	3	0.067

Mo	70.00	3	0.067
Ni	20.0	4	0.089
Pb	10.0	5	0.111
Sb	20.0	2	0.044
Se	40.0	3	0.067
Sr	2000.0	4	0.089
U	30.0	5	0.111
Zn	5000	3	0.067
Total	-	45	1.000

HPI is based on the weighted arithmetic quality mean that assigns a rating or unit weightage (Wi) for each heavy metal. Equation (1), and was applied:

$$\mathrm{HPI} = \frac{\sum_{i=1}^{n} Wi * \mathrm{Qi}}{\sum_{i=1}^{n} Wi} = \frac{Wi * \mathrm{Qi}}{1} \quad (1)$$

where *Wi* and *Qi* are the unit weight and sub-index of the i^{th} parameter, respectively, and n is the number of parameters considered. Unit weightage *Wi* is inversely proportional to the *Si*, the Mongolian standard permissible limit of i^{th} parameter in micrograms per liter, of all the selected heavy metals and was calculated by using Equation (2):

$$Wi = \frac{wi}{\sum_{i=1}^{n} wi} \quad or \quad Wi = \frac{K}{Si} \qquad (2)$$

where K is the constant of proportionality, the value of which ranges from 0 to 1. where *Qi* is the sub-index of the i^{th} parameter, *Wi* is the unit weightage of the i^{th} parameter, and *n* is the number of parameters considered. The sub-index (*Qi*) of the parameter is computed by Equation (3):

$$Qi = \frac{Vi * 100}{Si} \qquad (3)$$

Table 2. Classification of water based on HPI [12].

HPI	**Quality of Water**
<25	Very good
26-50	Good
51-75	Poor
76-100	Very poor
>100	Unsuitable

3 Results and discussion

3.1 Hydrochemical characteristics

A piper diagram is one of the most effective graphical representations in demonstrating the groundwater geochemical characteristics. The dominant hydrochemical types of groundwater were Ca-HCO_3 (97.8%), followed by Na-HCO3 (1.09%), and Ca-S

(1.09%). In the case of mineralization, about 67% of samples is determined as very fresh.

The anion content followed the order $HCO_3^- > SO_4^{2-} > Cl^-$ and their average mass concentrations were 109.6 mg/L, 8.36 mg/L, and 7.23 mg/L, respectively. The Cl^- concentration ranged between 1.8 and 64 mg/L (mean of 5.3 mg/L). All of the samples of Cl^- concentrations not exceeded the standard limit (i.e., 350 mg/L).

Ca^{2+} is the dominant cation representing 98.9% of the total cations. The cation content followed the order $Ca^{2+} > Mg^{2+} > Na^+ + K^+$, and their average mass concentrations were 30.74 mg/L, 3.46 mg/L, and 9.92 mg/L, respectively, and HCO_3^- is the dominant anion (Fig.2).

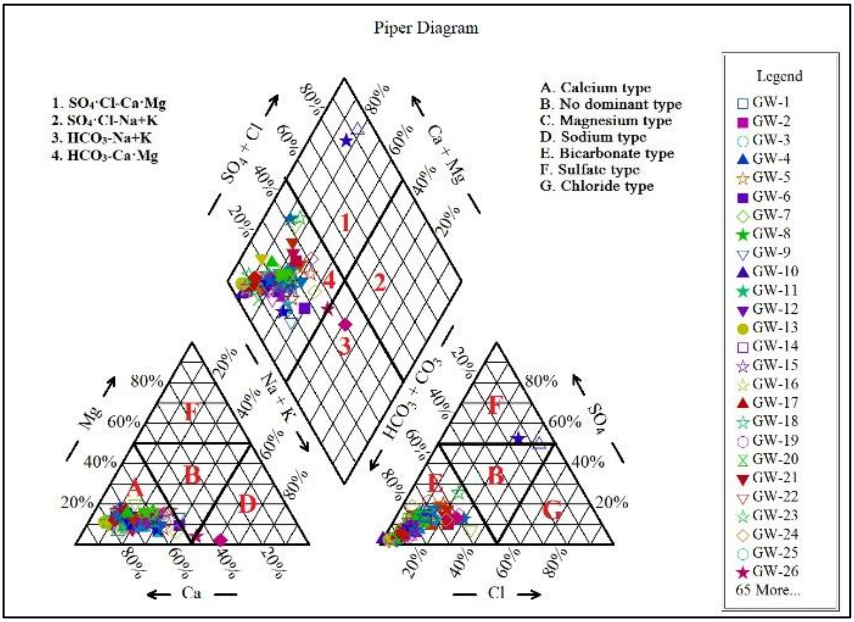

Fig.2. The piper diagram illustrates the classification of groundwater

Total hardness (TH) represents alkaline earth elements, such as magnesium and calcium within the water resources (Fig.3).

