The hydrochemical evaluation of groundwater quality in the Harzandat plain aquifer, Northwest of Iran

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Abstract

The Harzandat plain is part of the East Azarbaijan province, which lies between Marand and Jolfa cities, northwestern of Iran, and its groundwater resources are developed for water supply and irrigation purposes. For hydrogeological consideration and optimum management of groundwater resources a mathematical model as an efficient and economical tool was prepared. In order to evaluate the quality of groundwater in study area, 36 groundwater samples were collected and analyzed for various parameters. Chemical indexes like sodium adsorption ratio, percentage of sodium, residual sodium carbonated, permeability index (PI) and chloroalkaline indexes were calculated. Based on the analytical results, groundwater in the area is generally very hard, brackish, high to very high saline and alkaline in nature. The abundance of the major ions is as follows: Cl> $HCO_3 > SO_4$ and Na > Ca > Mg > K. The dominant hydrochemical facieses of groundwater is Na-Cl type and alkalis (Na, K) and strong acids (Cl, SO_4) are slightly dominating over alkali earths (Ca, Mg) and weak acids(HCO_3,CO_3). The chemical quality of groundwater is related to the lithology of the area and the residence time of the groundwater in contact with rock materials. The results of calculation saturation index by computer program PHREEQC shows that the nearly all of the water samples were supersaturated 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 unsuitable for drinking and agricultural uses.

Keywords: Groundwater quality, Harzandat plain, Hydrochemistry, Model, Saturation index

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 (Freeze & Cherry, 1979; Domenico and Schwartz, 1990; Kortatsi, 2007). Groundwater chemistry 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 (Guler and Thyne, 2004). 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

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arid and semi-arid regions of Iran while putting these resources at greater risk to contamination (Aghazadeh, 2004; Asghari and Najib, 2006). In this study, physical, hydrogeological, 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.

2. Description of study area

The study area is part of the Aras river drainage basin and lies between latitudes 38°,35' to $38^{\circ},45'$ N and $45^{\circ},30'$, to $45^{\circ},45'$ E (Fig.1). The climate of the study area is semi-arid and it's average annual rainfall and temperate is about 280 mm, 13.2C° respectively. Groundwater is an important water resource for drinking, agriculture and industrial uses in study area. Low precipitation and over-exploitation of groundwater resources in recent years has caused an extensive groundwater level decline in this plain prohibiting further development of the aquifer. From a geological point of view, the investigated area is located in the Alborz-Azarbijan zone of the Iran (Nabavi, 1976). The exposed lithological units of the Harzandat plain range in age from Devonian to Quaternary and have different hydrogeological characteristics (Fig.1). The groundwater of the study area occurs under unconfined conditions. The result obtained form drilled wells indicate that the thickness of the alluvium aquifer is average 65m (Azarbaijan Regional Water Authority, 2004). According to the results obtained from groundwater flow modeling of the study area, the values of hydraulic conductivity and the specific yields ranges from 0.5 to 2.5 md^{-1} and 1 to 4 percent, respectively (Asghari moghaddam and Aghazade, 2006). The general groundwater flow direction in the aquifer is from SE to NW (Fig.2) and depth to water table varies from 6 to 46 m below ground level.

3. Materials and methods

For to design mathematical model of the aquifer, all the necessary hydrological, climatological, geophysical and geological data were collected and analyzed. Based on this data the mathematical model of the aquifer was prepared by VISUAL MODFLOW software. In order to evaluate the quality of groundwater in study area groundwater samples were collected from 36 shallow and deep wells and springs of the area during May 2003(Fig.2). 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 cations and anions using the standard methods as suggested by the American Public Health Association (APHA, 1995).

4. Results and discussion

The abundance of the major ions in groundwater is in following order: Na>Ca>Mg>K and Cl> HCO_3 > SO_4 >CO₃. Figure 3 shows that Na and Cl are dominant cations and anion, respectively and the median values of Cl exceeded 50 % of total anions in milli-equivalent unit. Minimum, maximum and average values of physical and chemical parameters of groundwater samples are presented in Table 1. The large variation in EC is mainly attributed to geochemical processes prevailing in this region and high concentrations of Na in the groundwater are attributed to cation exchange among minerals. The concentration of dissolved ions in groundwater samples are generally governed by lithology, velocity and

quantity of groundwater flow, nature of geochemical reactions and solubility of interaction rocks. The dissolution of evaporate minerals such as halite and gypsum influences the chemistry of the water in the Harzandat plain aquifer.

Saturation indexes are used to evaluate the degree of equilibrium between water and minerals (Langmuir, 1997; Drever 1997; Coetsiers and et al., 2006). The saturation indexes were determined using the hydrogeochemical equilibrium model, PHREEQC for Windows (Parkhurst and Appelo, 1999). The saturation index of a mineral is obtained from equation (Garrels and Mackenzie, 1967). $SI = \log (IAP/Kt)$ where IAP is the ion activity product of the dissociated chemical species in solution and Kt is the equilibrium solubility product for the chemical involved at the sample temperature. In Table 1 the SI for calcite, dolomite, anhydrate and gypsum are shown. Nearly all water samples were supersaturated 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. The values obtained from the groundwater samples analyzing, and their plot on the Piper's diagrams (Piper, 1944) reveal that the major cation is Na and the anion is Cl (Fig.4). In the study area, the major groundwater type is Na-Cl, and alkalis (Na, K) are significantly dominating over the alkaline earth metals (Ca, Mg). The sodium-chloride water type in study area is due to the low velocity of groundwater, long time contacts of water and formations as well as the type of the rocks.

