

ARTICLE

THE HYDROCHEMICAL EVALUATION OF CASPIAN SEA COASTAL AQUIFER BY STATISTICAL METHODS (CASE STUDY; GHAEMSHAR-JOYBAR'S AQUIFER; NE OF IRAN)

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ABSTRACT

Ghaemshahr-Joybar plain is located in northeastern Iran, Mazandaran province on the shore of the Caspian Sea. The study area lies from 35'-44' to 36'-47' North latitudes and 52'-35' to 53'-23' East longitudes. The sample is determined after experiment of 22 points for different physicochemical. Groundwater quality by various physical and chemical parameters was tested. In this study, statistical methods with central indices such as mean, median, and mode are used. For distribution such as standard deviation and the relationship between variables, Pearson correlation coefficient, Skewness, Kurtosis and used. Kolmogorov and Smirnov method used to test the normal distribution of data. In these tests, values less than 0.05 as significant and considered acceptable. Given this assumption, all selected factors have approximate value (P -value < 0.05) more than test error (α), so there is no reason to reject the assumption of normality of the data. Statistical analysis shows that, this can complement conventional methods used in chemical assessment of groundwater. Based on the results analysis, ground water of dominant facies are composed of calcium and sodium bicarbonate and mixture of waters with calcium, magnesium, chloride, with sodium chloride. As a result, chemical reactions swap or reverse ion exchange in the study area of sodium result from salt-water intrusion and the amount of weathering of clay minerals, calcium, and magnesium from limestone and dolomite deposits. This study showed that statistical methods could be effective in analysis methods commonly used hydro-chemical.

INTRODUCTION

KEY WORDS

Ghaemshahr- Joybar,
heavy tailed, Skewness,
Kurtosis, Kolmogorov –
Smirnov

There are many variables associated with water quality, which are a function of wide fluctuations in time and space. Understanding these fluctuations and identifying whether the changes are natural or as the result of human activities can be a great challenge. The chemical composition of groundwater has many control factors including hydro climate, composition, and amount of rainfall, geological conditions, chemical composition of formations, topography, vegetation, and many other factors. One of the most important and complex issues in hydrogeological studies is the quality and suitability of the groundwater and protecting it, because most hydrology activities are done to supply water for various uses. In hydro chemical studies, using statistical methods such as correlation matrix, Skewness, kurtosis, and descriptive statistics can be an effective aid to common methods in the interpretation of data on water resources. Consider the analysis of the test data carefully for any assumption in any research is of great importance and as the main and most important part of each study. With the help of descriptive statistics such as central tendencies, for example mean, median, mode, variance dispersion such as standard deviation, and the like are data analysis. Descriptive statistics on the relationship between variables such as Pearson correlation, Skewness and Kurtosis are used. In this study, statistical methods and common hydro-geochemistry used to describe the situation. In this regard, there is a lot of research in Iran and the world. Among them, the studies by Burgohain et al. (2009) showed that statistical observations of the main ions and other parameters have almost uncoordinated distribution and their normal curve is asymmetrical. Comparing the contents of water according to the instructions provided for drinking for heavy elements is at warning level, which needs regular sampling to determine the concentrations of elements in the study area. Temporal and spatial measurements of chemical or physical processes usually cannot clearly reveal the main governing processes. Multi-variable analyses try to classify, interpret, or reveal the main processes governing by reducing data [18]. Due to the combined effect of multiple hydrologic, biogeochemical factors, it is very hard to determine the relationship between groundwater quality parameters and biogeochemical processes through graphical methods [11]. That another research [19], studied the quality changes in Suidish groundwater (Southern Sudan) in the period of 20 years for 77 stations using non-parametric method of Mann-Kendall, and the results showed a decreasing trend in the concentration of sulfate ion and no trend was observed in other alkaline ions. In southern Izmir (Turkey), Elci and Polat (2010) studied and assessed groundwater samples of 57 stations for qualitative variables through Kolmogorov-Smirnov method and t tests. The results obtained show a proper and coordinated process between the responses obtained from statistical parameters and common methods in hydro-geochemistry and qualitative variables. Another study is assessing hydro-geochemistry control agents of groundwater in Arak plain [9]. In this study, by establishing the correlation matrix, calculating the values of Skewness and kurtosis of hydro-geochemical parameters has assessed while comparing with conventional methods. Using statistical multivariate methods to help common hydro-geochemical methods, Moghimi et al. (2015) showed that proper and usable responses obtained. Faryabi et al (2009) compared hydro-geochemical methods with multivariate statistical methods and found that this method used in geology and water chemistry and their relationship with each other. One of the purposes of this article is in line with the use of statistical methods and their comparison with conventional methods used in hydro-geochemistry.

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Another goal is, whether we can rely on the results of statistical methods and based on a comprehensive analysis of hydro- climate, hydrology, geochemistry hydro-geochemical and geological be used.

Study and geological scopes

The studied area is until the Caspian Sea from the north and in the south, it is until of the Alborz mountain range. The study area lies from 35°-44' to 36°- 47' North latitudes and 52°-35' to 53°-23' East longitudes in Mazandaran. The total area of the basin is approximately 3348.1 square kilometers, of which 935.5 square kilometers is plains that makes up the study area and the rest is the Northern Alborz mountain range [Fig. 1]. Climatic conditions of the study area are affected by mountain and moist maritime climate with semi-humid climate.

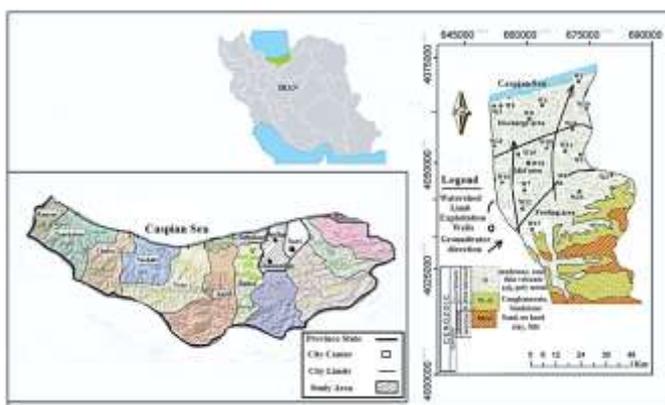


Fig. 2: Map of geographical location, geology, location of wells and the general direction of groundwater in Ghaemshahr- Joybar.

