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An Investigation of the Impacts by Hydro-geochemical Factors on Ghazvin Plain Groundwater Quality Indexes

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ABSTRACT─ In this study are used 42 exploiting wells statistics chemical parameters of groundwater for ten water years from 2003-2004 to 2013-2014 as a two-term average. Parameters with standards of WHO, Industrial Standards Institute and the Ministry of Energy's comparable quality indexes are calculated. In this study the effect of geology, hydro-geochemical and chemical reactions on quality index is investigated. Studies showed that ground water geology and chemical reaction with the dissolution, sedimentation in the underground water of the west and northwest to the southeast and the East is, effectively, and is increase underground water-soluble. Basic partly neutral pH due to the amount of carbonates, bicarbonates, and the dissolution of gypsum and halite increased the impact on TDS values visible. The issue in determining the type of water that derived from Piper diagram is evident. Type water shows water quality status of groundwater resources Ghazvin plain. Based in water year 2003 – 2004, 4.7% (excellent), 45.2% (good), 45.2%(weak) and 4.7% (very poor) and 2013-2014 water year in water quality index by 7.1% (excellent), 47.6% (good) , 26.2 % (weak),16.6%(very poor) and 2.3%has been found unsuitable. In this classification, most of the regions the water year 2013-2014 compared to 2003-2004 a better situation, but a very poor and unsuitable area has become worse. The main reasons for the changes in geological formations could be the impact of climate change and drought, excessive withdrawals of groundwater and reduce the volume of the reservoir will drop. Water Quality Index is a new method that requires perusing. It is necessary research according to the conditions of the study of the methods used or new ways to innovate and adapt to the study area.
KEYWORDS: Ghazvin Plain, WQI WHO, Piper Diagram, Iso- Water Quality Index

Introduction

Because of its geographical location, Iran has a rainfall average equal to one third of world average. This has brought about a dried to semi-dried climate for Iran, to which shortage of freshwater resources and excessive withdrawals out of groundwater and surface water resources are added. On the other hand, during the last forty years, increased population and expanded industries have caused infiltration of a huge amount of pollutants (natural and artificial) into surface and underground waters. As a result of this growth, significance of environmental issues has grown to be apparent. In different parts of the globe, various methods have been proposed to evaluate quality of surface and underground water resources and the effects caused by these factors. Water quality indices are beneficial instruments to determine conditions of water quality. They, just like other methods, require basic information about water and relevant factors (Nikbakht, 2004). There are indices which are determined for each parameter in order to obtain a general index called Water Quality Index after such indices are accumulated. The compounds which are available in water influence on its quality. Such compounds are divided into two general microbial and chemical categories. Containing bacteria, viruses, protozoa, and parasites, microbial factors have direct impacts on human health. Quality of waters which are infected by microbial factors is subject to quick changes in a broad range. The amount by which chemical factors leave impacts depends upon type of the chemical materials and the time during which human body is exposed thereto. According to WHO (2004) guideline on quality of freshwater, water qualitative factors are classified into following two categories:

Factors impacting on human health: These factors are those categories of chemical materials which might have direct effects on human health. Excessive intake of these materials for a short and long time might lead to extreme carcinogenicity and toxication, respectively. In the guideline on quality of freshwater provided by the WHO and Iran's National Standard, desirable amounts of these materials in freshwater are mentioned. Factors that increase these materials include type of geological formation, non-observance of hygiene threshold of water resources, excessive extraction of groundwater, and infiltration of household, agricultural, and industrial sewages into the underground waters.

Factors impacting on water salubrity: These factors do not have direct effects on human health. Even, at some cases, they are essential for health for having calcium and magnesium. However, they change water taste and acceptability. Although these factors do not have bad effects on human health, water users might prevent from consuming waters tinged by such materials and refer to waters whose salubrity is questionable. For the first time, Water Quality Index was measured by Horton (1965), who gave weight to each parameter under measurement in water, presenting aggregation function which defines qualitative characteristics of water. In developing qualitative index, Stigter et al. (2006a) described selection, standardization, and aggregation of involved parameters as the framework of three main stages. Following studies have been performed on water quality index:

In their article entitled "Determination of Water Quality Index Using Fuzzy Logic," Hasani et al (2013) used data on 9 parameters related to Yazd aqueducts in order to calculate qualitative index using the method proposed by the National American Institute of Health. Results showed that this method is applicable as a comprehensive instrument to determine qualitative index of waters consumable by human beings. Joodi and Zare (2009) conducted their investigation on "Introduction of GQI to Evaluate Groundwater Quality Used as Freshwater" in Feizabad Plain, (Khorasan Razavi, northeast of Iran). They indicated that this index is highly effective for evaluation of groundwater quality to be utilized as freshwater and locational changes using GIS. Results exhibited that these changes are made because of geological specifications of aquifer and are impacted by bedrock and introduction of desert saltwater. Hooshmand et al. (2007) investigated quality of Karoon River water using water quality indices provided by W.H.O, OWQI (Oregon), and CWQI (Canada). Results indicated that qualitative index specified by WHO was the best among others. Nasrabadi and Abbasimandeh (2013) examined quality of Tehran groundwater using the index presented by W.H.O in 2011 and 2012. Results indicated that these indices had better conditions in the north compared to eastern and southern regions, the incident which happened as a result of excessive water withdrawals from underground waters, drought, and pollutants like sulfate and nitrate that were generated by means of human activities. Continuation of this trend would exert more serious damages into Tehran groundwater resources. Behmanesh and Feizabadi (2013) conducted a study on qualitative index of Babolrood River using NSFWQI method and weighted arithmetic WQI, showing that qualitative values are variable between 48 and 80. They concluded that most sampling stations are acceptable, but they should be purified before domestic use. Using WQI, Bharti, and Katyal (2011) investigated qualitative water indices and vulnerability of surface waters. They, finally, determined their applied methods and relations and provided them with the researcher in order for him to get able to develop its intended method. Razi (2015), studying effects of drought on qualitative and quantitative conditions of Ghazvin Plain, showed that qualitative and quantitative changes of groundwater resources impacted by climatic changes and hydro-climatic conditions, especially rainfall, excessive withdrawals, population growth, agricultural fields, and industrialization of Ghazvin Plain surroundings have influenced on reduction of groundwater resources and quality of water resources. Abesi et al. (2012) carried out a study on development of WQI in Ghazvin Province groundwater resources. Qualitative indices were analyzed using some simple multivariable methods, and conditions and distribution of index were assessed by means of drawing related maps that were located near mineral waters. Evaluations indicated that groundwater resources WQI and qualitative indices of mineral waters are close to one another, and therefore drawn maps exhibit important points concerning water resources planning and management.

