

Assessment of Groundwater Quality and its Suitability for Drinking and Agricultural Uses in the Oshnavieh Area, Northwest of Iran

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Received December 8th, 2009; revised February 27th, 2010; accepted February 28th, 2010.

ABSTRACT

The Oshnavieh plain is part of the West Azarbaijan province, which is located; 100 km south of Urmia City, northwestern of Iran, and its groundwater resources are developed for water supply and irrigation purposes. In order to evaluate the quality of groundwater in study area, 31 groundwater samples were collected and analyzed for various parameters. Physical and chemical parameters of groundwater such as electrical conductivity, pH, total dissolved solids, Na, K, Ca, Mg, Cl, HCO₃, CO₃, SO₄, NO₃, NH₃, PO₄, Fe, F were determined. Chemical index like percentage of sodium, sodium adsorption ratio, and residual sodium carbonated, permeability index (PI) and chloroalkaline indices were calculated. Based on the analytical results, groundwater in the area is generally fresh and hard to very hard. The abundance of the major ions is as follows: HCO₃ > SO₄ > Cl and Ca > Mg > Na > K. The dominant hydrochemical facieses of groundwater is Ca-HCO₃ and Ca-Mg-HCO₃ type. According to Gibbs diagrams samples fall in the rock dominance field and the chemical quality of groundwater is related to the lithology of the area. The results of calculation saturation index by computer program PHREEQC shows that the nearly all of the water samples were saturated to undersaturated with respect to carbonate minerals and undersaturated with respect to sulfate minerals. Assessment of water samples from various methods indicated that groundwater in study area is chemically suitable for drinking and agricultural uses. Fluoride and nitrate are within the permissible limits for human consumption and crops as per the international standards.

Keywords: Groundwater Quality, Hydrochemistry, Hydrogeology, Oshnavieh Plain, Water Type

1. Introduction

Understanding the aquifer hydraulic properties and hydrochemical characteristics of water is crucial for groundwater planning and management in the study area. Generally, the motion of groundwater along its flow paths below the ground surface increases the concentration of the chemical species [1-3]. Hence, the groundwater chemistry could reveal important information on the geological history of the aquifers and the suitability of groundwater for domestic, industrial and agricultural purposes. Moreover, pumping tests with the drilling results are the most important information available for the groundwater investigations, as they are the only methods that provide information on the hydraulic behavior of wells and reservoir boundaries [4,5].

Hydrochemical evaluation of groundwater systems is usually based on the availability of a large amount of information concerning groundwater chemistry [6,7]. Quality of groundwater is equally important to its quan-

tity owing to the suitability of water for various purposes [8,9]. Groundwater chemistry, in turn, depends on a number of factors, such as general geology, degree of chemical weathering of the various rock types, quality of recharge water and inputs from sources other than water-rock interaction. Such factors and their interactions result in a complex groundwater quality [1,10,11]. The rapid increase in the population of the country has led to large scale groundwater developments in some areas. Intense agricultural and urban development has caused a high demand on groundwater resources in arid and semi-arid regions of Iran while putting these resources at greater risk to contamination [12-14]. Groundwater is an important water resource for drinking, agriculture and industrial uses in study area. In this study, physical, hydrogeologic, and hydrochemical data from the groundwater system will be integrated and used to determine the main factors and mechanisms controlling the chemistry of groundwater in the area. The relationship between groundwater flow, hydrogeologic properties and hydro-

chemistry has been studied by many researchers [2,15, 16]. The chemical quality of groundwater is related to the lithology of the area.

The Oshnavieh aquifer is part of the Gedar river drainage basin and lies between latitudes 36°57' to 37°05' N and longitudes 45°01', to 45°15' E. Oshnavieh plain covers an area of 120 km² and average elevation is 1450 m a.s.l. (Figure 1). The Gedar river basin covers approximately 2010 km² and river flow direction is almost west-east with utmost discharges into the Urmia lake. The most important drainage feature of the study area is the Oshnavieh, Nilvan and Sheykhhan rivers. The area has a cold temperate climate and the air temperature is highest in August (26.7°C) and lowest in January (-1°C) with an annual average of 13.3°C. The climate of the study area is semi-arid and it's average annual rainfall is about 422 mm, which 70% of it falls during the spring and winter seasons. The most important economic activity in the area is agriculture, with the chief crops being beet, wheat and pea.

2. Materials and Methods

Groundwater samples were collected from 31 shallow and deep wells and springs of the area during May 2006. The location of sampling points is shown in Figure 4. The pH and electrical conductivity (EC) were measured using digital conductivity meters immediately after sampling. Water sample collected in the field were analyzed in the laboratory for the major ions (Ca, Mg, Na,

K, HCO₃, CO₃, SO₄, Cl), nitrate, phosphate, ammonia, iron and fluorine using the standard methods as suggested by the American Public Health Association [17]. Sodium (Na) and Potassium (K) were determined by flame photometer. Total hardness (TH) as CaCO₃, Calcium (Ca²⁺), carbonate (CO₃), bicarbonate (HCO₃) and chloride (Cl) were analyzed by volumetric methods. Magnesium (Mg) was calculated from TH and Ca contents. Sulfates (SO₄) were estimated using the colorimetric technique. Nitrate (NO₃), phosphate (PO₄), ammonia (NH₃), iron (Fe) and fluorine (F) were determined by spectrophotometer. The saturation indexes were determined using the hydrogeochemical equilibrium model, Phreeqc for Windows [18].

