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Evaluation of groundwater quality for drinking purpose in Ardabil aquifer

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ABSTRACT

Ground water is an important component of fresh water resources. The use of ground water is of fundamental importance to human life and is also significant to economic vitality. This study attempt to evaluate ground water quality through Drinking water Quality Index (DWQI), referencing Institute of Standards and Industrial Research of Iran (ISIRI) and World Health Organization (WHO) guidelines, in Ardabil aquifer. In order to understand ground water quality, water samples were collected from 63 wells. The primary chemical parameters like pH, TDS, TH, Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, and F^- were analyzed for DWQI. Groundwater quality classification maps based on $DWQI_{ISIRI}$ and $DWQI_{WHO}$ were created by kriging method in GIS environment. Results indicated that the average values of the most chemical properties were above WHO and ISIRI standards except pH, Na^+, Cl^-, NO_3^-, and F^- which were within the WHO and ISIRI standards. $DWQI_{WHO}$ and $DWQI_{ISIRI}$ are strongly correlated with each other (R^2= 0.985) but in all samples the values of $DWQI_{WHO}$ were greater than the corresponding $DWQI_{ISIRI}$. TH and TDS had the greatest correlation with $DWQI_{WHO}$ and $DWQI_{ISIRI}$ and were considered as the main parameters controlling drinking water quality. Spatial distribution maps of $DWQI_{WHO}$ and $DWQI_{ISIRI}$ indicated that the areas occupied by different water quality classes are in the following order: Poor > Good> Very poor> Excellent. Poor water quality class has occupied 49.2 and 61.6 percent of the study area based on $DWQI_{ISIRI}$ and $DWQI_{WHO}$, respectively. Due to this quality deterioration of groundwater quality, an immediate attention should be employed in critical locations of the Ardabil Aquifer.

Key words : *Water quality, Drinking water, ISIRI, WHO, GIS, Ardabil Aquifer*

Introduction

Throughout the world, increasing demands for safe drinking water and healthy ecosystems are leading more attention about how to assess and manage our water resources. Fresh water is a valuable and limited resource which ensures sustainable development, economic growth, and social stability. Water quality has grown to become the major international issue in recent years (Rejith *et al*., 2009). Intensive agriculture, urban growth, and increased industrial activities have been recognized as drivers responsible for decreasing water quality (Patwardhan, 2003).

Iran's annual precipitation rate is somewhere between one-third and one-fourth of the world's average, and around two-thirds of the country receives less than the global norm. Furthermore, around 71 percent of this precipitation evaporates, and this number is likely to rise in the future. 50 percent of

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Iran's water comes from underground sources, but in many parts of the country underground water supplies are drying up.

Mismanagement of water resources has exacerbated problems related to the quality and quantity of water resources, and climate change is likely to significantly worsen the problem in the future. In arid and semi-arid areas, ground water is considered as the main source of water resources and the quality of this resource must be monitored and controlled to develop water policies and management practices. Water quality measurement also provides a tool to assess the influence of human activities on ecosystems. Functions and condition of aquatic ecosystems are evaluated by water quality. Efficient use of water strategies should help to reduce the escalating demand for irrigation water, complementarily between water pricing, water rights, and local water governance (Veettil *et al*., 2011).

To determine water quality for different uses such as drinking, agricultural, and industrial use, physical, chemical, and biological parameters should be considered (Boyacioglu, 2007). Traditional methods of evaluating water quality are based on the comparison of experimentally determined parameter values with guidelines (Tabesh *et al.*, 2011). These methods usually are confusing, and it's very hard to make a reliable decisions based on them because of the complicated results. To overcome these kind of problems, water quality index (WQI) has been introduced which serves as a useful and efficient method for assessing the suitability of water quality for various purposes. WQI method aims to give an index score to the water quality by translating the list of parameters and their concentrations in a sample into a single value. In other words, the indices are composite representations of a condition derived from a combination of several relevant observed measurements. The index number could be understandable, useful to technical and policy individuals as well as the general public who are interested in the water quality results. This is particularly important in reporting the state of the environment (Boyacioglu, 2007; Nagels *et al*., 2001).