Objectives of this study include examination of hydrochemical condition and Ghazvin Plain groundwater resources WQIs, hydro-geochemical effects of Ghazvin Plain groundwater resources on qualitative indices, impact of geological effects and hydro-climatic factors on qualitative indices of groundwater resources, and drawing subjective and locational maps to determine conditions of qualitative indices of Ghazvin Plain.

Geographical Location and Geological Setting of the Study Area

The area under investigation is located between eastern longitudes of 49°15′ to 50°40′ and eastern latitudes of 35°20′ to 36°30′. Catchment of Ghazvin is the plain is around 5534km^2 and in heights 3842km^2, which is totally 9376km^2. This catchment is formed in the area of plain mostly of quaternary alluvial sediments. Generally, however, Catchment of Ghazvin is geologically outcropped by Precambrian to Neogene formations. Most study areas' height above sea level is equal to 2971 meters and its minimum height is 1100 meters. Mean height of the area is around 1250 meters. This area is adjacent to Shahrood catchment from the north, to Abharrood catchment from the west, to Shoorchai, Gharebagh, and Gharechai catchments from the south, and Kordan and Karaj catchments from the east (Fig.1, right).

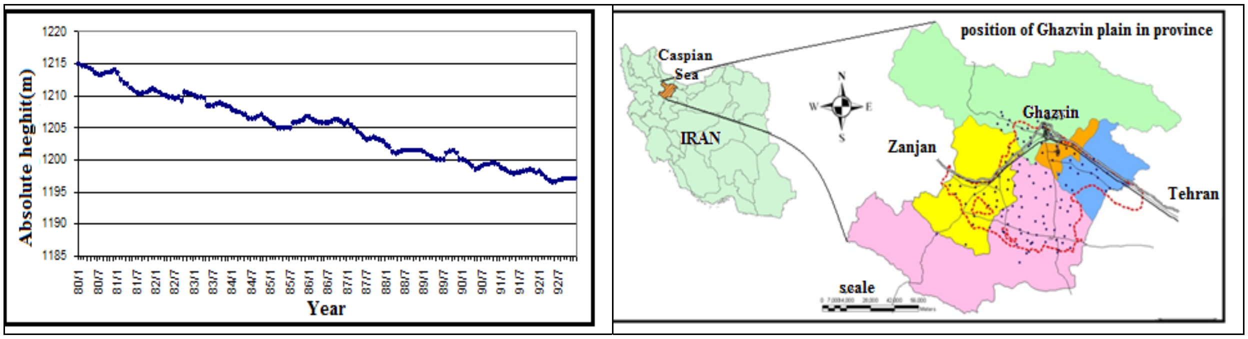


Fig.1 geographical condition, operation wells, and unit hydrograph of Ghazvin Plain aquifer

Climatically, with respect to location of Ghazvin Plain in southern slopes of Alborz, 10-year monthly average (2003 to 2013) of the coldest month of the year (February) is around 3 ºC to -3 ºC and monthly average of the hottest month of the year (July) is around 22 ºC to 27 ºC. Based on 10-year statistics, rainfall average was calculated to be around 261 millimeters. According to investigations, 77% of rainfalls are evaporated, 11% of rainfalls are infiltrated, and the rest of rainfalls are runoff form the study area. According to Ghazvin Plain hydrograph during 2003 to 2013, it is observed that drawdown of groundwater resources levels in this plain was 13.7 meters in intended time span, and downfall average was estimated to be around 1.37 meters for each year (Fig.1, left). One of the most important factors related to drawdown of groundwater table level was drought. SPI method indicted that the most continuance of drought happened during 2006 to 2013. The most severe drought in study area occurred in 2008 (Razi, 2015). The study area has a wide range of climatic diversity: dry-cold conditions in a wide range of areas, semi-dry and cold conditions in peripheral areas, and humid conditions in northern regions.