3. Results and Discussion

3.1 Geological and Hydrogeological Stting

From a geological point of view, the investigated area is located in the Khoy-Mahabad zone of the Iran [19]. Igneous, metamorphic and sedimentary rocks of different age's crop out in the basin and range in age from Precambrian to Quaternary. Precambrian sedimentary rocks consist of green to grey shale and siltstone. Cambrian formations in study area chiefly comprise crystalline limestone, siltstone, sandstone and dolomite in alternation with dark shale. The Ophiolite formation consists of crystallized limestone and shale with serpentinized ultramafic rocks, spite and some schist [20]. Igneous rocks of late Cretaceous age outcrop in many mountain and

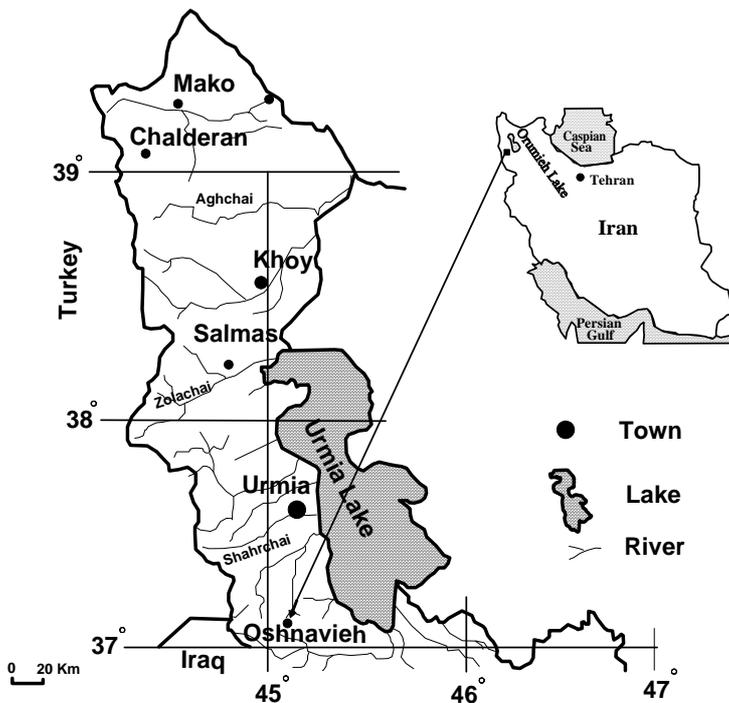


Figure 1. Location of study area in Iran

Oshnavieh aquifer is occurred in Quaternary sediments, which are distinguished by horizontal and vertical exchange of various lithological units. It is composed of Pleistocene and Holocene gravel-sand sediments and with silt-clay interbreeds. From field work and observations, groundwater occurs in the study area in two main water-bearing layers, a lower confined aquifer and an upper unconfined aquifer. Groundwater recharge is from rainfall. In the study area groundwater is an important source for domestic water supply. Groundwater and surface water of Gedar rivers use for agriculture uses. According to Azarbajian Regional Water Authority [22], 122 deep and 253 shallow active pumping wells operate in the aquifer. The water abstraction from the Oshnavieh aquifer during the 2003-2004 is about 30.738 million m³ and presented in **Table 2**. The hydraulic properties of Oshnavieh aquifer was determined using pumping tests data. The Oshnavieh aquifer is characterized by transmissivity that varies from 500-3000 m²/day and specific yield of about 3×10^{-2} [22]. One of the main imperative approaches for the identification of groundwater flow directions is the water level contour map, which has been used as a basis for evaluating groundwater recharge. Hence, water heads in meters above sea level (a.s.l.) in each piezometr were used to construct the piezometric surface contour map using the Surfer Software. The groundwater level contour map shown on **Figure 3** summarizes the distribution of piezometric head in the aquifer system within the study area. The general groundwater flow direction in the aquifer is from W to E, and depth to water table varies from 1.8 to 24.75 m below

ground level (**Figure 4**). Seasonal groundwater level fluctuations indicate that the water table tends to rise during November and April to reach peak in May and declines from January onwards to reach minimum in September [21].

3.2 Groundwater Chemistry

The chemical composition of groundwater results from the geochemical processes occurring as water reacts with the geologic materials which it flows [23]. The water quality analyses included all major anions, cations, nitrate, phosphate, ammonia, iron and fluorine. The allover groundwater pH and electrical conductivity (EC) values of the study area are ranging from 7.1 to 8.4 and 290 to 990 $\mu\text{S cm}^{-1}$, respectively. Total dissolved solids (TDS) in the study area vary between 182 to 582 mg/l. The groundwater in the study area falls under fresh (TDS < 1,000 mg/l) types of water [2]. The total hardness (as CaCO₃) ranges from 125 to 448 mg/l.