Caspian Sea coastal plains overlooking the sea gradually formed due to a drop in the sea. This loss along the coast is different. Along with the retreat of the sea, fresh water from the mountains has tried to wash and push back the salt water, but it has not completed and in here and there in alluvium, areas of salt water have remained [7]. Geology and hydrogeology studies conducted in the Caspian Sea coastal aquifers have proved some saltwater zone due to the Caspian Sea retreat. Geological formations have the most and major impact on water resources (quality and quantity) of Ghaemshahr- Joybar catchment. The heights of this area are mostly calcareous, marl, dolomite, and sandstone sediments (Mesozoic and Cenozoic). In the plain area from south to north in the foothills are the alluvial deposits that have high permeability and in the middle towards the coast in the plain, with reduced grain size, sediment such as sand, non-hard clay, silt, and thin layer of volcanic ash (new Caspian deposits with Quaternary age) prevail. Below these sediments is Absheron Formation made of clay, marl, non-hard sand, conglomerate, and a thin layer of volcanic ash with upper Pliocene-Quaternary age [Fig.1] [12].

According to geophysical studies, Ghaemshahr-Joybar coastal plain aquifer is like a bowl that has low thickness in the northern and southern ends and has the maximum thickness in the middle [17]. As a result, according to the geological situation and the direction of groundwater flow, water time of stay in the middle increases and this increases the chemical reactions in the middle section. In the study area, changes follow a certain order water table and affect the Earth's surface morphology and feeding of the aquifer (south area). Elevation of groundwater level curves varies between -25 to 60 meters and decrease from south to north. The general direction of groundwater flow in the area is from south to north and northeast [Fig. 1]. The focus in this research is to use descriptive statistical methods in the analysis of hydro chemical data of Ghaemshahr-Joybar and to compare them with conventional methods. The research objectives are assessment of the factors affecting hydro-geochemical status of Ghaemshahr-Joybar Plain aquifer using statistical methods and comparing the results of statistical methods with conventional hydro-geochemistry methods (Piper-Gibbs graph).

MATERIALS AND METHODS

Data and methodology

In order to investigate the quality of groundwater streams of Ghaemshahr-Joybar Plain through statistical procedures and common hydro-geochemical methods, the data of 22 exploitation wells used in the two sampling periods of 2003-2015 [Fig.1] [Table 1][1]. For chemical analysis is used APHA standards method [2]. Aqqa software is used in the determination of water type; SPSS-16 is used in the calculation and analysis of statistical methods to assess the chemical status of groundwater resources.

Table 1: Statistical Profile of Chemical analysis of selected sources in Ghaemshahr area (The values of elements and TDS in terms of mg / l and EC in terms of $\mu\text{S} / \text{cm}$ for 2003 and 2015) (R; Range, Min; Minimum, Max; Maximum, Me; Mean, Med; Median, Mo; Mode, SD; Standard Deviation, S; Skewness, K; Kurtosis, V; Variance,)

P	EC	TDS	P H	Ca	Mg	Na	K	HCO ₃	Cl	SO 4	TDI	SI c	SI d	SIha l	SI g	Alk	CA 1	CA 2	TH
2003																			
R	3278	2082	0.7	178	85.8	470	8	811.8	569.8	581	2111	1.3	1.8	0.05	14	640	1.65	0.4	1280
Min	792	522.5	7.5	74.8	31.6	22.7	2.2	250.1	35.01	73.9	571	0.41	6.51	-0.20	-16.2	212.2	-1.65	-0.4	572
Max	3885	2486.4	8.21	241.5	111.3	470.	10.	1037	577.5	624.7	2560	1.68	7.98	-0.14	-1.9	818.2	-0.06	0.0	1730
Me	2129.	1357	7.8	136.5	60.7	204	5.2	568.6	229	244	1450	1.2	7.41	-0.16	-6.2	453	-0.43	-0.1	988
Med	1855	1212	7.8	137.8	50.2	157	4.2	539.5	150.8	158	1292	1.2	7.3	-0.16	-4.0	427	-0.4	-0.1	927
Mo	1855	1212	7.8	88.5	42.7	143	3.9	381.2	46	160	560.7	1.3	6.3	-0.16	-16	208	-0.4	-0.2	879
SD	928	573.7	0.2	44.1	23.2	152	2.1	218.5	179.5	159	596.6	0.37	0.51	0.02	3.93	173.3	0.32	0.10	327.2
S	0.58	0.61	0.44	0.89	1.19	0.70	0.73	0.57	0.80	1.21	0.55	-0.5	-0.4	-0.16	-1.1	0.52	-2.0	-0.8	1.1
K	-0.49	-0.52	-0.3	0.79	0.41	-0.98	0.15	-0.25	-0.77	0.74	-0.53	-0.8	-0.5	-0.98	0.48	-0.36	6.15	-0.2	0.92
CV	0.435	0.422	0.02	0.32	0.38	0.74	0.4	0.38	0.78	0.65	0.41	0.3	0.07	-0.13	-0.6	0.38	-0.7	0.62	0.33
V	7.4E5	3.0E5	0.04	1.7E3	491.2	2. E4	4.0	4.1E4	2.8E4	3E4	3.08E5	0.12	0.22	0.00	13.4	2. E4	0.10	0.01	9. E4
2015																			
R	6480	4148.1	1.1	297	121	940.	2.5	818.6	1612.6	501.6	5757.4	1.43	1.88	0.07	10.4	638.1	0.70	0.64	2059
Min	868	554.4	7.52	74.8	29	22.7	3.43	255	31.2	47.5	686.4	0.07	5.74	-0.18	-11.5	193.3	-0.45	-0.12	552
Max	7014	4712.4	8.3	355	142.8	919.8	5.73	1024.8	1568.8	524	6152	1.50	7.62	-0.11	-1.1	793.7	0.25	0.51	2493
Me	1936	1244.1	7.85	145.1	58.9	154.8	4.2	554.5	254.7	128	1648	0.66	6.44	-0.15	-3.0	438	-0.0	-0.0	1021
Med	1480.8	946.5	7.79	136.7	49.4	73.1	3.72	510.8	127.2	94.1	1347	0.6	6.4	-0.16	-2.3	411.8	-0.4	-0.1	955
Mo	852.1	544.3	7.99	101.5	50.5	22.3	3.79	250.3	122	88.1	674	0.07	5.96	-0.16	-2.1	189.8	-0.2	-0.2	542
SD	1354	861.5	0.25	62	25.3	197.8	0.74	192.2	336.4	100	1180	0.38	0.54	0.02	2.12	151.6	0.15	0.12	434.4
S	3.02	3.05	0.07	2.22	2.16	3.26	0.79	0.93	3.37	3.4	3.1	0.58	0.81	0.76	-3.3	0.67	-0.6	3.17	2.27
K	11.02	11.26	0.52	6.68	6.27	12.4	-0.4	0.91	13.1	14.1	11.9	-0.4	-0.1	0.72	13.0	0.36	0.82	12.3	6.81
CV	0.7	0.69	0.03	0.42	0.43	1.27	0.17	0.34	1.32	0.78	0.71	0.57	0.08	-0.13	-0.7	0.34	-0.7	0.62	0.42
V	1.6E6	6.6E5	0.06	3340	560	3.6E4	0.49	3.4E4	1.0E4	8680	1.4E6	0.16	0.31	0.0	4.7	2.2E4	0.04	0.03	1.8E5