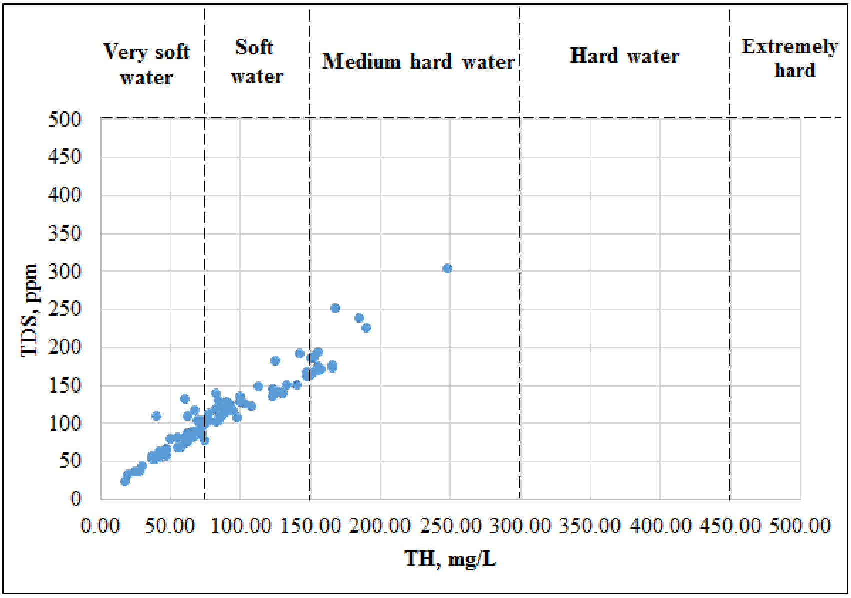

Fig.3. The graph of TDS vs total hardness in groundwater.

In terms of hardness, water was classified into the following types: very soft water (less than 75 mg/L), soft water (75–150 mg/L), medium hard water (150–300 mg/L), hard water (300–450 mg/L), and extremely hard water (greater than 450 mg/L).

TH of the natural water samples in the study area was between 17.4 and 247.8 mg/L, with an average of 91.03 mg/L, and the very soft water, soft water, and medium–hard water samples accounted for 47.2%, 35.1%, and 17.5% of the total water samples, respectively. Hard water and extremely hard water were not observed.

3.2 Statistical Analysis

The pH value of the drinking water samples in the study area was between 6.50 and 7.63, with a mean value of 7.0. The overall pH value was between weakly acidic to neutral. This indicates that all well water samples do not exceed the limit of 6.5-8.5 as per the Mongolian drinking water standard and WHO standard (Table 3).

The range of electrical conductivity (EC) was between 50.0 and 580.0 µS/cm, with an average value of 241.31 µS/cm. The variation range of TDS was between 25.0 and 305.0 ppm, and the average value was 116.5 ppm. After dividing water according to the TDS, freshwater accounted for 100%, and brackish water was not observed in the total water samples.

The content of NO_3^- was low, indicating the weak influence of human activities. Nitrate (NO_3^-) ranges between 0.0 mg/L and 20.0 mg/L, averaging 3.97 mg/L.

This indicates that all well water samples do not exceed the limit of physicochemical parameters as per the Mongolian drinking water standard and WHO standard for drinking purposes [8]. In contrast, fluoride, ammonium, and some heavy metals are beyond the maximum permissible limit in some of the samples.

The concentration of ammonium ranged from 0.0 to 4.5 mg/L (mean of 0.05 mg/L), and 1 sample exceeded the standard limit (1.5 mg/L). The highest level of ammonium (4.5 mg/L) at the GW-37 sampling point is 3 times higher than the Mongolian drinking water standard.