Table 2. Total Abstraction from Groundwater and springs during 2004

Water Re- source	Num.	Min.Dis- charge(lit/s)	Max.Dis- charge(lit/s)	Annual Dis- charge(MCM)	Agri- cultural uses (MCM)	Drinking uses (MCM)
Springs	23	1.5	35	6.927	6.341	0.585
Wells	375	2.4	44	23.811	19.26	4.55
Total	893	-	-	30.738	25.601	5.135

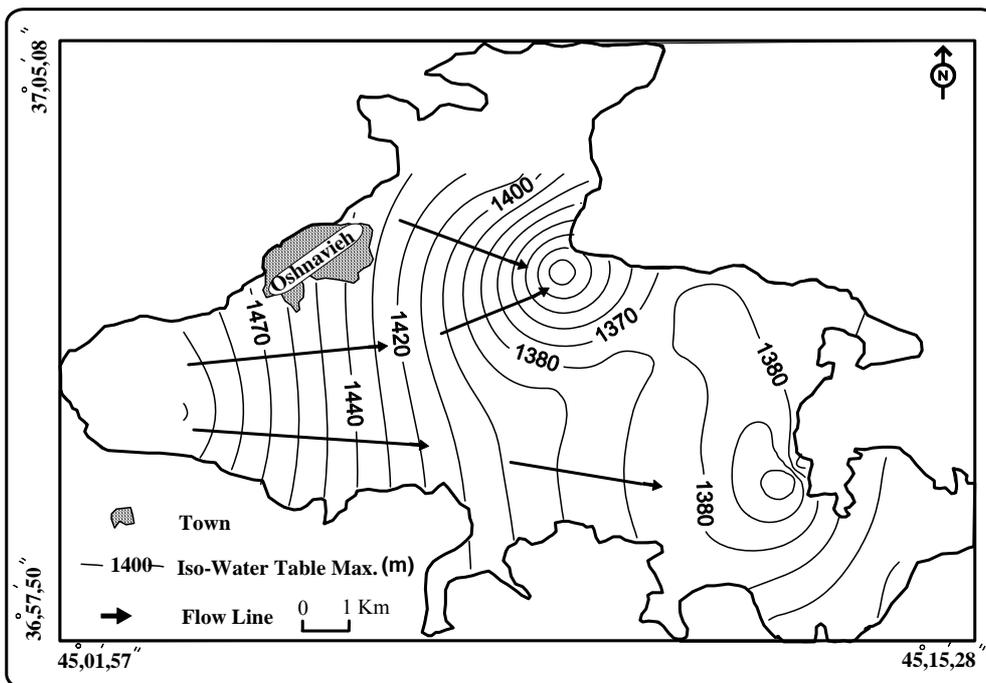


Figure 3. Groundwater level contour map of the aquifer system in the Oshnavieh plain (in meters above mean sea level)

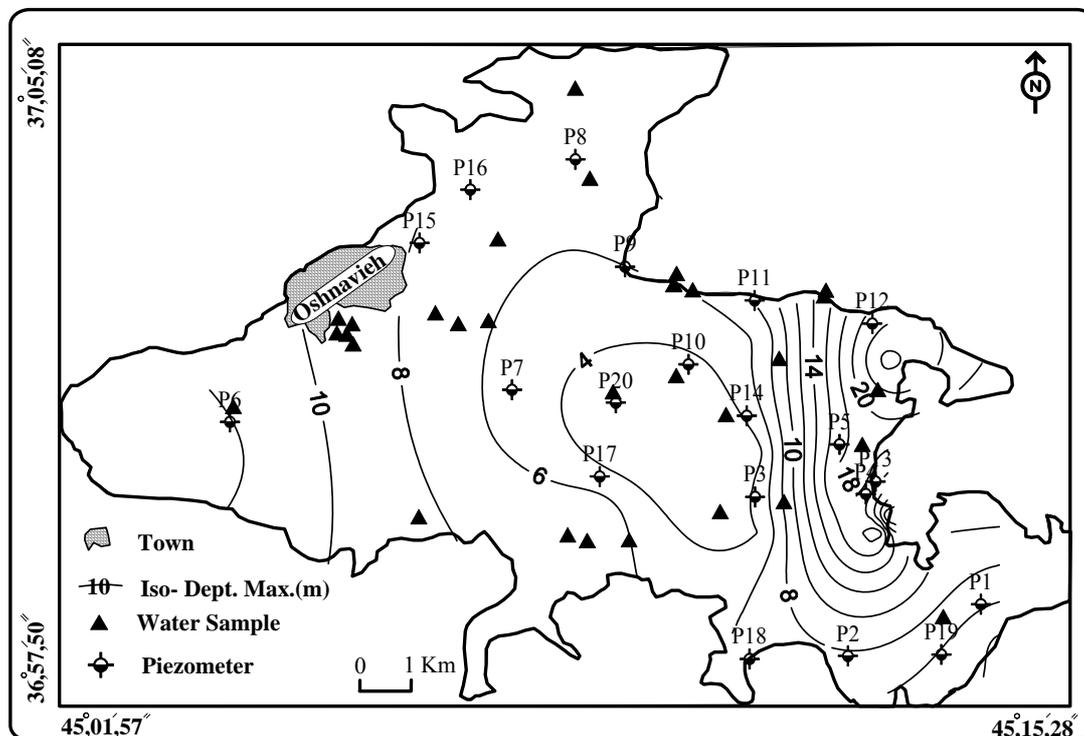


Figure 4. Depth groundwater contour map of the aquifer system in the Oshnavieh plain (in meters below ground level) and location of groundwater samples