The use of a WQI was initially suggested by Horton in 1965 and since then, different methods and indices have been developed. The main goal was to present a tool to simplify the reporting of water quality. These indices evaluate the suitability of water quality for different uses (Elango *et al*., 2003; Singh *et al*., 2008). For WQI formulation, water quality parameters are determined and some parameters of water quality are selected and a few of them judged more important than the others, so a weighted mean is used to combine the values (Dahiya *et al*., 2007; Alberta Sustainable Resource Development Communications 2012).

In this study groundwater quality in rural and urban areas of Ardabil region, Northwestern Iran, is evaluated by a general water quality index for drinking purpose (Anbazhagan & Jothibasu, 2014; Tiwari & Manzoor, 1988). The objectives are to compare the Drinking Water Quality Index (DWQI) values computed by referencing Institute of Standards and Industrial Research of Iran (ISIRI) and World Health Organization (WHO) standards and to determine the relationships between water quality parameters and DWQI.

Material and Methods

Study Area

The Ardabil plain aquifer is situated in the Northwest of Iran and lies approximately between latitude 38°07´06´´N to 38°25´37´´N and longitude 48°10´58´´E to 48°38´06´´E (Fig. 1). This plain has an aerial coverage of about 710 km^2. The region experiences pleasant summer and relatively long winters with an average annual precipitation of about 300 mm. The Ardabil plain is surrounded by elevations which are parts of Alborz Mountains. In the west of the plain, conglomerate with some tuff, volcanic ashes, and lahars are outcropped. Ardabil plain that has been formed out of Quaternary alluvial deposits, originated from alteration of surrounding mountains.

Sampling and Chemical Analysis

Groundwater samples were collected from 63 wells. The location of sampling points is shown in figure 1. The pH, electrical conductivity (EC), and total dissolved solids (TDS) of samples were measured insitu by using digital conductivity meters. To determine DWQI, each samples was analyzed for parameters such as calcium(Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), fluoride (F^-), and total hardness (TH). Na^+ and K^+ were determined by flame photometer and HCO_3^-, Cl^-, Ca^{2+}, and Mg^{2+} by the titration method. F^-, NO_3^-, SO_4^{2-} were determined by spectrophotometer. TH was

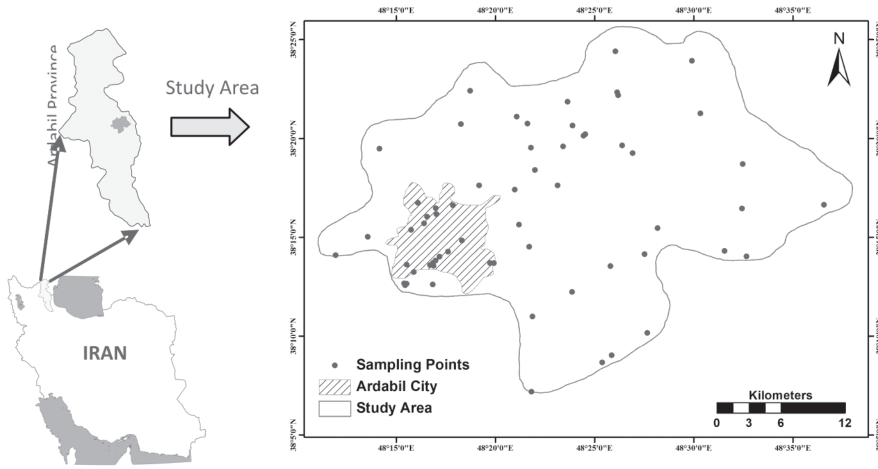

Fig.1. Geographical location of the study area with the distribution of sampling wells

calculated from the calcium and magnesium hardness which are the concentration of calcium and magnesium ions expressed as equivalent of calcium carbonate (APHA, 1998).

Calculation of DWQI

To evaluate the suitability of groundwater quality in the study area, DWQI has been calculated by referencing ISIRI and WHO standards for drinking aims. For the calculation of WQI, 12 parameters such as pH, total dissolved solids (TDS), Total hardness (TH), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), bicarbonate (HCO_3^-), chloride (Cl^-), sulphate (SO_4^{2-}), nitrate (NO_3^-), and fluoride (F^-) have been used.

To compute WQI, four steps are followed. In the first step, each of the 12 parameters has been assigned a weight (w_i) according to its relative importance in the overall quality of water for drinking objectives (Table 1). The maximum weight of 5 has been assigned to nitrate due to its major importance in water quality assessment and human health (Srinivasamoorthy *et al.*, 2008). Other parameters like calcium, pH magnesium, sodium, and potassium were assigned a weight between 1 and 5 depending on their importance in the overall quality of water for drinking purposes.