Table 3. Descriptive Statistics of the measured parameters of collected groundwater samples (n=91)

Parameters	*Min*	*Max*	*Mean*	*Std.Deviation*	*WHO 2011**	*MNS 0900:2018*	*% of unsuitable samples*
pH	6.50	7.63	7.00	0.34	6.5-8.5	6.5-8.5	-
TH, mg/L	17.4	247.8	91.03	46.1	500	7	-
EC, µS/cm	50.0	580.0	223.1	96.9	1500	1000	-
TDS, ppm	25.0	305.0	116.5	52.2	1000	-	-
Ca^{2+}, mg/L	6.00	75.2	30.75	15.4	75	100	-
Mg^{2+}, mg/L	0.60	14.6	3.46	2.10	30	30	-
Na^+, mg/L	3.70	28.7	9.92	5.23	200	200	-
HCO_3^-, mg/L	5.40	226.0	109.6	54.0	120		-
Cl^-, mg/L	1.80	64.0	7.23	8.34	250	350	-
SO_4^{2-}, mg/L	3.00	61.0	8.37	7.84	500	500	-
NO_3^-, mg/L	0.00	20.0	3.97	3.99	50	50	-
NH_4^+, mg/L	0.00	4.5	0.05	0.47		1.5	1.09%
F, mg/L	0.39	3.38	1.51	0.65	1.5	0.7-1.5	5.49% or 49.4%
As, µg/L	0.19	49.5	3.50	6.42	10	10	6.59%
Mn, µg/L	5.00	1599.0	38.73	172.21		100	6.59%
U, µg/L	0.07	642.0	43.23	101.85	30	30	30.70%
Be, µg/L	0.10	6.70	0.56	0.96		0.2	48.30%
Mo, µg/L	0.20	77.5	9.69	13.15		70	1.09%

Note: ''–'' suitable of Mongolian drinking water standard: MNS0900:2018 and WHO standard.

Fluoride: Fluoride (F^-) is another potentially toxic chemical that can negatively impact drinking water associated derived from mineral matter such as fluorapatite and fluorspar minerals [13]. The WHO and Mongolian drinking water standards MNS0900:2018 recommended limit for drinking water fluoride is between 0.7-1.5 mg/L [8, 9].

The F^- concentrations varied between 0.39 and 3.38 mg/L (mean of 0.65 mg/L). According to the results of the analysis, 54.9% of all water points with low fluoride (F 0.39-0.6 mg/L) and high fluoride (F 1.51-3.38 mg/L) content do not meet the standards, while 45.1% within the standards of drinking water (F 0.7-1.5 mg/L).

3.3 Distribution maps of trace elements and heavy metals

The levels of many trace elements were found to be low with the mean concentrations (ranges in brackets) being 196.4 (37-921) μg/L for strontium (Sr); 38.7 (6.0-1599) μg/L for manganese (Mn); 0.11 (<0.06-1.57) μg/L for Cobalt (Co); 52.8 (<5.0-478) μg/L for zinc (Zn); 1.0 (<0.2-6.7) μg/L for selenium (Se); and 0.03 (<0.01-0.17) μg/L for cadmium (Cd). The levels of uranium were surprisingly elevated (mean, 14.8 μg/L; range 0.073-642 μg/L), with the values for many samples exceeding the World Health Organization's guideline of 30 μg/L for uranium in drinking water (Fig.4).

The Nickel (Ni) ranged from 0.3 to 8.1 μg/L (mean of 1.31 μg/L). All of the samples of Ni concentrations have not exceeded the standard limit (i.e., 20 μg/L).

Manganese (Mn) concentration varied between 6.0 and 1599 μg/L, and 6 samples exceeded the standard limit (100 μg/L). The highest level of Mn (1599 μg/L) was recorded at the GW-81 sampling point.

The concentration of Mo ranged from 0.2 to 77.5 μg/L, with a mean concentration of 9.69 μg/L. Compared to the standard, only 1 sample exceeded the standard (70 μg/L). The highest level of Mo (77.5 μg/L) was recorded at the GW-80 sampling point.

Uranium (U): The uranium content in the groundwater and public water supply samples ranged from 0.073 to 642 μg/L with a mean value of 43.2 μg/L (Fig.4).

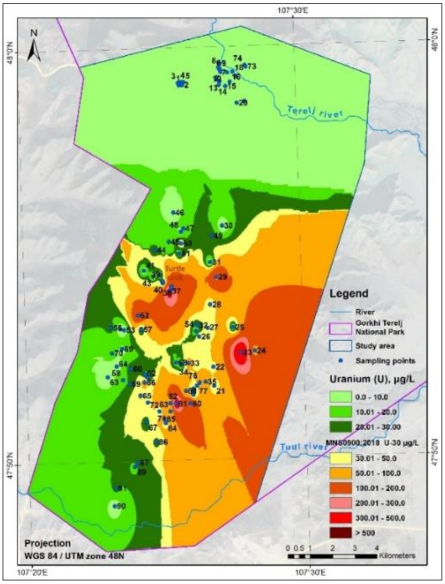

Fig.4. Geospatial distribution of Uranium

According to the WHO 2011 guidelines and Mongolian drinking water standards, the maximum permissible limit is 30 mg/L [8, 9]. Such as 30.7 % of the samples have uranium concentration higher than the recommended guideline value of 30 µg/L by the WHO and Mongolian drinking water standard. The uranium high concentrations in drinking waters have been earlier observed only in some parts of Mongolia [13].