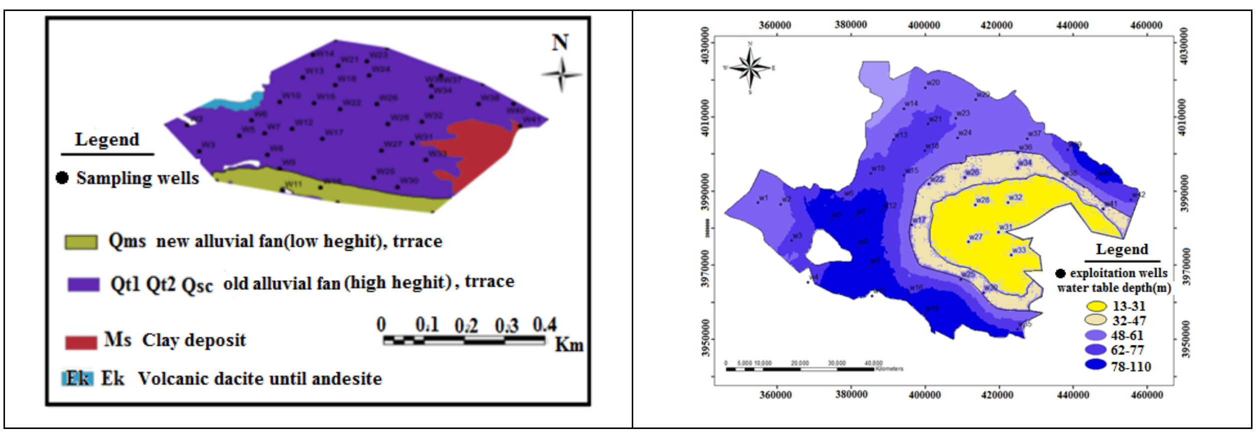


Fig.2 depth of groundwater contact (right) and geological map of Ghazvin Plain area (left)

According to general surveys in Ghazvin Plain conducted in 2009, a number of 7,654 deep and semi-deep wells, a number of 253 flumes, and a total of 1,981 active streams are available therein. In addition, total volume of extracted water from these resources was around 1,644.25 MCM. From the total volume of extracted water, around 4.6% are allotted to beverage purposes, 1.2% to industrial purposes, 86.2% to agricultural objectives, and the rest to other consumptions (Ghazvin Regional Water Organization (2015)). Based on surveys since 1966 (extraction from 400 MCM) so far, withdrawal amounts show a fourfold increase during these years. Due to the importance of Ghazvin Plain for agricultural and industrial purposes and increased urbanization degrees during the last 40 years, excessive water withdrawals have caused a decrease in quality of groundwater resources.

Region of alluvial Ghazvin Plain is formed as a result of a tectonic subsidence by the materials carried off from adjacent heights. Alluvial sediments around the Ghazvin Plain are composed of Precambrian to Neogene formations (sediment and volcanic materials). Sediments in north western region are in from of coarse- grained and alluvial fans (recharge zone), and their thickness at 300 meters. As we move to south eastern regions (discharge zone), grains become finer, and their thickness is highly decreased to some ten meters. Under these conditions, a considerable groundwater with suitable groundwater resources is formed. Generally, in alluvial fans regions of Ghazvin Plain, depth of water level is more than 100 meters, and it discharge zone into less than 15 meters. Direction of groundwater flow in this plain is from west and northwest to south east and east (Fig.2, right) (according to the slope topography is plain). Geologically, Ghazvin Plain catchment is composed of Precambrian to Neogene formations. In northern heights (west to east), of limestone, dolomite, and marl deposits are widely observed. In of Ghazvin Plain, however, deposits are mainly quartz sediments made of terraces and old and new alluvial fans, silty-clay sediments with salt deposits (Qc, Qt1, Qt2, Qms, and Qsc), gypsum (discharge area), heightened red conglomerates including conglomerate, marl, chalk marl, and sandstone, which are outcropped in southern parts of the Ghazvin Plain.

Methodology

In this research, geological, hydrogeological, and hydro-geochemical information is applied to examine chemical features of the groundwater. Information of water samples from 42 operation wells during water years 2003-04 to 2013-14 was collected and analyses were conducted based on average of each intended water year. Analysis of water samples includes measure of main cation and anion concentrations and parameters such as EC, T.D.S., and pH,. Hardness and alkalinity are calculated through two chemical analyses and chemical relations together with Sodium Adsorption Ratio (SAR). Analyses are carried out based on the methods defined by the Iran Institute of Industrial Standard (Fig. 1), standards values provided by the WHO (1993), Institute of Standards and Industrial Research of Iran (2009) (Circular 1053), and Department of Energy. Descriptive statistics of the parameters available in groundwater resources are mentioned in the Table 2.

Table 1 The method to measure elements and materials existing in groundwater resources

Elements and materials	Method	Elements and materials	Method
Magnesium, sodium, and potassium	Atomic absorption and spectrometry	EC,TDS	Portable field device
Bicarbonate and chloride	Titration	pH	Portable field device
Sulfate	Spectrophotometer	Calcium, rigidity, alkalinity	Titration method

Table 2 Statistical specifications of chemical analysis for selected resources in Ghazvin Plain area (amount of elements and TDS in terms of mg/L and EC in terms of µS/cm for 2003-04, 2013-14 water years (Ghazvin Regional Water Organization, 2015)