In the second step, the relative weight (W_i) is computed using a weighted arithmetic index method given below (Brown *et al.*, 1972; Horton, 1965; Tiwari & Manzoor, 1988) in the following steps:

Table 1. WHO and ISIRI standards, weight (w_i), and relative weight (W_i) for each parameter

Chemical parameter	WHO (2006) standard (S_i)	ISIRI (2008) standard (S_i)	Weight (w_i)	Relative weight (W_i)
pH	8.5	6.5-8.5	4	0.105
TDS	500	1000	4	0.105
TH	100	200	2	0.053
Ca^{2+}	75	300	2	0.053
Mg^{2+}	30	30	2	0.053
Na^{+}	200	200	2	0.053
K^{+}	10	10	2	0.053
HCO_3^-	300	300	4	0.105
Cl^-	200	250	3	0.079
SO_4^{2-}	200	250	4	0.105
NO_3^-	50	50	5	0.132
F^-	1.1	1	4	0.105
Total			Σw_i=38	ΣW_i=1

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \quad .. (1)$$

Where, W_i is the relative weight, w_i is the weight of each parameter and n is the number of parameters.

In the third step, a quality rating scale (Q_i) for each parameter is calculated in percent by dividing its concentration in each water sample by its respective standard according to the guidelines of ISIRI and WHO and multiplying by 100:

$$Q_i = \left(\frac{C_i}{S_i}\right) \times 100 \quad .. (2)$$

Where Q_i is the quality rating, C_i is the concentration of each chemical parameter in each water sample in mg/L, and S_i is the ISIRI and WHO drinking water standards for each chemical parameter in mg/L according to Table 1.

In the fourth step, the SI is first determined for each chemical parameter, which is then used to determine the WQI as per the following equation:

$$SI_t = W_t \times Q_t \quad .. (3)$$

SI_i is the sub index of parameter i and Q_i is the rating based on concentration of parameter i. The overall DWQI was calculated by adding together each sub index values of each groundwater samples as follows:

$$DWQI = \sum_{i=1}^{n} SI_i \quad .. (3)$$

Because of the difference between the S_i in ISIRI and WHO standards (Table 1), two different values of DWQI was computed for each water sample which were named $DWQI_{ISIRI}$ and $DWQI_{WHO}$ According to the ISIRI and WHO standards. Computed DWQI values are subdivided into four classes (Table 2): excellent, good, poor, and very poor for drinking purposes (Sahu and Sikdar, 2008; Ramakrishnaiah, *et al*., 2009).

Results

A statistical summary of chemical parameters from groundwater samples is presented in Table 3. The average ranges for Na^+, K^+, Ca^{2+}, and Mg^{2+} in terms of mgL^{-1} are 160.39, 23.70, 162.15, and 50.64, respectively. The predominant cations trend in the study area is $Ca^{2+} > Na^+ > Mg^{2+} > K^+$. The average ranges for Cl^-, HCO_3^-, NO_3^-, F^-, and SO_4^{2-} in terms of mgl^{-1} are 184.73, 474.45, 39.19, 0.7, and 373.01. The abundance of the major anions in groundwater samples of Ardabil is in the following order: $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^- > F^-$. TDS values of the groundwater samples of the study area range from 148 to 3716 mgL^{-1} and pH values lie between the ranges of 6.44 to 8.19. The pH has lowest and Cl^-, SO_4^{2-}, and NO_3^- have the greatest variability among the water chemical properties.

Table 2. Classification of DWQI values

WQI range	Type of water
<50	Excellent
50-100	Good
100-200	Poor
>200	Very poor

The average values of the most chemical properties were above WHO and ISIRI standards except pH, Na^+, Cl^-, NO_3^-, and F^- which were within the WHO and ISIRI standards. In the case of Ca^{2+}, the average value in water samples were above the WHO standard but it's within the ISIRI standard.