In the study area, the Na and K concentrations in groundwater range from 2 to 52 and 0 to 11.7 mg/l, respectively. The concentrations of calcium range from 20 to 142 mg/l, which is derived from calcium rich minerals like feldspars, pyroxenes and amphiboles. The major source of magnesium (Mg) in the groundwater is due to ion exchange of minerals in rocks and soils by water. The concentrations of Mg and HCO_3^- ions found in the groundwater samples of study area are ranged from 12–51 and 140 to 506 mg/l respectively. The concentration of chloride ranges from 3.5 to 43 mg/l and increases from the recharge to discharge area. Sulfate varies from 8 to 48 mg/l. The nitrate concentration in May 2006 groundwater samples range from 8 mg/l to 62 mg/l with an average value of 16.6 mg/l. The source of nitrate in area is N fertilizers (commonly urea, nitrate or ammonium compounds) that are used for agricultural practices. Fluoride is one of main trace elements in groundwater, which generally occurs as a natural constituent. Bedrock containing fluoride minerals is generally responsible for high concentration of this ion in groundwater [24,25]. The concentration of fluoride in groundwater of the study area varies between 0.11-0.42 mg/l during May 2006 with an average value of 0.22 mg/l and all samples groundwater in study area are suitability for drinking. **Figure 5** shows that Ca, Mg and HCO_3^- are dominant cations and anion,

respectively. A further illustration of this is shown in **Figure 5** where the median values of HCO_3^- exceeded 50% of total anions in milli-equivalent unit. The abundance of the major ions in groundwater is in following order: $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{CO}_3^{2-}$. Minimum, maximum and average values of physical and chemical parameters of groundwater samples are presented in **Table 3**. The concentration of dissolved ions in groundwater samples are generally governed by lithology, nature of geochemical reactions and solubility of interaction rocks. The functional sources of dissolved ions can be broadly assessed by plotting the samples, according to the variation in the ratio of $\text{Na}/(\text{Na}+\text{Ca})$ and $\text{Cl}/(\text{Cl}+\text{HCO}_3^-)$ as a function of TDS [26]. The Gibbs plot of data from study area (**Figure 6**) indicates that rock is the dominant processes controlling the major ion composition of groundwater.

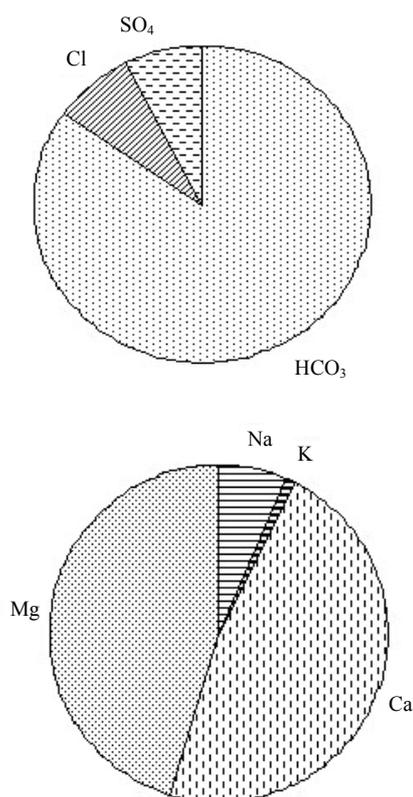
3.3 Saturation Index

Saturation indexes are used to evaluate the degree of equilibrium between water and minerals. Changes in saturation state are useful to distinguish different stages of hydrochemical evolution and help identify which geochemical reactions are important in controlling water chemistry [27–29]. The saturation index of a mineral is obtained from Equation (1) [30].

Table 3. Minimum, maximum and average values of physical and chemical parameters of groundwater samples

Parameters	Units	Minimum	Maximum	Average
pH	-	7.1	8.4	7.52
EC	S/cm μ	290	910	592
TDS	mg/l	182	582	374
Na	mg/l	2.63	34.78	7.14
K	mg/l	0	11.7	1.91
Ca	mg/l	20	142	45.16
Mg	mg/l	12	51	25.9
Cl	mg/l	3.5	43	17.97
HCO ₃	mg/l	140	506	297.6
CO ₃	mg/l	0	60	2.1
SO ₄	mg/l	8	48	23.75
TH	mg/l	125	448	294
SAR	-	0.074	1.8	1.25
%Na	%	2.63	34.78	7.14
RSC	meq/l	-2.93	2.3	-1.01
PI	%	30	66	42.9
CAL,1	meq/l	-0.7	0.64	-0.33
CAL,2	meq/l	-0.44	0.37	-0.18
SI _{calcite}	-	-0.82	0.12	-0.24
SI _{dolomite}	-	-1.84	-0.12	-0.62
SI _{gypsum}	-	-2.82	-1.77	-2.26
SI _{anhydrate}	-	-	-	-

EC: Electrical conductivity
 TDS: Total dissolved solids
 TH: Total hardness
 SAR: Sodium adsorption ratio
 RSC: Residual sodium carbonate
 PI: Permeability index
 CAL: Chloro alkaline index
 SI: Saturation index