P	TDS	EC	pH	Na	K	Mg	Ca	SO4	Cl	HCO3	TH	SAR	Alk	WQI
(2003-2004)														
Min	230	358	7.2	23.7	0.78	4.32	10.6	12.4	10.6	97.6	44.2	0.74	73.8	39.8
Max	2724	4256	9.7	530.8	25.3	84.96	211.4	772.8	1150.2	372.1	791	9.78	340	273.2
Mean	976.6	1526	8.2	198.	3.4	35.7	66.1	227.	221.1	223.4	312.5	5.03	199.7	113.
STD	604.6	948.1	0.4	128	3.9	23.9	48	175	139.3	59.6	202.4	2.3	53.7	56.6
(2013-2014)														
Min	257	432	7.3	23	0.78	9	11.2	19.6	20.9	89	74.4	0.64	24.9	40.87
Max	4090	6523	8.1	1030	9.4	198	307	920	1605	486.7	1272.8	12.51	1039.7	458

Mean	1035.5	1657.5	7.7	188.5	2.15	49.7	80.4	252	255.3	241.8	405.8	3.95	208.2	123.7
STD	773.4	1231.8	0.24	175	1.68	36.9	65	209	316.4	66.1	283.6	2.12	212.1	84.5

According to hydro-geochemical statistics, a number of 42 wells were used for determination of qualitative WQIs. Structurally different methods to determine water quality indices (WQI) have been tried, all of them have been obtained through statistical methods. Distribution of sampling wells in area of Ghazvin Plain is shown in the Fig. 1. As presented in this section, standards freshwater values are provided by the WHO (1993), Institute of Standards and Industrial Research of Iran (2009) (Circular 1053), and Department of Energy.

Hydro-geochemical investigation of Ghazvin Plain aquifer: Hydro-geochemical statistics of Ghazvin plain groundwater are analyzed for two water years 2003-04 and 2013-14 with a 10-year time distance from mean of measured parameters. In doing so, minimum, maximum, and average descriptive statistics are calculated using SPSS, ver. 16. TDS and pH maps for spatial and temporal distribution of these two important parameters were drawn using Schoeller Standard (1962). Determination of ion ratio Na/(Na+Cl) to determine ion displacement was applied to specify the relation between geological formations and the plain's groundwater resources. Determination of SAR ratio (sodium absorption ratio) is very important in evaluation of water's impacts on soil and qualitative index. Piper diagram (1944) was used to determine type of water and its changes along with groundwater currents and chemical reactions in the study area.

Development of groundwater quality index: There are different methods to determine qualitative indices using statistical methods in various parts of the world. Horton (1965) was one of the first researchers who presented relation 1 using WQI and weighted arithmetic method.

$$\mathbf{WQI_A} = \sum_{i=1}^{n} wiqi \quad (1)$$

Brown et al. (1970) improved Horton's method as an incremental index, calculating the qualitative index using weighted geometric method (relation 2).

$$\mathbf{WQI_M} = \prod_{i=1}^{n} qi^{\,wi} \quad (2)$$

In these two methods, all parameters are able to have different weights based on importance of water's qualitative condition in the area under study. In front of these two methods are calculated using geometric squares weightless method, which is calculated by adding sub-indexes. This method is proposed for two weighted arithmetic and geometric methods (Relation 3).

$$\mathbf{WQI} = \sqrt{n} / \sum_{n=1}^{n} 1/SIi^2 \quad (3)$$

Based on different methods concerning determination of WQIs, various countries and organizations have presented different methods as proportionate with the *status quo* in their states and regions. Development of qualitative indices whereby all parameters impacting on water consumption contain of a certain function is now regarded as a common method in evaluation of surface and underground waters. Stigter et al. (2006a) described selection, standardization, and aggregation of involved parameters as the framework of three main stages. The first stage includes selection of a number of water quality parameters as many as required for intended function. In standardization phase, each parameter is given weight with regard to its importance (wi). Division of given weight by total weight of parameters (∑wi) would result in relative weight (Wi) (Table 3). Finally, in the third stage, values of sub-index calculated in the previous stage are aggregated by a mathematic operator or one of geometric, arithmetic, or harmonic mean calculation methods with regard to relative weight of each parameter. Then, a separated parameter called water quality index is resulted. This method is also known as WHO method (1993). In this study, with regard to statistics of parameters available in study area, above method and weighted arithmetic method were applied. In this method, at least three parameters are required. Quality of freshwater is determined somewhere between *zero* and *infinite* based on the weight which is given to each parameter and freshwater standards provided by WHO, Iran Industrial Research Standard, and Department of Energy. To determine quality of freshwater, weight is given to parameters available in water concerning their importance and role in qualitative and quantitative measurements. According to accumulated parameters and importance of each parameter from one (low importance) to five (high importance), weights are assigned. The higher the value of indices, the lower the quality would be (Nasrabadi, 2013).

In the method suggested for Ghazvin Plain, above-mentioned model is applied as the standard method to develop approved qualitative indices. In selection stage, a group of qualitative parameters are selected and, in the next stage, each qualitative index parameter is obtained using the method for division of measured densities (ci) in terms of desirable recommended values (Sdi) applying existing standards provided by WHO, Iran Industrial Research Standard, and Department of Energy. Simply put, following relations and values of qualitative index of each well are specified and same-index maps are drawn in order to determine each index's locational and time condition. Following relations are used to calculate qualitative index:

$$\mathbf{Wi} = \mathbf{wi} / \sum_{i=1}^{n} \mathbf{wi} \quad \textbf{(4)}$$

$$\mathbf{qi} = \left(\frac{\mathbf{Ci}}{\mathbf{Sdi}}\right) \mathbf{100} \quad \textbf{(5)}$$

$$\boldsymbol{SIi} = \boldsymbol{Wi} * \boldsymbol{qi} \quad \textbf{(6)}$$

$$\text{GWQI} = \sum_{i=1}^{n} \mathbf{SIi} \quad \textbf{(7)}$$

Where, *Wi* is relative weigh, wi weight of each parameter, *n* number of parameters, *qi* water quality rate, *ci* concentration of each parameter in sample (mg/L), and Sdi freshwater standard. Amounts of qualitative index are categorized in five levels, as shown in the Table 3. In this study, qualitative conations of water are hydro-geochemically investigated and amounts of soluble materials in water are examined for TDS and pH values and their effects in order to evaluate underground water quality indices of Ghazvin Plain using available information.