Empirical cumulative frequency distribution of DWQI values based on WHO and ISIRI standards represented in Figure 2. This figure contains detailed information about $DWQI_{WHO}$ and $DWQI_{ISIRI}$ values in 63 groundwater samples. $DWQI_{WHO}$ ranges from 46.7 to 454 and $DWQI_{ISIRI}$ ranges from 37.5 to 337. Lower values of DWQI indicate that the water is clear and is free of any impurities. According to the figure 2 and $DWQI_{WHO}$ distribution, it can be concluded that only a few percent of water samples

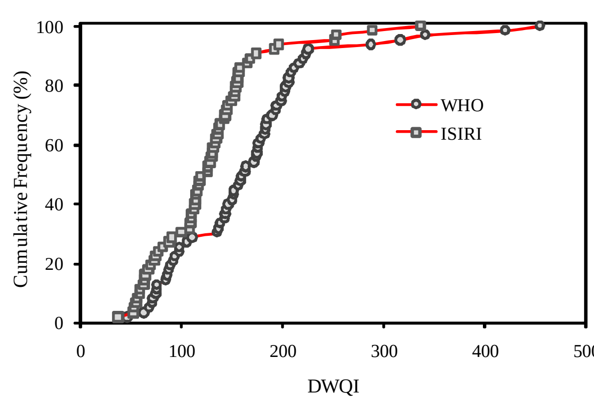

Fig. 2. Cumulative frequency percent in relation to DWQI

have excellent quality for drinking aims. Approximately, the frequency of water samples with good, poor, and very poor quality, based on WHO standards, were 23, 50, 24 percent, respectively. According to $DWQI_{ISIRI}$ distribution, less than 2% of the wells contain excellent water; 27% have good water; 65% have poor water; and 6.35% of samples contain very poor water.

$DWQI_{ISIRI}$ values of water samples were plotted against the corresponding $DWQI_{WHO}$ to show the correlation and quantitative difference between two approaches (Fig. 3). As it is apparent the figure, there is a strong linear relationship (R^2=0.985) between DWQI values derived from two standards. In all cases, $DWQI_{WHO}$ value is higher than the corresponding $DWQI_{ISIRI}$. The difference between two approaches is negligible in the relatively low values of DWQI (approximately less than 170) but with increasing the DWQI quantity, the difference between $DWQI_{ISIRI}$ and $DWQI_{WHO}$ values tends to be higher.

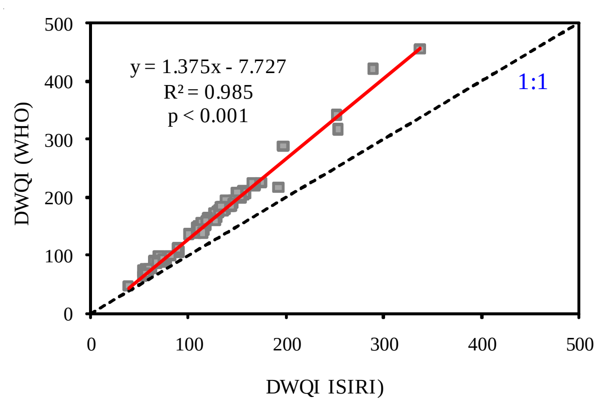

Fig.3. DWQI based on WHO in comparison with ISIRI

In order to analyze the groundwater quality parameters of the study region, correlation between various chemical parameters were calculated which are indicated in Table 4. According to the correlation analysis, most of parameters are positively related to one another except pH. TDS parameter has significant correlation at 0.01 levels with TH, Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}, F^{-} and significant correlation at 0.05 levels with HCO_3^{-} and NO_3^{-}. TDS has high correlation with Na^{+} and Cl^{-} in the cations and anions, respectively. It also distinguishes that TH has high correlation with Ca^{2+} and Mg^{2+} among the cations and Cl^{-} among the anions. It is noticed that the highest correlation is among TDS and Na^{+}, Mg^{2+}, Ca^{2+}, Cl^{-}. This indicates that these four parameters are the main contributors to TDS in the study area and they indicate the majority of salts in the groundwater samples. High correlation between Na^{+}, Mg^{2+}, and Cl^{-} also demonstrates this fact. Similar results reported by Saat-nori *et al.* (2014) in water samples of Saveh-Nobaran aquifer at the central Iran. $DWQI_{ISIRI}$ and $DWQI_{WHO}$ have highest correlation with TH and TDS which indicates the importance of these two parameters in water quality assessment for drinking purposes. Correlation of $DWQI_{WHO}$ with the chemical parameters is in the following order: TH> TDS> Mg^{2+}> Na^{+}> Ca^{2+}> SO_4^{2-}= Cl^{-}>F^{-}> NO_3^{-}> HCO_3^{-}> K^{+}> pH. In addition, similar results for $DWQI_{ISIRI}$ were observed.