Standard deviation is a measure of the dispersion of data around the mean. If data set standard deviation is small, they usually gather around the mean and if it is great, they are away from the mean.

Box-and-whisker plot: when the aim is emphasizing certain points of distribution, this plot is used to provide information. This plot enables comparisons between multiple data sets easily. Box-and-whisker plot has one rectangle (box) and two lines on two sides of the rectangle (whisker) that is drawn by the median, first (25%), third (75%) quartile, and minimum and maximum observed data. Using this plot, centrality, dispersion, and skewness of the data can be interpreted. Rectangle drawn has 25% and 75% length, which is equal to quartiles. Middle size is drawn as a line parallel to the width of the rectangle and thus rectangle is divided into two parts. On the other hand, using sorted data, minimum and maximum data that are within the inner borders are determined and a line from the middle of the rectangle is connected to these two points in form of a filled lines. These lines are called whiskers that start from the quartile and end in the above points. Each number located outside the inner borders is called outlier and if it is between inner and outer borders, it is a weak outlier shown with O. If it is over the border or in the external enclosure, it is called strong outlier (end) shown with (*). Using box-and-whisker plot, the following information is obtained:

- A) If the median is near the middle of the rectangle (box), data distribution is almost symmetrical.
- B) If the median is on the left of the middle of the rectangle, distribution is skewed to the right, and if the median is on the right of the middle of the rectangle, distribution is skewed to the left.

Skewness is an index to analyze the distribution and asymmetric symbol and the deviation from a normal distribution. Skewness studies the degree of symmetry or asymmetry of probable distribution of data around the mean.

Interpretation: If it is greater than zero, it has right skew distribution and most of the values are concentrated on the left part of the men along with maximum values and above on the right. If it is less than zero, it has left skew distribution and most of the values are concentrated on the right part of the men along with maximum values and above on the left. If the values are zero, the mean and median are equal and have symmetrical distribution around the average.

Kurtosis is a statistical graph used as an index to analyze the distribution of data as a sign of being smooth or without tipping in a distribution. Kurtosis is a measure of the steepness of the curve at the peak. The strain or chamfer of frequency curve compared to the normal curve is called kurtosis.

Interpretation: kurtosis greater than zero which is sharper than a normal distribution identified with values focused around the mean and a denser or heavy tail. This means that, it is likely that the maximum values are placed in this heavy tail. Kurtosis smaller than zero is wider than a normal distribution with a broad peak, probably maximum values are smaller than the normal distribution, and the values are widely scattered around the mean. In this distribution, variance is high. Kurtosis equal zero its shape is long and upward. Normal distribution is a correct sample for this type of distribution [Fig. 2].

The coefficient of variation (C.V.): This index calculated by dividing the standard deviation into the mean. It was use to compare two traits of a population with different units of measurement. It does not depend on unit of measurement. Observation data set with lower C.V has more consistency and homogeneity.

Correlation coefficient: Correlation coefficient shows two random variables X and Y by r in a population. Pearson correlation properties of elements and substances in the groundwater include: always $-1 \leq r \leq 1$ and independent of the measuring unit. When $r = 1$, the correlation between the two variables is strong and consistent. This means that the increase in one increases the other. When $r = -1$, the correlation between the two variables X and Y is severe and strong. This means that the increase in one decreases the other. When r is near to zero, correlation between the two variables is weak [Table 3]. In this table, the numbers significantly correlated are calculated with two stars with one percent error and one star with 5 percent error rate. As a result, significant numbers (from 0.4 to 0.75), if have two or one star can also show good correlation. While the ones with no stars, even if in the significant area can have a weak correlation. Negative values show reverse correlation with the intended parameters. However, values less than 0.4 mean linear or weak correlation, values between 0.4 to 0.75 mean significant linear correlation, and values between 0.75 and 1 are defined as strong linear correlation [16].

Table 2: Pearson correlation between groundwater quality parameters of Ghaemshahr-Joybar Plain(Slh;Sihalit, Slg; Slgypsum (2003 and 2015)