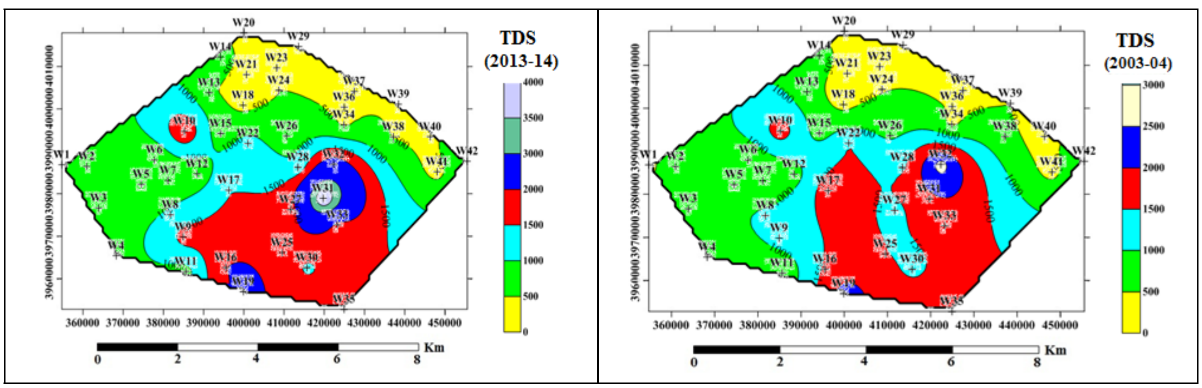
Table 3 Relative weight and standard applied for each parameter (Iran Standard and Industrial Research Institute[1], WHO[2], Department of Energy[3], and Richards[4], 1954) and categorizations of WQIs

Chamical parameters	Sdi (Standard)	Weight (wi)	Relative weight(Wi)	WQI	Class	Water quality
TDS[1]	500	5	0.0952	Less than 50	I	Excellent
EC[2]	1000	4	0.0952	50-100	II	Good
pH[1]	8.5	4	0.0952	100-200	III	Weak
Ca[1]	75	2	0.0476	200-300	IV	Very weak
Mg[1]	30	2	0.0476	Higher than 300	V	Unsuitable
Na[1]	200	3	0.0714			
K[3]	10	2	0.0476			
SO4[3]	250	3	0.0714			
Cl[1]	250	3	0.0714			
HCO3[2]	500	2	0.0476			
TH[3]	100	2	0.0714			
SAR[4]	10	3	0.0476			
Alkalinity[2]	200	3	0.0714			
		∑Wi=38	∑Wi=1			

Results

In this essay, information of water samples from 42 exploiting wells during water years 2003-04 to 2013-14 was collected and analyses were conducted based on average of each intended water year. It was attempted to take into consideration all important factors in freshwater and agriculture water to separate healthy water from ordinary water. These factors include all minerals in groundwater, TDS, and pH that are regarded as factors which determine desirable quality of groundwater resources in relation with waters used for beverage and agricultural purposes. Of course, not all minerals contain usable parameters, parameters such as pollutant resources and more heavy elements are of paramount importance in assessment of quality of groundwater resources, the agents which are beyond the scope of this article.

Ghazvin Plain Groundwater Hydro-geochemistry: A lookout into the Table 2 shows descriptive statistics of the parameters in groundwater resources. Averages of SAR, K, Na, and pH have been reduced since 2003-04 to 2013-14, while other parameters experienced considerable increase. Such increase is observed in EC and TDS values, also. During water years 2003 to 2013, groundwater solution had alkaline pH, the fact which shows existence of sediments of carbonates (Hounslow, 1995), since calcite is in oversaturation state. Aligned with this, TDS and pH maps have been draws due to their importance in determination of quality and indices of groundwater resources, chemical reactions, solutions and sediments, and ionic replacements (Fig. 3). TDS map is drawn based on Schoeller Standard (1962) and, as observed in the figure, its values are increasing from north to north western regions to south and southeastern areas. In middle points from 2003-04 to 2013-14, however, conditions are aggravated and reach from 3,000 to 4,000. Respecting standard, although, a wide area of the region is in desirable level (500mg/l), exceeding allowed range, i.e., 1,500 mg/l. It means that it is in desirable range and it is drinkable considering the parameters existing in water and the fact that it should not harm human health in neither short nor long terms. While in 2013 area of desirable region has been decreased, a broad are of the region is usable for drinking and agricultural purposes. Increase in TDS into discharge area ensues from dissolution of gypsum and halite in alluvial sediments and Upper Red Formations (Fig. 3, above). In pH map of 2003-04, although a wide area is in desirable level, a small region is in allowed range. In this year, groundwater solution goes from neutral to basic level (9.36-7.3), where carbonates deposit (calcite, dolomite, and megnesite) that are oversaturated in calcite study area. In 2003, the whole area was desirable: variable between 7.3 until 8.1. In this state, calcite is oversaturated and calcite depositing is observed. These minerals are formed as a result of limestone, dolomite, and marl outcropping in the north and northwest (Fig.3, below). According to Table 2, sodium, chloride, calcium, and sulfate ions are ions impacting on quality of resources. In study area, Na<Cl in almost 25% of wells, the fact that shows a reverse softening that originates from brines where vaporization and density are increased as a consequence of excessive withdrawals. In other wells, source of sodium, save for halite, ensues from plagioclases (existence of clay plates). In more than 30% of wells, we have Ca<SO4, the fact which indicates that removal of calcium and calcite deposit are natural. In other wells, calcium is originated from gypsum, calcite, dolomite lime, or silicates. With regard to geological conditions of deposits such as gypsum, clay, lime, shale, and silty-clay plates might work as ionic replacements in these chemical reactions, entering a considerable amount of different ions into water. This has left the highest effect on reduction of WQIs, causing Ghazvin Plain groundwater climatic conditions to be decreased as a result of excessive withdrawals. Piper diagram (Fig.4) in the interpretation and detection of chemical reactions carried out important information can be obtained in the study area. According to Piper diagram, type of water in 2003 was temporary rigid (Ca+Mg, HCO3), brine ((Na+K, Cl+SO4), and alkaline carbonate (Na+K, HCO3+CO3).



