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Research Article

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Hydrogeochemistry of high-fluoride groundwater at Roumeshgan plain's, Lorestan province, Iran

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ABSTRACT

The purpose of this study is to investigation the process of alteration main elements along with fluoride in the region's water, their relation with each other and also with geology and human made activities of this basin. In order to gain this purpose, 25 samples of groundwater were studied on December, 2013. Moreover, statistics methods such as correlation matrix, the main component analysis, and cluster analysis with the SPSS softer were used to evaluation of the relations between water resources and the elements dissolved in water. Result showed that fluoride concentration increase, from upstream to downstream (from 1 to 4 mg/L). Also result of the primary test showed that some of the main elements and physicochemical parameters such as sodium, sulphate, chlorine, electric conductive, and some of the soluble electrolyte increase, from upstream to downstream while bicarbonate decreases. The result taken from the main component analysis represents the presence of different elements in different groups. Furthermore, the cluster analysis categorizes the water resources into 3 classes and it represented that water resources in downstream are completely different from the other resources in their constructive elements. The correlation coefficient of ions showed that correlation of Fluorine with calcium sodium and sulphate was positive and with bicarbonate a pH was negative. Piper's diagram also showed that faces and types of upstream samples are Bicarbonate Magnesia - calcic and sodic and downstream samples are sulphate sodic. Result showed that fluoride concentration in the region's water (2 to 8-fold) more than normal range in in the region's water the level found in the water with fluoride concentration normal range (0.5 mg /L). These findings provide a basis for further studies on evaluation of serum and urine fluoride concentration of animals and humans that use in the region's water.

Keywords: Roumeshgan; Elements; Fluoride; Geology; Water.

INTRODUCTION

The population growth increasingly and its consequent using ground water for different usage, especially in arid and semiarid regions, draws the attention toward these valuable water resources. Better understanding of ground waters about their quality and quantity, the sediments around them and their feeding resources causes a better management of using them. In Iran and most parts of the world, overusing ground water resources and, on the other hand, the increasing of man–made pollutant resources, such as agriculture, has cause a wide pollution in water resources [1-5]. In spite of the high importance of ground waters in arid and semiarid regions (like Iran), there is little information about the effect of natural and man – made phenomena on the quality of these resources [6]. The chemical compound of ground waters is determined by factors such as the rainfall water compound, geological and mineralogical construction of the basin the chemical process along the water passing [7]. In studies done on hydrochemical of the regions in which ground waters are the main resource, in addition to the amount of main ions and parameters, the studies done on subsidiary anions attentively, because of their importance specially fluoride and nitrate on the life of the residences [8]. Fluoride is one of the subsidiary anions existing in water whose concentration. Varies based on geology conditions and man – made activities, its amount has been reported from about zero to 15 mg/l [9]. Fluoride, in the environment, is more in a form of free ion of fluoride (F^-), but in certain conditions this element makes a complex with elements such as aluminum, beryllium, boron, silicon [10]. Generally, water resources existing in arid and semiarid regions, crystalline stones, and alkali soils have high fluoride [11]. One of the most important man – made factors which increases the concentration of fluoride in water is using phosphate fertilizers in agriculture [12]. The other factors increasing the concentration of fluoride are: the high rate of evaporation and transpiration, long time irrigation and over using agricultural fertilizers [13]. Getting fluoride less than its usual amount (0.5 ppm) by human and especially by children causes lack of consistency in bones and teeth. On the other hand, if fluoride is used in a large amount (more than 1.5 ppm) causes diseases in bones and teeth of children and adults [14, 15]. Nowadays, multivariative statistical analyses make a significant help in recognizing the main reactions which affect the chemistry of water. If hydrochemical analyses are coupled with a complete knowledge of geology and hydrology conditions, multivariable statistics methods can define the amount of the relation of ground water resources with the mentioned factors very well [16-20]. Purpose of the present research is to understand the process of controlling the under study region's water quality with focusing on fluoride element. This significant factor was done by sampling from water and analyzing them, geological studies, and finally multivariative statistical methods such as principal component analysis (PCA) and cluster analysis (CA).

EXPERIMENTAL SECTION

Study area

Roumeshgan plain's basin which is located in south west of Lorestan Province and between longitude 47º 33´ to 47º 66´ and latitude 33º 22´ to 33º 38´, has a population about 47000 people. The estimated space of this basin and Roumeshgan plain are 384 and 153 square kilometers respectively. The average calculations taken from the adjacent stations of this region in a 40 – year statistics shows that the average of the rainfall in this region is 544 milliliter and the average of the region's temperature is 17.1º centigrade. Hence, In De Martonne's climatology divisions, this region's climate is Mediterranean climate [21]. Roumeshgan region is located in the zone of fold Zagros. Different formations which present in this region are: Talehzang formation, Kashkan formation, Asmari formation, Asmari – Shahbazan formation, Aghajari formation, and Gachsaran formation (Figure 1). Asmari, Asmari – Shahbazan and Gachsaran formations and also alluvial sediments of Quaternary are appear in a large part of the region and they are considered as the most important formations of the region.