2015	EC	TDS	PH	Ca	Mg	Na	K	HCO ₃	Cl	SO4	TDI	Slc	Sld	Slh	Slg	Alk	CA1	CA2	TH	2003
EC	1	0.1 ^{**}	0.05	0.7 ^{**}	0.7 ^{**}	0.9 ^{**}	0.8 ^{**}	0.55 ^{**}	0.9 ^{**}	0.7 ^{**}	0.1 ^{**}	0.43	0.6 ^{**}	0.9 ^{**}	-0.77 ^{**}	0.5 ^{**}	0.02	-0.6 ^{**}	0.74 [*]	EC
TDS	0.1 ^{**}	1	0.027	0.7 ^{**}	0.7 ^{**}	0.9 ^{**}	0.8 ^{**}	0.5 ^{**}	0.9 ^{**}	0.8 ^{**}	0.1 ^{**}	0.4	0.6 ^{**}	0.9 ^{**}	-0.77 ^{**}	0.5 ^{**}	0.03	-0.6 ^{**}	0.74 [*]	TDS
PH	0.2	0.2	1	0.18	-0.03	0.04	-0.13	0.03	0.1	-0.02	0.06	0.7 ^{**}	0.5 [*]	0.13	0.03	0.07	.06	0.07	0.1	PH
Ca	0.9 ^{**}	0.9 ^{**}	0.21	1	0.8 ^{**}	0.41	0.7 ^{**}	0.62 ^{**}	0.31	0.7 ^{**}	0.7 ^{**}	0.6 ^{**}	0.8 ^{**}	0.43 [*]	-0.66 ^{**}	0.6 ^{**}	-0.1	-0.07	0.98 [*]	Ca
Mg	0.96 [*]	0.96 [*]	0.26	0.96 [*]	1	0.38	0.77 [*]	0.6 ^{**}	0.38	0.68 [*]	0.72 [*]	0.41 [*]	0.73 [*]	0.41	-0.66 ^{**}	0.6 ^{**}	0.03	-0.03	0.93 [*]	Mg
Na	0.99 [*]	0.99 [*]	0.19	0.9 ^{**}	0.9 ^{**}	1	0.60	0.35	0.97 [*]	0.63 [*]	0.89 [*]	0.23	0.4	0.94 [*]	-0.64 ^{**}	0.35	0.06	-0.7 ^{**}	0.42	Na
K	0.78 [*]	0.77 [*]	0.34	0.78 [*]	0.77 [*]	0.75 [*]	1	0.55 ^{**}	0.57 [*]	0.68 [*]	0.8 ^{**}	0.34	0.57 [*]	0.63 [*]	-0.67 ^{**}	0.55 [*]	0.05	-0.3	0.76 [*]	K
HCO ₃	0.74 [*]	0.72 [*]	0.16	0.8 ^{**}	0.8 ^{**}	0.65 [*]	0.68 [*]	1	0.22	0.08	0.61 [*]	0.68 [*]	0.75 [*]	0.41	-0.045	0.1 ^{**}	-0.5 [*]	-0.4	0.6 ^{**}	HCO ₃
Cl	0.98 [*]	0.97 [*]	0.19	0.88 [*]	0.9 ^{**}	0.99 [*]	0.74 [*]	0.59 ^{**}	1	0.67 [*]	0.86 [*]	0.2	0.35	0.9 ^{**}	-0.67 ^{**}	0.23	0.25	-0.6 ^{**}	0.4	Cl
SO4	0.92 [*]	.92 ^{**}	.17	0.9 ^{**}	.9 ^{**}	.91 ^{**}	.64 ^{**}	.59 ^{**}	.90 ^{**}	1	.74 ^{**}	.15	.41	.58 ^{**}	-.99 ^{**}	.082	.26	-0.2	0.7 ^{**}	SO4
TDI	0.99 [*]	0.98 [*]	0.16	0.9 ^{**}	0.95 [*]	0.98 [*]	0.74 [*]	0.68 ^{**}	0.98 [*]	0.93 [*]	1	0.47 [*]	0.68 [*]	0.87 [*]	-0.7 ^{**}	0.6 ^{**}	-0.04	-0.6 ^{**}	0.77 [*]	TDI
Slc	0.6 ^{**}	0.6 ^{**}	0.78 [*]	0.7 ^{**}	0.7 ^{**}	0.5 [*]	0.67 [*]	0.7 ^{**}	0.51 [*]	0.5 [*]	0.55 [*]	1	0.93 [*]	0.33	-0.11	0.7 ^{**}	-0.3	-0.1	0.6 ^{**}	Slc
Sld	0.77 [*]	0.76 [*]	0.61 [*]	0.8 ^{**}	0.86 [*]	0.7 ^{**}	0.77 [*]	0.83 ^{**}	0.67 [*]	0.66 [*]	0.73 [*]	0.95 [*]	1	0.48 [*]	-0.37	0.77 [*]	-0.2	-0.17	0.8 ^{**}	Sld
Slh	0.87 [*]	0.87 [*]	0.22	0.8 ^{**}	0.86 [*]	0.86 [*]	0.8 ^{**}	0.7 ^{**}	0.85 [*]	0.67 [*]	0.86 [*]	0.57 [*]	0.75 [*]	1	-0.6 ^{**}	0.41	0.03	-0.7 ^{**}	0.4 [*]	Slh
Slg	-	-0.9 ^{**}	-0.17	-0.9 ^{**}	-0.9 ^{**}	-0.9 ^{**}	-0.6 ^{**}	-0.57 ^{**}	-0.9 ^{**}	-0.1 ^{**}	-0.9 ^{**}	-0.5 ^{**}	-0.6 ^{**}	-0.7 ^{**}	1	-0.05	-0.3	0.24	-0.7 ^{**}	Slg

	0.9**																			
Alk	0.66*	0.66*	0.12	0.8**	0.7**	0.57*	0.72*	0.89**	0.52*	0.57*	0.6**	0.64*	0.75*	0.61*	-0.56**	1	-0.5*	-0.4	0.64*	Alk
CA1	0.3	0.29	-0.12	.28	0.2	0.27	0.37	0.01	0.33	0.27	0.34	-0.01	0.11	0.38	-0.27	0.14	1	0.45*	-0.06	CA1
CA2	0.3	0.3	0.12	0.22	0.2	.340	0.38	-0.16	0.43*	0.21	0.34	.058	0.13	0.43*	-0.21	-0.12	0.7**	1	-0.06	CA2
TH	0.96*	0.95*	0.22	0.99*	0.98*	.9**	0.8**	0.8**	0.9**	0.9**	0.9**	0.7**	0.85*	0.8**	-0.9**	0.77*	0.3	0.2	1	TH

** . Correlation is significant at the 0.01 level (2-tailed). * . Correlation is significant at the 0.05 level (2-tailed).

DISCUSSION

In Ghaemshar-Joybar study area, hydro-geochemical and physicochemical data are used with the help of statistical methods such as range, minimum, maximum, mean, median, mode, standard deviation, Pearson correlation, Skewness and kurtosis and conventional hydro-geochemical methods such as Piper and Gibbs for use in analysis, groundwater chemistry control mechanisms, and the factors affecting. Due to the geological status and retract of the middle part and the accumulation of water in the direction of groundwater flow, water stay time rises and this increases chemical reactions. For this reason, in the analysis of these graphs, the relationship between geological conditions, hydro-climate, saltwater and saline fossil groundwater intrusion, excessive exploitations, the reaction between water and rocks, and other effective factors in the control mechanism of groundwater can be used [8].