Figure 5. Pie diagram of median values of major ions

$$SI = \log (IAP/Kt) \quad (1)$$

where IAP is the ion activity product of the dissociated chemical species in solution, Kt is the equilibrium solubility product for the chemical involved at the sample temperature. An index (SI), less than zero, indicate that the groundwater is undersaturated with respect to that particular mineral. Such a value could reflect the character of water from a formation with insufficient amount of the mineral for solution or short residence time. An index (SI), greater than zero, specifies that the groundwater being supersaturated with respect to the particular mineral phase and therefore incapable of dissolving more of the mineral. Such an index value reflects groundwater discharging from an aquifer containing ample amount of the mineral with sufficient resident time to reach equilibrium. Nonetheless, super saturation can also be produced by other factors that include incongruent dissolution, common ion effect, and evaporation, rapid increase in temperature and CO₂ exsolution [23,29]. In **Table 2** the SI for calcite, dolomite, anhydrate and gypsum are shown. **Figure 7** shows the plots of SI against TDS for all the investigated water. Nearly all water samples were saturated to undersaturate with respect to calcite, dolomite and aragonite and all samples undersaturated with respect to gypsum and anhydrite, suggesting that these carbonate mineral phases may have influenced the chemical composition of the study area. In Ca-HCO₃ water type the

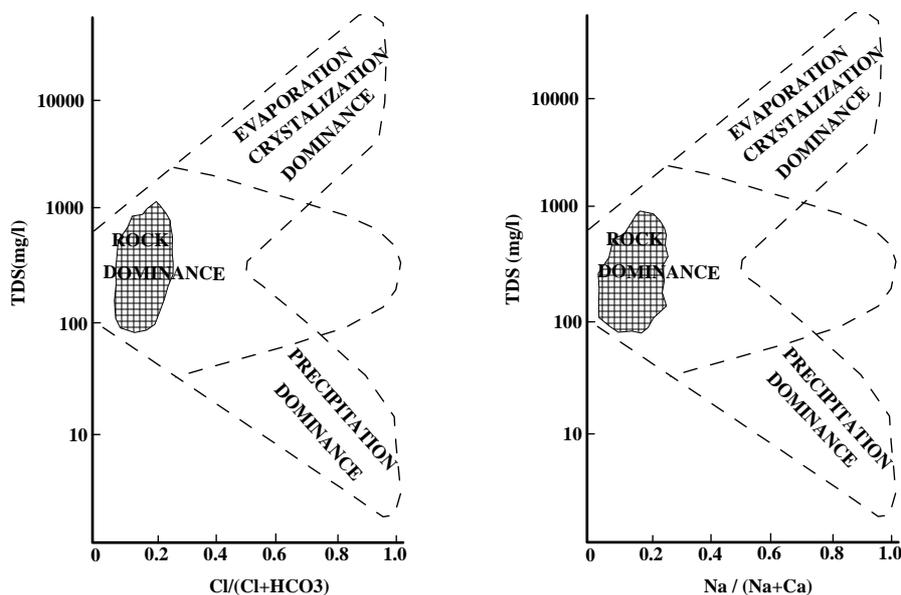


Figure 6. Mechanisms governing groundwater chemistry (after gibbs, 1970)

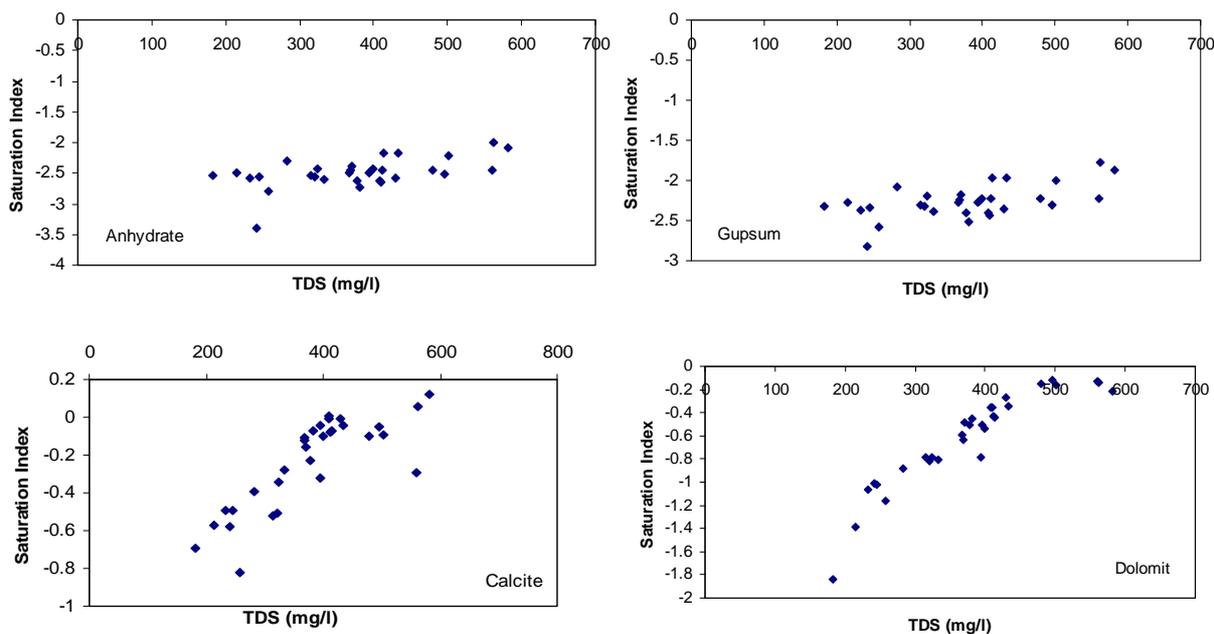


Figure 7. Plots of saturation indexes with respect to some carbonate minerals against total dissolved solids (TDS)