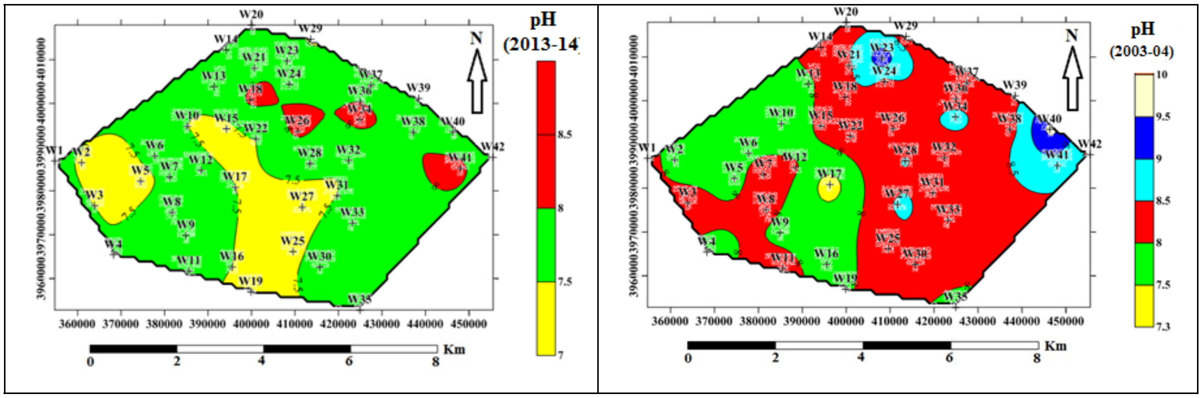


Fig.3 Map of changes TDS (above) and pH (below) in study area (Ghazvin Plain)

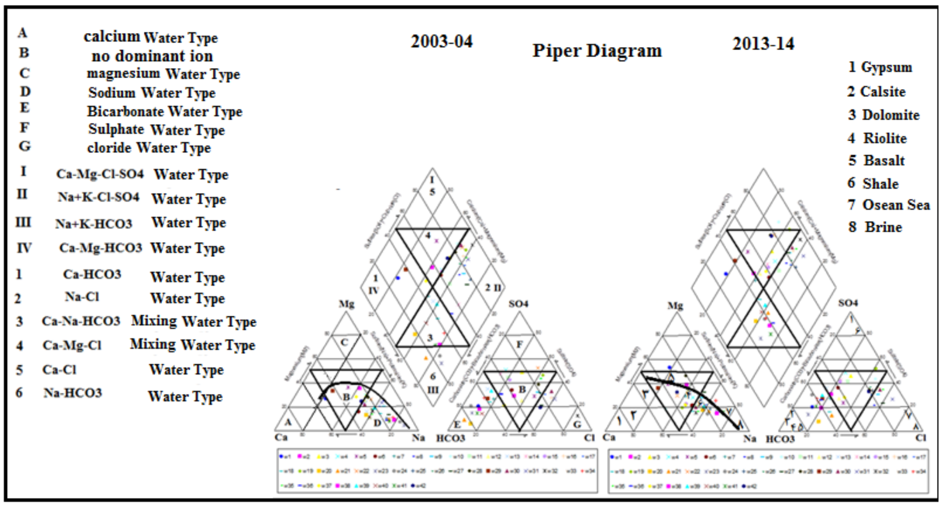


Fig.4 Piper diagram groundwater samples in Ghazvin Plain for water years 2003-04 and 2013-14