The constructive materials of alluvial sediments of Quaternary are Gravel, sand, silt and clay. The direction of flow of the ground water in this region is from carbonate formations toward Gachsaran formation. The studies show that the depth of ground water in this region has down turned about five meters during 8 years.

Sampling of the under studied region's ground waters and Physical and chemical analysis

In order to determine the hydrochemical quality of ground waters of Roumeshgan, 25 wells which had suitable dispersion all over the region were selected and taken samples from (Figure 1). Some physiochemical parameters such as pH and electrical conductivity (EC) were sampled and calculated with pH – EC meters model WT – 410 i at the place of sampling. In order to transfer samples to laboratory, two completely clean polyethylene containers for each sample were used, and all of the samples were taken at least 10 minutes after the turning of the wells on.

To calculate cations, the sample's pH, were brought lower than 2 with nitric Acid 25% by coupled plasma atomic emission Spectrometry, the concentrations of Sodium, Calcium, Magnesium in water samples were determined. The concentrations of anions of chlorine, sulphate and fluoride were calculated with Ion chromatography (IC). Bicarbonate was also determined with potensiometric and total dissolved solids (TDS) were calculated with evaporation and the remained amount. The errors of the test for anions and cations was calculated with Ion Balance Error (IBE) based on milligram per liter and in all of these samples these numbers were less than ±5 [22]. Table 1 represents the results of chemical analysis from the taken sample in Roumeshgan region's ground waters.

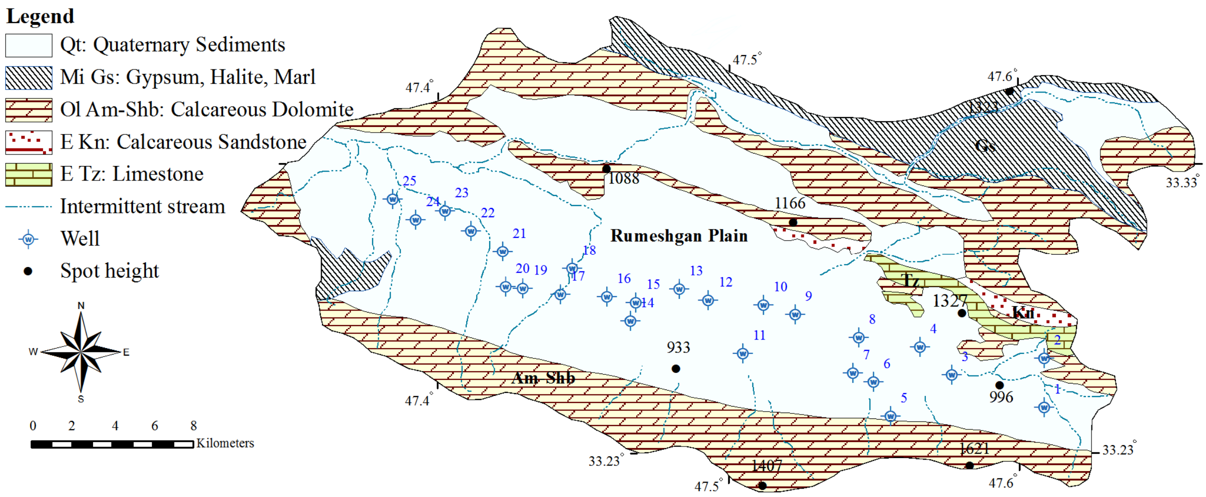


Figure 1. The geology map and the location of the sampling places of ground water resources in Roumeshgan plain's aquifer

Statistical analyses

Multivariative analysis is a quantitative and independent approach which categorizes ground water resources based on correlation between chemical parameters. Using different methods of multivariative analyses such as principal component analysis (PCA) and correspondence analysis (CA) causes a better understanding of the alterations of the quality of water and better comparison of samples with each other [23, 24].