mean values of SI_{cal} , SI_{dol} , SI_{gyp} , SI_{anhy} are -0.24 , -0.617 , -2.26 and -2.49 , respectively.

3.4 Hydrochemical Facies

The values obtained from the groundwater samples analyzing, and their plot on the Piper's diagrams [31] reveal that the dominant cation is Ca and the anion is HCO_3 . In the study area, the major groundwater type is Ca- HCO_3 and Ca-Mg- HCO_3 (Figure 8). Chadha [32] has proposed new diagram for geochemical data presentations. The

proposed diagram is a modification of Piper diagram with a view to extend its applicability in representing water analysis in the possible simplest way. Results of analyses were plotted on the proposed diagram to test its applicability for geochemical classification of groundwater and to study hydrochemical processes (Figure 9). The plot shows that all of the groundwater samples fall under the subdivision of alkaline earths exceeds alkali metals and weak acidic anions exceed strong acidic anions (Ca-Mg- HCO_3 water type).

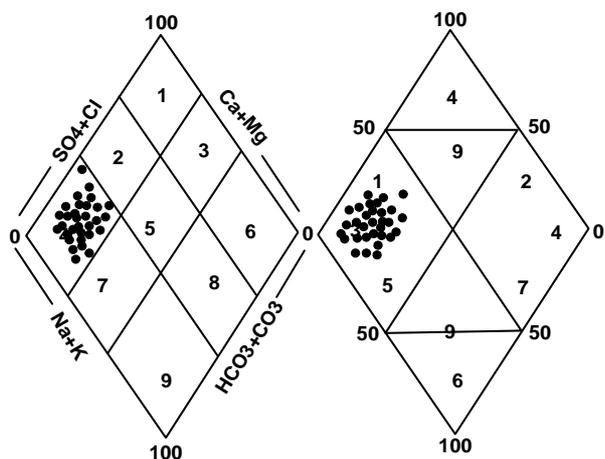


Figure 8. Chemical facies of groundwater in piper diagram

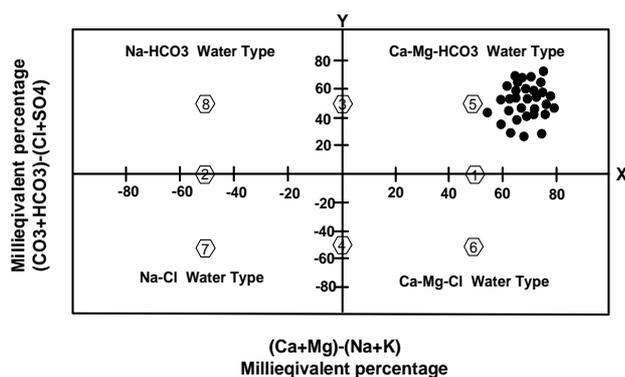


Figure 9. Diagram showing geochemical classification and hydrochemical parameters of groundwater (after Chadha, 1999)

3.5 Drinking and Irrigation Water Quality

The analytical results have been evaluated to ascertain the suitability of groundwater of the study area for drinking and agricultural uses. The drinking water quality is evaluated by comparing with the specifications of TH and TDS set by the World Health Organization [33,34]. According to WHO specification TDS up to 500 mg/l is the highest desirable and up to 1500 mg/l is maximum permissible (Table 4). Based on this classification, 87% of samples are belonging to highest desirable category and remaining samples are belonging to maximum permissible category. The hardness values range from 125 to 448 mg/l during May 2006. The classification of groundwater based on total hardness [35] (Table 5) shows that 59% of the groundwater samples fall in the very hard water category, 35% hard category and remaining samples fall in moderately hard category (Table 5). Maximum allowable limit of TH for drinking is 500 mg/l and the most desirable limit is 100 mg/l as per the WHO international standard. Based on this classification it in

Table 4. Groundwater samples of the study area exceeding the permissible limits prescribed by WHO for drinking purposes

Parameters	WHO international standard (1971, 1983)		
	Most desirable limits	Maximum Allowable limits	Amount in Groundwater samples
PH	7–8.5	9.2	7.1–8.4
TDS(mg/l)	500	1500	182–582
TH(mg/l)	100	500	125–448
Na(mg/l)	-	200	2–52
Ca(mg/l)	75	200	20–142
Mg(mg/l)	50	150	12–51
Cl(mg/l)	200	600	3.5–43
SO ₄ (mg/l)	200	400	8–48
NO ₃ (mg/l)	45	-	8–62
NH ₃ (mg/l)	0.05	0.5	0–0.05
F(mg/l)	-	1.5	0.115–0.425
Fe(mg/l)	0.1	1	0–0.141

Table 5. Suitability of groundwater based on hardness

Total hardness as CaCO ₃ (mg/l)	Water class
<75	Soft
75–150	Moderately hard
150–300	Hard
>300	Very hard

icates that all of the groundwater samples are not exceed the maximum allowable limits.