Statistical analysis: Statistical characteristic of chemical analysis of the study area can be seen in [Table 1]. In this table, the values of range, minimum, maximum, mean, median, mode, standard deviation, Skewness, kurtosis, and coefficient of variation of chemical parameters are provided. Given the normal test and assuming normal test error (α) 0.05, all selected factors have approximate value (P-value) more than test error (α), so there is no reason to reject the assumption of normality of the data (Table-2). By drawing bar graph of the elements and materials measured and calculated in groundwater, normal curve is compared with them. These graphs are drawn after normal test using Relation 1 and with the help of SPSS software after the data have been normalized and standardized. After applying the above, measured and calculated data are analyzed using statistical methods. The following is obtained by comparing statistical values for 2003 and 2015 [Table 2]:

- In both years, minimum values have not changed much, but maximum values in 2015 have increased in form of spots (16th well), especially in discharge area, while this increase has largely not reflected in the mean values. As a result, the radius of influence of these cases is not high and the wells around have normal trend.

- Relative harmony of the mean and median in 2003, and mean, median, and mode in 2015 shows relative homogenization of the solutions entering the aquifer in input in the direction of groundwater flow to drains. In the meantime, the most appropriate method for determining the measure of central tendency of water quality is median values.

- Higher ion frequency is based on the median values in 2003 as Na + K > Ca > Mg, HCO₃ > SO₄ > Cl in 2015 are: Ca > Na + K > Mg, HCO₃ > Cl > SO₄ [13, 14].

In [Fig. 2], box-and-whisker plot for 19 different parameters for 2003 and 2015 have been drawn. According to the figure, the data from these wells due to being out of quartiles and maximum are introduced as outliers, and as the distance increases, outlier of data increases. In this study, in 2003, wells including 18 and 9 (center and drain) and in 2015, wells 11 and 20 (drain) have strong outliers. Weak outlier data in 2003 includes wells 14 (input), 9 and 20 (drain) and in 2015 includes wells 20 and 21 (drain) [Fig.3]. Strong and weak outlier data in 2015 have been drawn into drain. This issue in 2015 can be due to increased pressure of bicarbonate solution (calcium and sodium) from input to drain. As seen in [Fig. 3], the line inside the rectangle shows the median. The medians of all major ions and substances such as TDS, EC, are TDI are located on the left side of the rectangle. This means that the slope of most of the parameters is towards percentile 25. The slope of this line that shows the groundwater quality-variables changes in 2003 and 2015 is positive or zero. The slope of the median line zero in 2015 has rather been more than 2003 and this represents the entry of almost uniform solutions (considering mean, median and mode parameters) making changes in the concentration of qualitative variables of the plain and making them fairly homogeneous. The length of the rectangles represents and index for the variance of the values of each variable from 25 to 75 percentile. The increase in length in 2015 compared to 2003, it clearly was saw in the parameters EC, TDS, and TDI. In [Fig. 3], the bar graph of the normal curve of the elements and substances in the groundwater of Ghaemshahr-Joybar has been drawn and the following is remarkable:

- In the height and number of columns peaks in 2003 and 2015 some differences in some parameters are observed. These differences are due to concentration of input solutions in various forms such as the influence of rainfall, input from the adjacent aquifers, leak, or spray from fossil saline aquifers and seawater intrusion into the aquifer. In the direction of groundwater flow due to the geology, the solution causes chemical

reactions between water and rock. Given the high depth and high stay time in the central parts towards the output, high the water stagnation leads to evaporation from that surface and the collection of these elements in different parts of the aquifer changes the concentration of the mixed solutions. The frequency (or columns height) and saturation parameters such as pH decreased, dolomite saturation did not change, but the rest of the parameters had change from limit low (HCO₃) to very high. In the meantime, EC, TDS, Cl, and Na show two to three times increase. The number of peaks in the histogram in most of the parameters from 2003 to 2015 shows a decline. Major cations and anions with EC and TDS in 2003 have two peaks, and only pH has three peaks. The peak can be caused by the arrival of three separate sulfate compounds, bicarbonate, and sodium chloride into the aquifer. However, the lack of homogeneity in the column of concentrations, especially in large amounts, is due to excessive increase of values along the study area from the end of the middle towards discharge. In 2015, pH had two peaks and EC, TDI, Ca, Mg, HCO₃ one point and one-sided columns, all from left to right, meaning right and positive skew are formed (TDS, Na, Cl, SO₄).

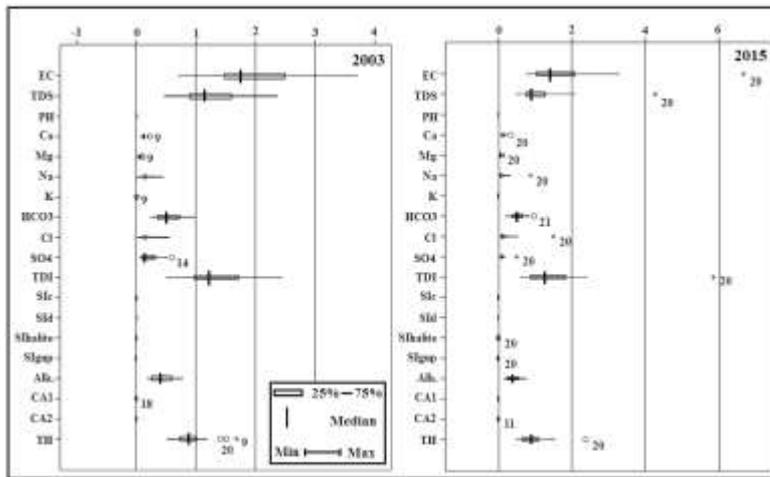


Fig. 2. Box-and-whisker plot for the various parameters of Ghaemshahr-Joybar (M;Mean, S; Skewness, K; Kurtosis, SD, Standard deviation, C.V.; Coefficient variance) (2003-2015).