Groundwater quality classification maps based on $DWQI_{ISIRI}$ and $DWQI_{WHO}$ were created by kriging method in GIS environment for determining their spatial variation in the study area (Figure 4). Figure 5 also indicates the relative percentage of study area occupied by each class of water quality. According

Table 3. Summary statistics of the analytical data and groundwater samples of the study area

Parameter	Units	Min	Max	Average	CV# (%)
pH	-	6.4	8.19	7.5	4.00
TDS	mgL^{-1}	148	3716	1005	64.28
TH	mgL^{-1}	68.8	1964.4	607.3	58.57
Ca^{2+}	mgL^{-1}	6.6	438.2	162.1	52.50
Mg^{2+}	mgL^{-1}	1.3	210.9	50.6	78.06
Na^{+}	mgL^{-1}	23.9	621.4	160.4	70.45
K^{+}	mgL^{-1}	0.4	107.6	23.7	42.62
HCO_3^{-}	mgL^{-1}	218.7	1014.1	474.4	53.14
Cl^{-}	mgL^{-1}	20.9	1077.1	184.7	91.82
SO_4^{2-}	mgL^{-1}	0.0	1973.2	373.0	89.20
NO_3^{-}	mgL^{-1}	0.0	143.6	39.2	85.71
F^{-}	mgL^{-1}	0.0	1.4	0.70	42.86

Coefficient of variation

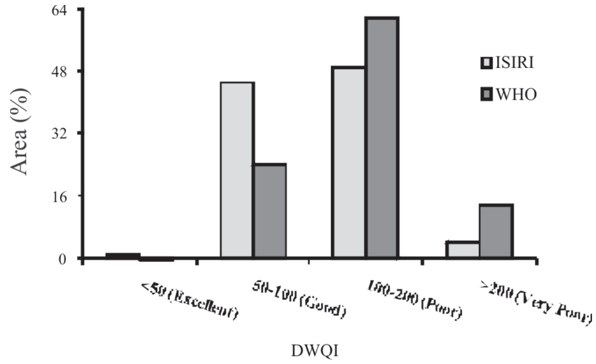

Fig. 5. Relative percentage of area occupied by different DWQI classes based on ISIRI and WHO standards

to the distribution maps and figure 5, the area occupied by different water quality classes in both of $DWQI_{ISIRI}$ and $DWQI_{WHO}$ is in the following order: Poor > Good> Very poor> Excellent. Good water quality was observed mainly in the eastern parts of the study area. Central parts have poor water quality and a narrow border in northern and southern parts of the region has very poor quality for drinking. It should be noticed that the area of each class is different when considering $DWQI_{ISIRI}$ and $DWQI_{WHO}$. For example, the relative percentage of area with good water quality is in 45.3 for $DWQI_{ISIRI}$ and 24.4 for $DWQI_{WHO}$. Poor water quality class has occupied about 49.2 and 61.6 percent of the area for $DWQI_{ISIRI}$ and $DWQI_{WHO}$, respectively. Ardabil city lies in area with poor water quality based on $DWQI_{ISIRI}$. When considering $DWQI_{WHO}$, Ardabil city lies in area with poor and very poor water quality.

Discussion

Groundwater is increasingly gaining importance as a main solution of water supply in Iran. This study aims to evaluate the water quality for drinking purposes by referencing ISIRI and WHO guidelines. The average values of Mg^{2+}, SO_4^{2-}, K^+, HCO_3^-, TH, and TDS were above the permissible limits of ISIRI and WHO guidelines.