Salinity and indices such as, sodium absorption ratio (SAR), sodium percentage (Na %), residual sodium carbonate (RSC), and permeability index (PI) are important parameters for determining the suitability of groundwater for agricultural uses [36,37]. Electrical conductivity is a good measure of salinity hazard to crops as it reflects the TDS in groundwater. The US Salinity Laboratory [38] classified ground waters on the basis of electrical conductivity (Table 6). Based on this classification, 16% of samples are belonging to the doubtful category and 84% to good category. Sodium adsorption ratio (SAR) is an important parameter for determining the suitability of groundwater for irrigation because it is a measure of alkali/sodium hazard to crops [9]. SAR is defined by

Table 6. Classification of groundwater for irrigation based on EC, SAR

Quality of water	Electrical conductivity (S/cm)	Sodium adsorption ratio(SAR)
Excellent	<250	<10
Good	250–750	10–18
Doubtful	750–2250	18–26
Unsuitable	>2250	>26

Karant [39] as Equation (2).

$$SAR = Na / [(Ca + Mg) / 2]^{1/2} \quad (2)$$

where all ionic concentrations are expressed in meq/l. The SAR values range from 0.074 to 1.84 and according to the Richards [40] classification based on SAR values (Table 6), all of samples are belong to the excellent category. SAR can indicate the degree to which irrigation water tends to enter into cation-exchange reactions in soil. Sodium replacing adsorbed calcium and magnesium is a hazard as it causes damage to the soil structure and becomes compact and impervious [37]. The analytical data plotted on the US salinity diagram [40] illustrates that 77% of the groundwater samples fall in the field of C2S1, indicating medium salinity and low sodium water, which can be used for irrigation on all types of soil without danger of exchangeable sodium (Figure 10). The sodium percent (%Na) is obtained by the Equation (3).

$$\%Na = [Na] \times 100 / [Ca + Mg + Na + K] \quad (3)$$

where all ionic concentrations are expressed in meq/l.

The Wilcox [41] diagram relating sodium percentage and total concentration shows that 26% of the groundwater samples fall in the field of good to permissible and 74% of the groundwater samples fall in the field of excellent to good for irrigation (Figure 11).

Residual sodium carbonate (RSC) has been calculated to determine the hazardous effect of carbonate and bicarbonate on the quality of water for agricultural purpose and has been determined by the Equation (4).

$$RSC = (CO_3 + HCO_3) - (Ca + Mg) \quad (4)$$

where all ionic concentrations are expressed in meq/l [42]. The classification of irrigation water according to the RSC values is waters containing more than 2.5 meq/l

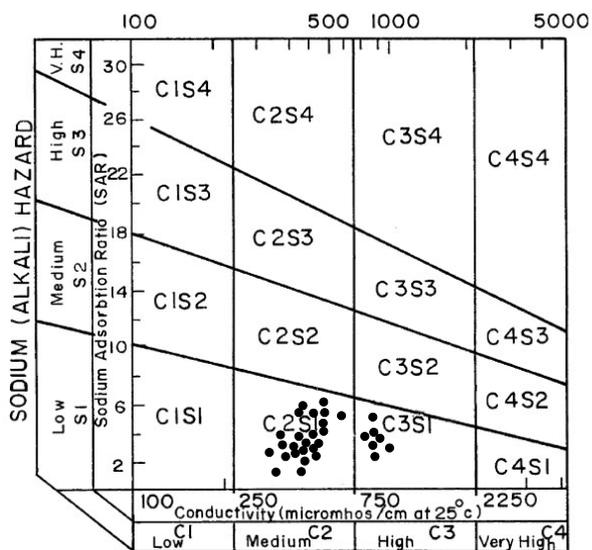


Figure 10. Rating of groundwater samples in relation to salinity and sodium hazard