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 WHO (1989). Assessment of water samples according to exceeding the permissible limits prescribed by WHO for drinking purposes indicated that all of the groundwater samples is very hard water and groundwater in study area is chemically unsuitable for drinking uses (Table2). Salinity and indexes 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 (Ragunath, 1987; Srinivasa, 2005; Subramani, 2005; Raju, 2006). The SAR values range from 1.2 to 19.2. According to the Richards (1954) classification based on SAR values, %83 of samples is belong to the excellent category, %11 of them is belong to good category and the remaining samples are belong to the doubtful category. The Wilcox (1955) diagram relating sodium percentage and total concentration shows that %27 of the groundwater samples fall in the field of good to permissible, %16 of the groundwater samples fall in the field of doubtful to unsuitable and %53 of the groundwater samples fall in the field of unsuitable for irrigation. Residual sodium carbonate (RSC) has been calculated to determine the hazardous effect of carbonate and bicarbonate on the quality of water for agricultural purpose (Eaton, 1950). The classification of irrigation water according to the RSC values show that, %5 samples belongs to the good category,%16 samples belongs to the doubtful category and %79 belongs to unsuitable category. According to permeability index (PI) values, the groundwater of in the study area can be designated as class II (25–75%) indicate that the groundwater is unsuitable for irrigation excepting the two samples, which classified as class I (>75%).

5. Conclusions

Interpretation of hydrochemical analysis reveals that the groundwater in study area is very hard, fresh to brackish and alkaline in nature. The results of calculation saturation index show that the nearly all of the water samples were supersaturated with respect to carbonate minerals and undersaturated with respect to sulfate minerals. In the study area, the dominant hydrochemical facieses of groundwater is Na- Cl. Ionic concentrations, TDS, EC and water quality suggest that groundwater residence time is primarily controlled by the occurrence of different hydrochemical facies. The chemical quality of groundwater is related to the lithology of the area and the residence time of the groundwater in contact with rock materials. Assessment of water samples for drinking purposes indicated that groundwater in study area is chemically unsuitable for drinking uses. Assessment of water samples from calculation of chemical indexes indicated that groundwater in study area is chemically doubtful to unsuitable for irrigation.

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Parameters	Units	Minimum	Maximum	Average
pН	-	6.8	8.2	7.52
EC	S/cmµ	990	6220	3489
TDS	mg/l	653	4000	2300
Na	mg/l	66	1127	471
K	mg/l	1.17	50	11
Ca	mg/l	54	287	161
Mg	mg/l	30	205	78
Cl	mg/l	115	1611	637
HCO3	mg/l	212	1488	479
CO3	mg/l	0	60	10
SO4	mg/l	125	1248	490
TH	mg/l	325	1720	724
SAR	-	1.2	19.2	7.6
%Na	%	28	79	55
RSC	meq/l	-30.4	4.5	-6.46
PI	%	43	82	63.7
CAI,1	meq/l	-1.2	0.44	-0.33
CAI,2	meq/l	-0.44	0.37	-0.18
SI calcite	-	-1.08	1.5	0.35
SI dolomite	-	-0.7	2.95	0.85
SI gypsum	-	-3.5	-0.32	-1.71
SI anhydrate	-	-3.27	-0.5	-1.34
EC:	Electrical	SAR: Sodium adsorption ratio		
conductivity		RSC: Residual sodium carbonate		
TDS: Total	dissolved	PI: Permeability index		
solids TH: Total hardness		CAI: Chloro alkaline index SI: Saturation index		

 Table 1 Minimum, Maximum and average values of physical and chemical parameters of groundwater samples

Table 2 Groundwater samples of the study area exceeding thepermissible limits prescribed by WHO for drinking purposes

Parameters)WHO international standard (1983,1989				
	Most	Maximum	Amount in		
	desirable	allowable	groundwater		
	limits	limits	samples		
PH	7-8.5	9.2	6.8-8.2		
TDS(mg/l)	500	1500	653-4000		
TH(mg/l)	100	500	325-1720		
Na(mg/l)	-	200	66-1127		
Ca(mg/l)	75	200	54-287		
Mg(mg/l)	50	150	30-205		
Cl(mg/l)	200	600	115-1611		
SO4(mg/l)	200	400	125-1248		

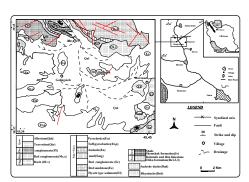


Fig.1.Geology and hydrogeology units of the study area.

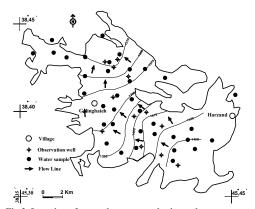


Fig.2. Location of groundwater samples in study area.

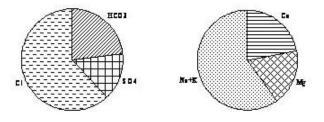


Fig.3. Pie diagram of median values of major ions.

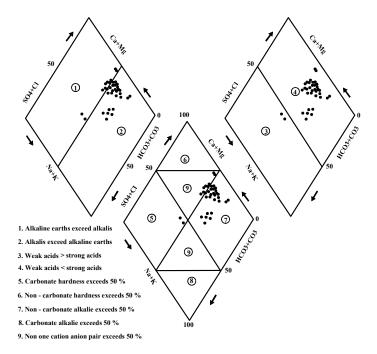


Fig.4. Chemical facies of groundwater in Piper diagram.