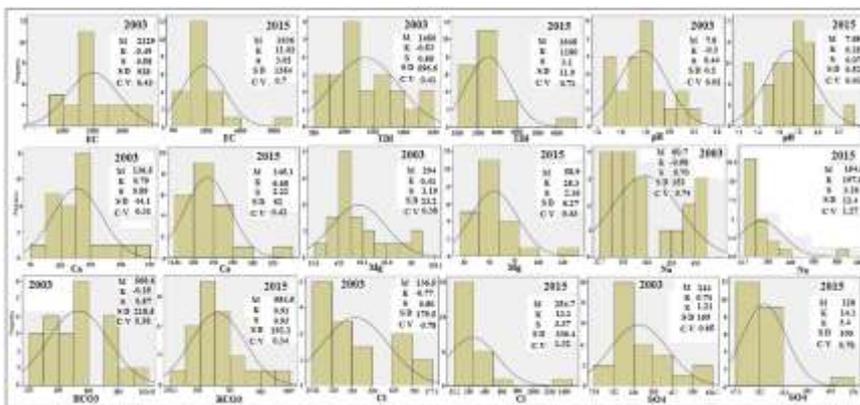


Fig. 3: Normal and bar curves of elements and substances in groundwater in Ghaemshahr-Joybar aquifer (2003-2015).

In this case, high values are placed at the end of the heavy tail of the distribution curve. Given that skewness values in the elements and materials measured are all positive, so the skew is right. Positive skew values in the curve of statistical distribution show that the bottom (heavy tail) on the right (in line with high values) is more than its left side and the bulk of the values (even taking into account the average) than the mean of each parameter tend to the left of the curve. Negative skew values indicate that the ending part is the higher than the distribution graph from the left and the bulk of the values are drawn towards the right of the mean. In positive Skewness, first, small amounts are relatively more than large amounts. Secondly, it represents the last section of the kurtosis curve of this statistical distribution to the right in line with the large amounts skewed, which are longer than the left side, and thirdly, the bulk of the values are drawn towards the left of each parameter. In fact, these three concepts can be due to different solutions, and in some areas from their mixing in the aquifer [Fig.3]. Thus, positive skewness values can be divided into low, middle, and high categories, each of which contains one group and one resource.

Continuity of the columns has reduced, which represents an increase of dispersion of high values in more areas of the study area. In this year, the number of tipping points shows the entry of calcium and sodium bicarbonate solution (from the southern part of plain and mountains of limestone, dolomite and marl) and sodium chloride solution (end of the middle section from the spill and spray of sodium chloride ions of saline fossil groundwater and discharge section and mixing it with saltwater intrusion). Another important aspect is the increase of rocks-water reaction and the formation of sodium bicarbonate and sodium chloride solutions, one part of whose sodium has derived from sodium-rich clay minerals (plagioclase). However, in general, unlike 2003, in 2015, two solutions and their mixing in the area play a central role in the formation of type of water. In hydraulic terms, the formation and composition of these solutions are due to reduction of the pressure of the water column in sweet aquifer due to excessive harvests and almost vertical rising of these ions into the aquifer. Because of water level drawdown in discharge zones, saltwater intrusion pressure enters into aquifers in almost a horizontal position. The combination of these factors along with the evaporation of salty water table in the discharge areas lead to increased intrusion of saline region in the area.

In general, the reduction of coefficient of variation is a reason for homogenization of the set of values along the study area. In the study area, values of the coefficient of variation (CV) in 2003 varied between 0.78 to minus 71.0 and in 2015 between 1.32 to minus 0.71. However, pH values have shown the lowest coefficient of variation in positive values [Table 1] representing a homogenous solution and almost neutral along the area. The standard deviation of cations and anions in both 2003 and 2015 is highly variable. In 2015, calcium cations (40%), sodium (29.3%) and magnesium (7%) had the highest increase, and potassium has dropped nearly 65%. The chloride anions (87%) increased, bicarbonate (12%), and sulphate decreased 37%. The standard deviation of pH is almost the same and low. It shows that, pH is around the center of the mean, which means good and uniform dispersion (neutral pH in both years) in the total study area [Table 1].

Reactions created can also be caused due to constant pH value (at neutral level) during these two years. The standard deviation of the main elements can be the possibility of the highest combination between chloride and sodium (from two sources, from the middle to drain), calcium, and sodium bicarbonate (from input to the middle section) and the mixing of cations and anions remaining in the area of the plain (calcium, magnesium, chloride, and sulfate). In fact, the removal of some compounds is due to lack of sufficient amounts of soluble anions and cations for chemical reactions. In general, the reduction of bicarbonate anion can be derived from the relative decline of rainfall and subsequent dissolution. Sulfate, with reduction of approximately 40% (based on mean, median and mode values) has had the largest decline. Although there is no gypsum deposits, the reason of reduced sulfate is probably the optimum consumption of sulfate fertilizers, absorption of part of it through the roots, and lack of enough solution for chemical composition, which have caused small amounts of sulfate ions to enter into the water. EC and TDS, almost have 0.62 relationship, the increase of standard deviation values from 2003 to 2015 has, respectively been 46% and 50%. This much increase reflects the large changes and number variety, especially from the middle part towards discharge and the homogenization in high amounts. These changes are created due to mixing of seawater and brackish fossil aquifers, indiscriminate harvesting, evapotranspiration, and water level drawdown. High and positive kurtosis values in 2015 are more than in 2003 representing a somehow pointed distribution tending towards the middle that have concentrated in lower part of the tail or heavy tail. Negative or low kurtosis shows a flat distribution, this means data set with little kurtosis tend a high oblong. By comparing the Skewness, it can be said that kurtosis follows the same pattern [Fig. 4] [Table 1].

To illustrate this pattern, skew curve relative to kurtosis is drawn in [Fig. 4]. Correlation of the graph is quadratic of share type. Share figure in 2015 is more complete and has a very high correlation coefficient. By comparing the charts of these two years with [Table 1], significant changes are observed in the study area.