Chemical reactions of Mg^{2+} in the groundwater are similar to those of Ca^{2+} (Akoteyon, 2013). Mg^{2+} normally occurs at about half the concentration of Ca^{2+}; however in the study area average Mg^{2+} concentration was slightly less than the half of Ca^{2+}. High concentrations of Ca^{2+} and Mg^{2+} are important factors, which increase the hardness of waters (Ravikumar *et al*., 2010). The presence of sulfate in

Table 4. Correlation matrix between groundwater quality parameters of Ardabil province

	pH	TDS	TH	Ca	Mg	Na	K	HCO_3	Cl	SO_4	NO_3	F	$DWQI_{WHO}$	$DWQI_{ISIRI}$
pH	1													
TDS	-0.357**	1												
TH	-0.264*	0.894**	1											
Ca	-0.316*	0.786**	0.933**	1										
Mg	-0.240	0.898**	0.903**	0.727**	1									
Na	-0.228	0.909**	0.834**	0.679**	0.902**	1								
K	-0.200	0.179	0.095	0.073	0.099	0.124	1							
HCO_3	-0.431**	0.269*	0.307*	0.309*	0.207	0.302*	0.152	1						
Cl	-0.081	0.756**	0.717**	0.589**	0.758**	0.743**	0.044	0.037	1					
SO_4	-0.110	0.607**	0.643**	0.533**	0.680**	0.683**	-0.117	0.252*	0.541**	1				
NO_3	-0.263*	0.261*	0.387**	0.433**	0.236	0.212	0.032	0.468**	0.114	0.398**	1			
F	-0.165	0.552**	0.476**	0.388**	0.514**	0.548**	0.229	0.140	0.572**	0.192	0.079	1		
$DWQI_{WHO}$	-.330**	0.915**	0.931**	0.833**	0.899**	0.881**	0.307*	.405**	0.734**	0.732**	0.466**	0.531**	1	
$DWQI_{ISIRI}$	-0.336	0.882**	0.886**	0.778**	0.870**	0.860**	0.390**	.437**	0.705**	0.717**	0.488**	0.539**	0.993**	1

*and ** correlations are significant at 0.05 and 0.01 levels, respectively.

drinking water can cause noticeable taste, and very high levels might cause a laxative effect in unaccustomed consumers (Sadat-Noori *et al.*, 2014). Based on taste considerations Environmental Protection Agency (EPA) recommended an upper limit of 250mgl^{-1} of sulfate in drinking water. Sulfate concentration in drinking water exceeding 500mgl^{-1} is associated with diarrhea in adults and infants (Heizer *et al.*, 1997). Potassium is an essential element in humans and is seldom, if ever, found in drinking water at levels that could be a concern for healthy humans. The recommended daily requirement is greater than 3,000 mg (WHO, 2006).

$DWQI_{WHO}$ and $DWQI_{ISIRI}$ are strongly correlated with each other but there was quantitative difference between the values of DWQI considering two approaches. The dissimilarities in the permissible values of TDS, TH and Ca (Table 1) in two guidelines cause the difference in quantitative values of $DWQI_{WHO}$ and $DWQI_{ISIRI}$. The correlation of $DWQI_{WHO}$ and $DWQI_{ISIRI}$ with chemical parameters also indicated the highest correlation of water quality indices with TH and TDS which distinguishes the main impact of these two parameters. TH is primarily caused by the presence of cations such as calcium and magnesium; and anions such as carbonate, bicarbonate, chloride, and sulfate (Ravikumar *et al.*, 2010). According to the grading standards of TH, groundwater can be divided into soft water (TH<150 mgL^{-1}), moderately hard water (150<TH<300 mgl^{-1}), hard water (300<TH< 450 mgL^{-1}), extremely hard water (TH>450 mgL^{-1}). In the study area, TH varies between 68.8 and 1964.4 mgL^{-1} (Table 3), considering 3 percent of samples is in the soft category and 65 percent is in the extremely hard category. These results clearly point out the importance of TH in the study area and emphasis on the TH as the main controlling factor of water quality in the study area. The water with hardness above 200mgL^{-1} may cause scale formation in the distribution system. The high hardness of 150–300mgL^{-1} and above may cause heart diseases and kidney problems (Ramesh & Elango, 2006).

Spatial distribution maps were shown that most parts of the study area have undesirable water quality for drinking purposes; but to some extent, the eastern parts of the area are of good quality. Groundwater quality for drinking consume exacerbates from central to North and to South-west of the study area. Similarly, Daneshvar-Vousoughi *et al.*, (2013) have reported that groundwater wells of North and South-west in Ardabil plain haven't desirable quality for agricultural consumption. In this study, Groundwater of Ardabil city lies in the poor category which should be taken into account for water supply of the city population. These findings may help to improve groundwater resources assessment to support governance and policy. The results clearly indicate that the main parts of the aquifer have undergone significant amount of deterioration which requires immediate attention.

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