As the solution as alkaline (pH between 7.25 and 9.68) in 2003-04, existence of alkaline carbonates, calcite saturations, dolomite, megnesite, and deposits are not non-expectable. While in 2003-04, pH of solution was between 7.3 and 8.1, alkalinity was relatively neutral, in which bicarbonate was the dominant anion and calcium and magnesium were the dominant cation. In Table 2, values of these ions are increased and samples are placed in temporary rigidity and brine range (Piper diagram) that is ensuing from salty and gypsum deposits in middle sections to discharge (Hounslow, 1995). On the other hand, Piper diagram is able to determine type of water. As shown in Fig. 4, in cation triangle in 2003-04 to 2013-14, the drawn line has changed as a result of ionic exchange and this parallel line starts with a fixed magnesium line and curves into apex of sodium. This shows a higher calcium rather than magnesium exchange. Most samples are placed in B and D ranges, showing that no ion and type of sodium water is dominant. On the other hand, most type of water is impacted by dolomite deposits (3), magnesium-bearing minerals (mica and amphibole), rhyolite (4), basalt (5), shale (6) from the Karaj Formation, and evaporate deposits of salt and gypsum (8) (Upper Red Formation and part of the quaternary sediments) respecting geological conditions of study area. In 2013, although drawn line has less sloped, the procession is along the sodium apex. Based on Piper diagram (Fig.4), most samples are in area 3 (Ca-Na-HCO3) and area 4 (Ca-Mg-Cl). And, number of samples in area 3 is higher than them in area 4. Afterwards, area 2 (Na+K-Cl-SO4) (Na-Cl), area 6, and area (Ca-Mg-HCO3) (Ca-HCO3) are placed. The year 2013 is much like 2003 saves for area 6, with the difference that type of mixing water is much more limited than area 4, and area 2 is decreased as to year 2003. The factors which are involved in these waters are ion exchange mostly for cation exchange (replacement of calcium and magnesium for sodium), since ion ratio Na/Na+Cl in 2003 of wells W5, W32, and W42 and in 2013 of wells W5, W10, W22, W27, W28, W32, W33, and W42 were less than 0.5 and the rest more than 0.5. This indicates a ion exchange in most regions of study area (Hounslow, 1995). Deposition (saturation and deposit of calcite, dolomite, and monazite) causes these types of waters to be directed from groundwater currents to discharge. Regarding arrangement of samples in Piper diagram diamond, type of water along groundwater currents from west to northwest into east and southeast is impacted from feeding area to discharge respectively through calcium bicarbonate and magnesium bicarbonate, calcium deposits affected by limestone, dolomite, and marl in the highlands of the catchment. Mixing waters mostly include Ca-Na-HCO3 and Ca-Mg-Cl that might play a significant role in these chemical reactions along with pH changes. On the other hand, due to importance of SAR values in groundwater resources and its impact on soil and agriculture, these values are used in determination of qualitative indices. In the water years under study, SAR values are variable between 5.03 (2003-04) and 3.95 (2013-14). Because of reduction in sodium abruption rates, sodium and calcium + magnesium amounts are reduced; thereby water conditions are improved for agricultural purposes.

WQI in Ghazvin Groundwater Resources: With respect to hydro-geochemical specifications of study area, reactions occurred along groundwater currents are one of the most influencing factors on quality of these resources. Since solutions and sediments and materials in water have direct connection with WQIs. To determine these indices, analysis of 42 selected wells in Ghazvin Plain were separately examined. Each index was representative of qualitative conditions of wells and groundwater under investigation. According to Table 3, relative weight and standards are applied in development of groundwater WQI as proposed by WHO in water years 2003-04 and 2013-14. To ascertain and develop the proposed method, hydro-geochemical studies were conducted in order to obtain a more suitable view out of changes made in these indices and their relation with geological conditions. One of the most important parameters is changes in TDS values and their comparison with indices' locational changes. A look into TDS (Fig.3) and WQI (Fig.5) maps shows suitable congruence between changes occurred in these two figures. Since values 1000 mg/l are positioned in excellent and good range (desirable range for drinking purposes is 1000 mg/l). Values between 1000 and 1500 mg/l are unsuitable and amounts higher than 1500 mg/l signify bad and undrinkable ranges. It means that TDS changes are able to specify conditions of qualitative indices in the study area. Respecting pH conditions and chemical reactions (ion exchange) and resolution (halite and gypsum) and sediment (calcite, dolomite, and magnetite), they play a significant role in increased soluble materials in groundwater resources. Together with natural resources, excessive withdrawals are also of paramount importance in study area that cause reduction of the intended groundwater and increased density of materials in water. Ghazvin Plain WQIs are calculated to be based on desirable standards (Fig.3). Accordingly, in water year 2003-04 percentage of WQI was excellent (4.76%) (2 wells), good (45.23%) (19 wells), weak (45.23%) (19 wells), and very weak (4.76%) (two wells). While in water year 2003-04, excellent range is reduced to 7.14%, good range increased to 47.62%, and weak range reduced to 26.19%. Very weak range is increased to 16.66% and unsuitable range is added thereto. (Fig.4). It means that excellent, good, and weak areas that are related to heights, alluvial fans, and primary areas of the plain signify suitable conditions respecting withdrawal and feeding. While, very weak and unsuitable ranges have increased, geological formations (silty-clay, halite, and gypsum plates), excessive withdrawals (increased density of ions and reduced size of groundwater), and mixture of urban, rural, agricultural, and industrial wastewaters have the highest effects (Fig. 5). According to obtained ranges, qualitative changes diagram as to wells is drawn in Fig. 6, which shows that the highest effects in water year 2013-14 are related to wells W35, W31, W27, W25, W19, W16, and W10 and in water year 2003-04 related to wells W35, W32, W25, W22, W19, and W10, most of which being located in middle area into the outlet side. This is except for well 10 in the water year 2013-14 that is located in the area of feeding and is rooted in non-natural pollution, as observed in the Fig.5.