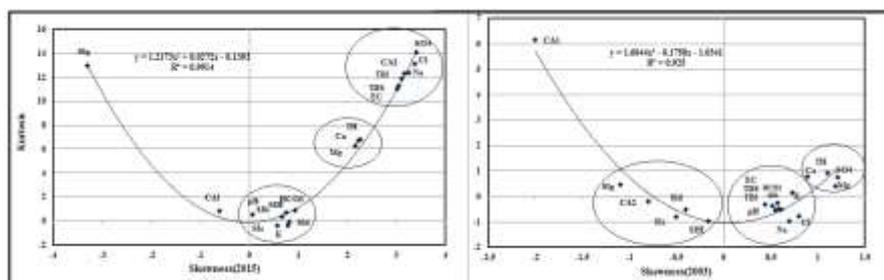


Fig. 4: Kurtosis to skewness chart in Ghaemshahr-Joybar study area (2003-2015).

Increased skewness and kurtosis in 2015 compared to 2003 reflects the diversity of chemical reactions. In 2003, elements and materials measured are nearly concentrated in one area and possibly chemical reactions take place within a specified range. This is while, in 2015, it is as three separate sets and evidently each group is the representative of chemical reactions in groundwater in the direction of the flow. In 2015, precisely ion exchange and the reverse (almost 50% displacement of soluble calcium and magnesium with

deposits sodium and potassium, and 50% reverse chemical reactions takes place) in the sodium chloride solution and its relationship with other groups can will be seen in [Fig. 4]. Given that in 2003, all chloro-alkaline are negative ion exchange prevails. In general, the concentration of ions in one area can be derived from the confluence of three solutions. In 2015, the completion of the curve and its proper distribution can be somewhat due to homogenization of the solution in the input to the aquifer. From figure 3, the type of solution is visible. Sodium chloride solution is due to spray of saltwater intrusion and leakage of chloride sodium ions from brackish fossil aquifers and the bicarbonates is due to dissolution of calcareous, dolomite, and marl sediments and communication of the solutions with each other. In 2015, the amount of pH (7.85) is somewhat more neutral compared to 2003 (7.8), and more homogeneous solution runs in the aquifer. In [Table 2], correlation matrix of data for different hydro chemical parameters of groundwater resources of Ghaemshahr-Joybar plain is provided. From the correlation matrix for 2003 and 2015, the following points have been obtained:

- Most data has positive relationship that reflects the direct relationship with the same hydro chemical data, except for parameters such as pH in 2003 that was negatively correlated with magnesium, potassium sulphate, and in 2015 with chloroalkane, and gypsum saturation profile (Sig), which means by increasing the pH, the ions and parameters listed decrease and or vice versa.

- The correlation coefficient in 2003 varies from 0.022 (a weak positive relationship between the EC-CA1) to 0.999 (strong positive relationship between HCO3-Alk). In 2015, the least correlation 0.003 was calculated for HCO3-CA1, and maximum correlation 0.997 between TDS-EC. In general, Sigup has a reverse correlation with all parameters in both years.

- A strong positive correlation is seen between TDS and EC with most of the parameters except for chloro-alkaline. This strong correlation is observed for both years, with the difference that in 2015 the correlation is much stronger and has increased compared to 2003. Of course, in [Table 3], correlation is obtained with one percent of errors (two stars) and 5% (a star) that can be significant. This means that even small amounts can show a good correlation. Generally, PH has been variable in the range of 7.5 to 8.2 in 2003, and 6.9 to 7.9 in 2015. This means that, it has changed from very weak alkaline state to neutral in 2015. In fact, in the entire study area, the moving solution has been homogeneous and uniform. Except for saturated calcite and dolomite, it has no correlation with any of the elements and materials, and it can be due to the consumption of the solution in saturated calcite and dolomite leading to neutralization of PH solution. However, significant correlations are observed between sodium, magnesium, and calcium with bicarbonate and sodium chloride and calcium, and sodium with magnesium as well as calcium, magnesium and sodium with sulfate (year 2015). The cases are weak in 2003 except for calcium with magnesium and sodium with chloride. In fact, these issues are under the influence of geological formations (water-rock reactions), evaporation and crystallization reactions, intrusion of salt water, and spray of sodium and chloride ions from saline fossil aquifers [Table 2].

Piper chart: according to mean values, ion frequency in 2003 is Na + K> Ca> Mg, HCO3> SO4> Cl and in 2015 is; Ca>Na + K> Mg,HCO3>Cl>SO4. In order to understand the natural status of groundwater in terms of chemical better, using Piper chart(1944), and determining main anions and cations on the charts, one can determine facies of the study area [Fig.5].

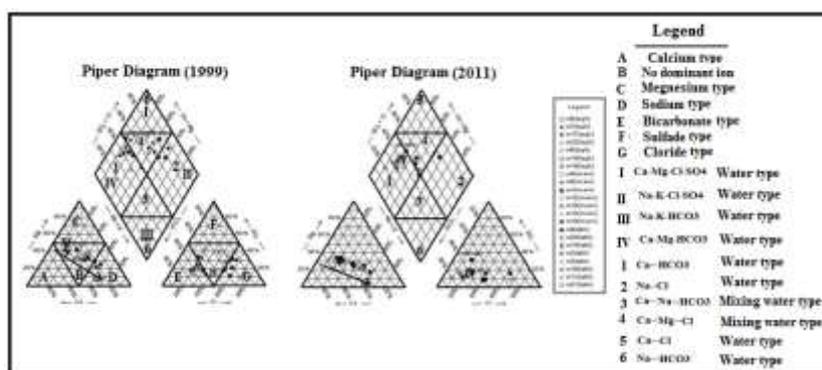


Fig. 5: Classification of ions in triangle diagrams and in Piper rhombus and anionic and cationic charts facies in the study area (2003 in 2015).