Beryllium (Be): Beryllium (Be) is a relatively rare element and occurs naturally in the Earth's crust, in coal, and in various minerals, including beryl, bertrandite, bromellite, chrysoberyl, and beryllonite [14]. Beryllium (Be) is the smallest of all the metal cations and is relatively immobile in natural waters at neutral pH [15].

Hard rock aquifers of Lower Paleozoic age and granites have the highest values, with concentrations up to 4 µg/L. For example, in the noncarbonate groundwaters in the UK, beryllium was detected in aerobic waters from three aquifers the Namurian (Carboniferous) grits, the Devonian red sandstone, and the Cretaceous Lower Greensand Chalk [16].

The levels of concentration of Be were found between <0.1 and 6.7 µg/L, with a mean concentration of 0.56 µg/L (Fig.5).

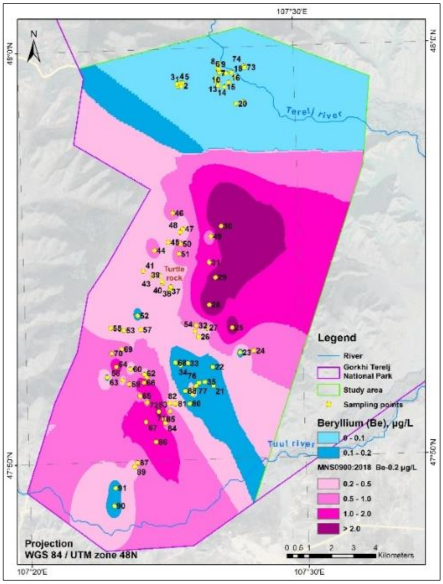

Fig.5. Geospatial distribution of Beryllium

Arsenic (As): The concentration of As was found between 0.19 and 49.5 µg/L, with a mean concentration of 3.5 µg/L. In response to health concerns about arsenic in drinking water, the World Health Organization has an upper threshold of 10 µg/L, while the value of As concentration in Gorkhi Terelj National Park 6 groundwater samples exceeded this value.

The highest level of As (49.5 μg/L) was recorded at the GW-52 sampling point. The second-highest level of As (25.5 μg/L) was recorded at the GW-26 sampling point (Fig.6).

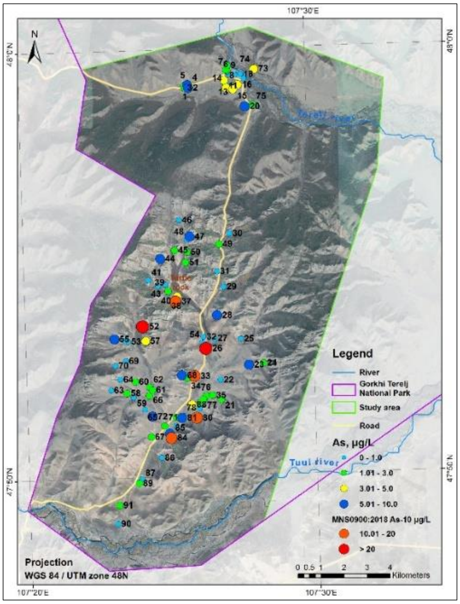

Fig.6. The concentration of Arsenic

The causes of high-arsenic groundwater are mainly a result of natural activities [17].

3.4 Heavy metal pollution index

The relative weighted index was used to assess the groundwater's suitability for drinking and irrigation purposes.

Table 4. Water quality classification as HPI

HPI	**Quality of Water**	No.of samples	Sampling points
<25.9	Very good	57	The rest of the others
26-50.9	Good	18	GW-14, GW-15, GW-24, GW-33, GW-35, GW-36, GW-44, GW-50, GW-59, GW-64, GW-65, GW-70, GW-72, GW-76, GW-82, GW-83, GW-84, GW-88
51-75.9	Poor	7	GW-25, GW-26, GW-38, GW-67, GW-71, GW-85, GW-86
76-100	Very poor	1	GW-66
>100.1	Unsuitable	8	GW-23, GW-28, GW-29, GW-30, GW-37, GW-52, GW-80, GW-81

Seeing from Table 4, the calculation of the heavy metal pollution index (HPI) showed that 62.6% of the samples showed "very good", "good" (19.7%; HPI 26.67-50.72), "poor" (7.69 %; HPI 52.19-74.81), "very poor" (1.09%; HPI 88.21), and 8.79% of the samples showed unsuitable for drinking purpose (HPI 110.4-304.9).