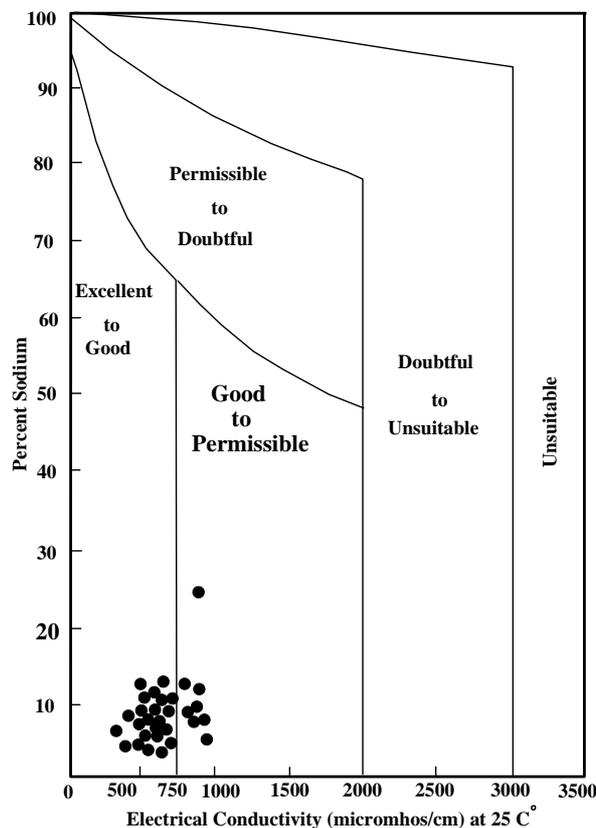


Figure 11. Rating of groundwater samples on the basis of electrical conductivity and percent sodium (after Wilcox, 1955)

of RSC are not suitable for irrigation, while those having -2.93 to 2.3 meq/l are doubtful and those with less than 1.25 meq/l are good for irrigation. Based on this classification, all of groundwater samples belong to the good category except one sample. The permeability index (PI) values also indicate that the groundwater is suitable for irrigation. It is defined as follows (Equation (5))

$$PI = 100 \times \frac{[Na] + [HCO_3]^{1/2}}{[Na] + [Ca] + [Mg]} \quad (5)$$

where all the ions are expressed in meq/l [44]. WHO [45] uses a criterion for assessing the suitability of water for irrigation based on permeability index. The PI range from 30% to 66% and the average value is about 43% during May 2006. According to PI values, the groundwater of in the study area can be designated as class II (25–75%) that shows the groundwater in study area is suitable for irrigation purposes.

3.6 Chloroalkaline Indices (CAI)

It is essential to know the changes in chemical composition of groundwater during its travel in the sub-surface [45]. The Chloro-alkaline indices CAI 1, 2 are suggested by Schoeller [46], which indicate the ion exchange between the groundwater and its host environment. The

Chloro-alkaline indices used in the evaluation of Base Exchange are calculated using the Equations (6,7).

1) Chloro Alkaline Indices

$$I = [\text{Cl}-(\text{Na}+\text{K})] / \text{Cl} \quad (6)$$

2) Chloro Alkaline Indices

$$2 = [\text{Cl}-(\text{Na}+\text{K})]/(\text{SO}_4+\text{HCO}_3+\text{CO}_3+\text{NO}_3) \quad (7)$$

If there is ion exchange of Na and K from water with magnesium and calcium in the rock, the exchange is known as direct when the indices are positive. If the exchange is reverse then the exchange is indirect and the indices are found to be negative. The CAI 1, 2 are calculated for the waters of the study area as given in **Table 2**. Chloro Alkaline Indices 1, 2 calculations shows that 26% of the groundwater sample is negative and 74% positive ratios.

4. Conclusions

Interpretation of hydrochemical analysis reveals that the groundwater in study area is fresh, hard to very hard. The sequence of the abundance of the major ions is in the following order: $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$ and $\text{HCO}_3 > \text{SO}_4 > \text{Cl}$. Alkali earths slightly exceed alkalis and weak acids exceed strong acids. Falling of water samples in the rock dominance area in Gibbs plot indicates the interaction between rock chemistry and the chemistry of the percolating precipitation waters in the sub-surface. The results of calculation saturation index show that the nearly all of the water samples were saturated to undersaturated with respect to carbonate minerals (calcite, dolomite and aragonite) and undersaturated with respect to sulfate minerals (gypsum and anhydrite). In the study area, the dominant hydrochemical facieses of groundwater is Ca- HCO_3 and Ca-Mg- HCO_3 . Distribution of the groundwater samples in rectangular diagram reveals that all of the groundwater samples fall under the calcium-magnesium-bicarbonate category. According to classification of water based on TDS, 87% of samples are belonging to highest desirable category and remaining samples are belonging to maximum permissible category. Irrigation waters classified based on SAR has indicated that 83% of samples belong to the excellent, 11% samples good and remaining samples belong to doubtful category. The Wilcox diagram relating sodium percentage and total concentration shows that 26% of the groundwater samples fall in the field of good to permissible and 74% of the groundwater samples fall in the field of excellent to good for irrigation. The analytical data plotted on the US salinity diagram illustrates that 77% of the groundwater samples fall in the field of C2S1, indicating medium salinity and low sodium water. Base on the classification of irrigation water according to the RSC values, all of groundwater samples belongs to the good category. According to PI values, the groundwater of in the study area can be designated as class II (25 - 75%) that shows the groundwa-

ter in study area is suitable for irrigation purposes. Assessment of water samples from various methods indicated that groundwater in study area is chemically suitable for drinking and agricultural uses. Chloroalkaline Indices 1, 2 calculations shows that 26% of the groundwater sample is negative and 74% positive ratios. The positive values indicate absence of base-exchange reaction.

5. Acknowledgements

This study was supported by the Islamic Azad University of Urmia. The authors gratefully acknowledge the Azarbaijan Regional Water Authority for supplying the existing relevant data and also wish to thank Ms. Hajilar for the water chemistry analysis. We would like to thank Mr. E. Eliassi for their kindly help during the field visits and the collection of data.

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