According to [Fig. 5], in 2003 and 2015, facies cationic form nearly moves in a straight line from calcium and magnesium side to sodium and potassium corner, which reflects the cationic change from bicarbonate calcic and magnesium (input) towards the sodium chloride (discharge) that is caused by changes in the composition of water on the cation exchange process [10]. This change is in the middle section, which is the deepest part

of the plain and the long lasting time of solutions. By combining the bicarbonate water (calcic and sodic) and intrusion of fossil salt water and seawater, the mixing water are formed and thus no ion is dominant, and towards output, sodium chloride waters are formed. In anionic bicarbonate facies, more bicarbonate and non-dominance of none of the ions and to some extent chloride was saw. Composition and water type in 2015 is similar to 2003, except that; Na-K-Cl-SO₄ type of water has been greatly reduced and most dominant form of water type is bicarbonate (calcic and sodic) and mixing of Ca-Mg-Cl with sodium chloride, along with calcium and sodium sulphate on the spot in the western part (well; 22) in input area, and end of the discharge on the beach (well 11) have been observed. These two wells have converted 2015 with cation exchange bicarbonate calcic (well 22) and sodium bicarbonate (well 11). According to the above description in the Piper rhombus in 2015, the water type of feeding water to drain is bicarbonate calcic (as point sodium bicarbonate) and mixed sodium chloride type. As a result, most type of waters in the study area are formed in the direction of groundwater flow from input to drain including Ca- HCO₃ (4 and IV) with Na-K-Cl-SO₄ (2 and II) (mostly sodium chloride) with a mixture of Ca-Mg-Cl water types prevailing. This can be due to a solution, which is alkali-rich in some places and is rich of alkali soils along the way. As a result, exchange and reverse ion exchange in rock-water weathering reactions play an important role in terms of exchange.

Gibbs graph: Gibbs (1970) explained a general model in relation to major anions of water chemistry to recognize these reactions. According to the results, he offered three major hydrological processes that include input from the atmosphere, weathering of rocks (reaction and interaction between water and rock), and evaporation and crystallization [Fig. 6]. Ghaemshahr Plain, due to humid conditions, with relatively good vegetation and rivers full of water, but due to rice cultivation, which requires a high consumption of water, high water table in the output of the plain, relatively high evaporation of groundwater, and saltwater intrusion has caused %50 of selected samples (11 wells) to be fall in water-rock reaction area in Gibbs diagram and the rest within the evaporation area (year 2015). The value in 2003 was about 45%. As a result, in the last 12 years, 5% has been added to evaporation and crystallization. However, the chemical weathering of minerals forming the rock, which is geology of the heights and alluvial deposits and evaporation- crystallization, is the main driving force controlling groundwater chemistry of the study area [13, 14].

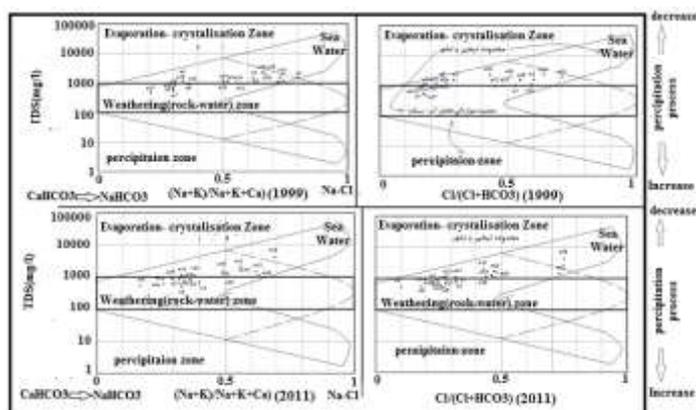


Fig. 6: Gibbs charts (anionic and cationic) in Ghaemshahr-Joybar study area.

RESULTS

Camel According to studies, the following results were obtained

Kolmogorov–Smirnov test with significance level of 95% and decision criteria of 5% was run to determine the normality of the data. Accordingly, there is no reason to reject the null hypothesis, and this means that the intended samples follow a normal distribution.

In this study, median and mode have been more effective in determining the ion frequency and have been of great help to common methods. Ion frequency obtained represents a performance increase of chloride ion and reduction of sulfate ion entry to the study area from 2003 to 2015. Given that in the area, there are no deposits of gypsum and the like, the reduction of the amount of sulfate compounds in groundwater in 12 years (2003-2015) can be caused by lack of adequate solution suitable PH conditions for the reaction. The existence of chloride is due to two sources of fossil water through leaks or spray of solution of sodium chloride and seawater intrusion into the aquifer. Pearson correlation showed that the main ions have a very strong correlation with each other, which confirms the geological relationships with groundwater and saltwater intrusion and saline fossil groundwater effects. In this connection, EC and TDS have a very strong correlation with all anions and cations and their sum (TDI) except PH. On the other hand, a strong correlation between sodium and chloride and calcium and magnesium with bicarbonate and to a lower extent sodium with

bicarbonate in both years shows the groundwater that result from limestone, dolomite and marl structure and their mixing in the mid-range in line with groundwater flow direction with fossil groundwater brackish and saltwater intrusion. Histograms and frequency charts with normal curve represent the number of solutions input and their scattering along the study area. By comparing the histogram and frequency curve with skewed, kurtosis, and the coefficient of variation values, generally increase of these parameters indicates asymmetry in the distribution. The presence of high spot samples causes the deviation of the distribution toward these values (high), as a result, the ending part or the heavy tail of the curve is related to high values. This in fact represents at least two or at most three very different populations, which probably stems from two or three sources of solution. Kurtosis can also follow this pattern, because according to the skewness-kurtosis connection diagram, it is a quadratic equation with a correlation coefficient above.

Piper method in 2003 shows the existence of three bicarbonate solutions (from the southern highlands including calcareous, dolomite, and marl sediments), sulfates (penetration of urban, rural, agricultural, and industrial wastewater and input through seawater intrusion), and intrusion of the sodium chloride solution through saline fossil aquifers and seawater. In 2015, bicarbonate solution and two different sodium chloride solutions are created. In 2003, reverse ion exchange prevailed, while in 2015 this amount reached 50% and includes the rest of ion exchange. This is justified as follows:

- In 2015, the governing reactions are unilateral ones between dissolved calcium and magnesium (dissolution of calcareous, dolomite and marl sediments in the study area) with sodium (rainwater) and solid potassium (marl, Na-feldspar) and deposits. In 2015, this reaction became bilateral and according to assimilation of water-rock reactions, suitable condition for the movement is created.

- Sulfate shows relative 40% decrease in 2015 compared to 2003, given that there are no deposits of gypsum in the range, this reduction could probably be due to reduced consumption of sulfate fertilizers or optimized fertilizer consumption. On the other hand, absorption causes a significant portion of the reduction of these ions in groundwater. Studying statistical methods with commonly used method in hydro geochemistry and their comparison represent a relatively good coordination between the two. Thus, statistical methods can be used as an adjunction in analysis in the studies to achieve better results.

CONFLICT OF INTEREST

There is no conflict of interest.

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FINANCIAL DISCLOSURE

None

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