3.5 Weathering and Gibbs Diagram

Gibbs diagram suggested that atmospheric precipitation, rock weathering, and evaporation crystallization were the three major mechanisms controlling the chemistry of groundwater and surface water bodies. Weathering of different host rocks can yield different producing various combinations of dissolved cations and anions [18].

Fig.7 shows that the majority of the samples are plotted in the field of the rock dominance area, showing that rock-water interaction is the primary geochemical activity in the study area. Most of the samples show rock dominance, which shows that the chemical weathering of rock-forming minerals contributes to the groundwater chemistry in the studied area (Fig.7).

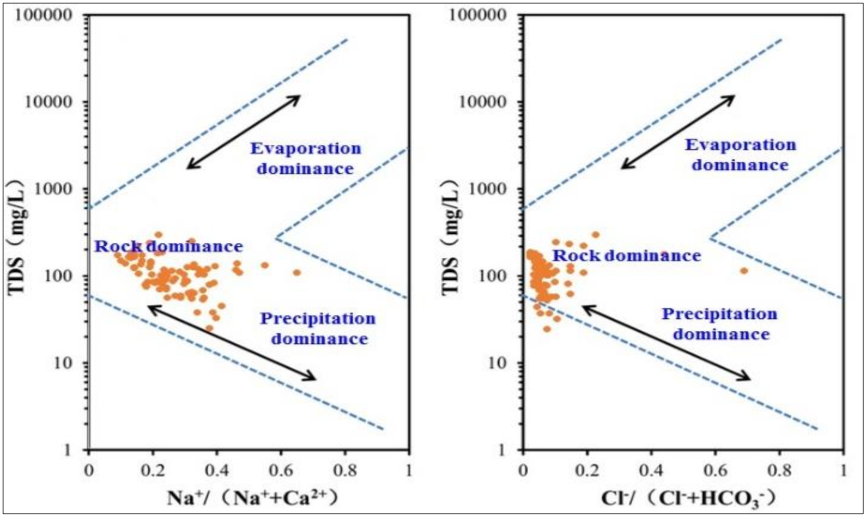

Fig.7. Gibbs diagram were used to explain groundwater chemistry and geochemical process in the study area.

High concentrations of heavy metals and chemical constituents in drinking water are derived from rock weathering, industrial wastewater discharges, and agricultural runoff.

4 Conclusion

In this study, 91 wells of water were collected and analyzed to evaluate groundwater quality in the area of Gorkhi Terelj which is one of the major National Parks in Mongolia. The composition of groundwater depends on the geological formations and rocks of the environment. The findings of the study are summarized as follows:

The hydrochemical data of the groundwater samples from the district of Gorkhi Terelj reveals that it is slightly acidic to neutral in nature and very fresh to fresh, very soft to medium hard type. The predominant hydrochemical types of groundwater were Ca-HCO_3 (97.8%). In the case of mineralization, about 67% of groundwater wells show very fresh, 32.9% fresh. In the case of hardness, 47.2% is very soft, 35.1% soft, and 17.5% medium-hard. Also pertaining to TDS concentration, total hardness, mineralization, and main cation, anion; All the samples taken from the study area were found to be below acceptable levels and suitable for drinking. But some heavy metals in the samples were very high.The uranium concentration varied from 0.073 to 642 µg/L; it surpassed the WHO drinking water standard (30 µg/L) at 30.7% of sampling sites. The concentration of arsenic (As 0.19-49.5 µg/L) in 6 water samples was 1.45-4.95 times higher than the WHO level and MNS0900:2018, molybdenum (Mo 0.2-77.5 µg/L) was 1.1 times higher in 1 sample, and manganese (Mn 6.0-1599 mg/l) was 1.1-15.9 times higher in 6 water samples. The heavy metal relative weighted index was used to assess the groundwater's suitability for drinking and irrigation purposes. The HPI values ranged between 4.05 and 304.9 with 8, 1, 7, 18, and 57 sampling points classified as unsuitable, very poor, poor, good, and very good water quality, respectively.

This study will provide baseline data for the assessment of groundwater quality and heavy metal pollution in groundwater in Gorkhi Terelj National Park Zone. Furthermore, continuous research should be implemented.

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