Table 4 Qualitative classification of Ghazvin Plain groundwater based on world health index

WQI	**Class**	**Water quality**	**No. of samples**	**Percentage of No. of samples (2003-04)**	**No. of samples**	**Percentage of No. of samples (2013-14)**
50>	I	Excellent	2	4.76	3	7.14
50-100	II	Good	19	45.23	20	47.62

100-200	III	Weak	19	45.23	11	26.19
200-300	IV	Very weak	2	4.76	7	16.66
300<	V	unsuitable	--	---	1	2.38

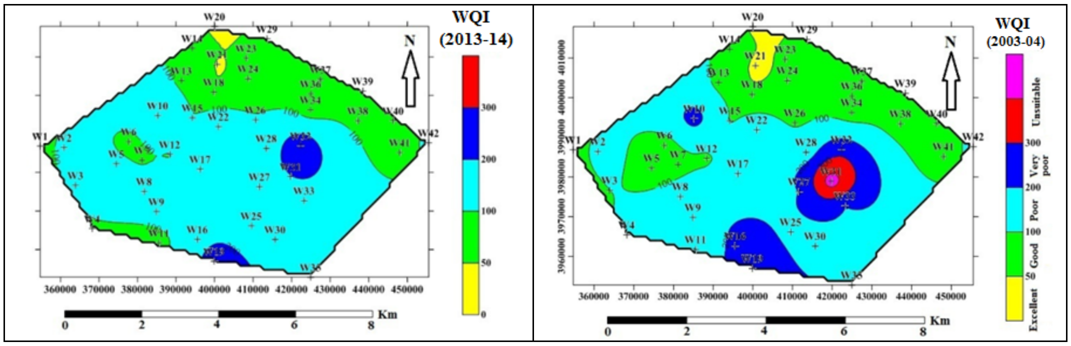


Fig.5 The map for qualitative changes in Ghazvin Plain groundwater's WQI

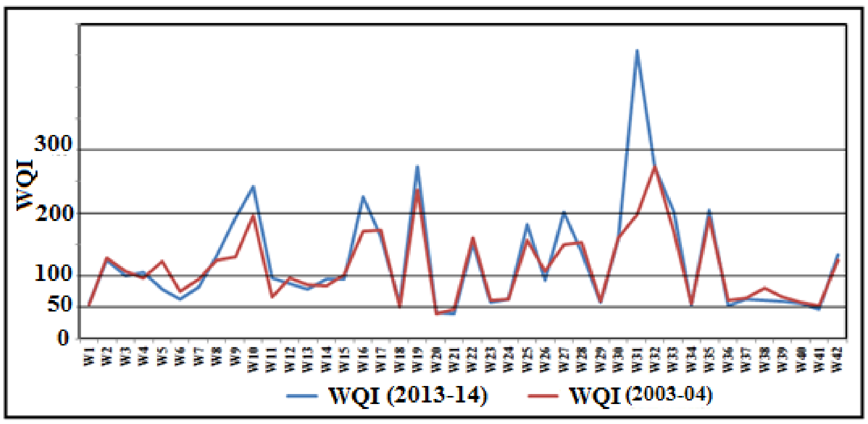


Fig.6 Changes in WQI values at the Ghazvin Plain groundwater resources (2003-04 and 2013-14)

Discussion and Conclusions

In this study, statistics related to water years 2003-04 to 2013-14 associated with 42 wells were used to examine Ghazvin Plain groundwater WQI. In order to conduct a more in-depth investigation, study area was divided into three sections: feeding area, middle area, and discharge area. According to obtained statistics, WQI was calculated using the method presented by the WHO and weighted arithmetic method. This index is determined using the standards by WHO, Iran Industrial Research Standard, and Department of Energy. With regard to excessive fourfold withdrawal during 45 years since 1966 to 2011 and downfall of mean as 1.33 meters during 2003 to 2013 per year due to several reasons in changes in groundwater qualitative water from west and northwest to southeast to east. The most important reasons in changes in Ghazvin Plain groundwater resources include:

1. During ten past years, climatic conditions provoked several droughts, reduced rainfall rates, and increased vaporization and heat temperature. This causes a quick advance in saltwater basin in southeastern region toward the groundwater, causing an increase in minerals in the groundwater. Population growth as well as increased industries and withdrawals have brought about a reduction in volume of groundwater resources and an increase in chemical density of groundwater. Because of absence of a system to recollect consumed urban, rural, industrial, and agricultural waters, pollutions find a direct route in the groundwater and change quality of groundwater resources and WQI.

2. Time and location statistical analyses which are obtained using GIS are indicative of changes in qualitative factors. It seems that geological impacts constitute the major cause of a downfall quality of water in the Plain from feeding to

discharge, because of existence of calcareous and dolomite sediments in Karaj formation (tuff, limestone, basalt, andesite, rhyodacite, and shale) in northeast and west, evaporate formations (halite, gypsum, and clay) in middle parts along the outlet regions, and clay-silt plates in outlet regions. Because of these two factors in northern regions, water quality is relatively suitable for beverage and agricultural purposes. While the major part of study area is located in weak to unsuitable classification, persistence of this condition would cause an advancement of saltwater basins into the groundwater, and downfall of quality of groundwater resources due to excessive withdrawals would bring about dire and irreparable complications. Senior managers are required to quickly take measures to make changes in agricultural patterns (type of implantation methods and irrigation systems) and reverse water recollection methods (beverage, industry, and agriculture). WQI is one of the modern methods that needs precise investigations. Researchers are required to either make use of present methods or invent new ones in order to make them compatible with their study areas.

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