Standardizing the data

Standardizing the data decreases the effect of variables with high variance and increases the effect of variables with low variance. Furthermore, by deleting different parameters, standardizing can have a better explanation of the relation between them. In order to make multi variative statistical analysis, the data should be standardized at first. Standardizing is done with the following formula:

$$X = (X - \mu) / \sigma$$

X = represents the primary amount of the calculated parameter
μ = the average of all calculated parameters in all of the samples
σ = the standard deviation of the parameter. [25]

RESULTS AND DISCUSSION

Hydrochemiacal data

Hydrochemical combinations of ground waters in Roumeshgan plain depend on different factors such as the construction of sediments in contact with water, durability of ground waters, and man – made activities (specially in downstream of the basin). The reaction between the mentioned factors causes ground waters with different combinations. Table 1 represents the characteristics of water resources and the primary results of sample analyzing. In figure 2 co – concentration lines for elements such as sodium, bicarbonate, sulphate, chlorine, EC, fluoride, magnesium and calcium in Roumeshgan plain have been represented. A brief look to these data shows that concentration of some parameters such as sodium, sulphate, chlorine and TDS increases from the upstream to downstream of the basin and also concentration of carbonate and bicarbonate

decreases. In other words, as we go forward from carbonate formations toward evaporative formations, the concentration of sulphate, sodium and chlorine increases intensely and the concentration of bicarbonate decreases. As it can be seen in table 1, the amount of fluoride in the most of samples is less than the determined amount with the universal health organization (1.5 mg/l). It can also be seen that the amount of fluoride suddenly increases in the basin's exit. Because of the sediment construction of the region's all formations and consequently the lack of enrichment of fluoride in the sediments , and also the growth of agriculture in the region and overusing of phosphate fertilizers, it seems that the other factors – along, man–made factors interfere the high concentration of this element in the basin's water resources.

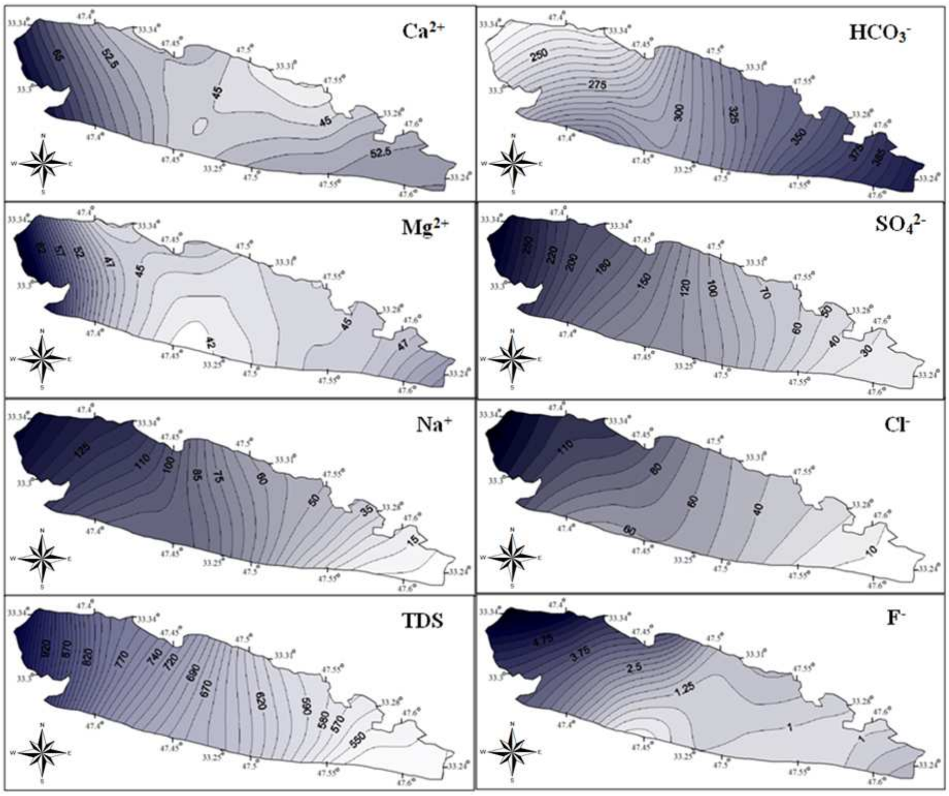


Figure 2- The map of the alteration of some existing ion's concentration in Roumeshgan plain's ground waters

The statistical results for chemical and physical parameters of Roumeshgan plain's ground water are represented in table 1. According to the statistics, the average alteration of fluorine in Romeshgan plain's ground waters is 3.75 milligram per liter which is too higher than universe standards [25] in which the standard concentration of fluoride for drinking use is 1.5 ppm.

Saturation Index

Saturation Index is represented as $SI = \text{Log}\ \frac{IAP}{kt}$ in which IAP is the amount of ion acivity and kt is equibriumsduability constant. If water is exactly on the maximum of saturation, SI will be equal to zero. If SI is positive, it shows the over saturation of the mine in water and its tendency to sedimentation and if SI is negative, it shows the under saturation of that mine and its tendency to solution [26]. Figure 3 represents the saturation index for main mines and also fluorite. As it can be viewed, among the main mines, carbonates, sulphates and chlorides have the highest saturation respectively. In other words, carbonates, sulphates and chlorides have the least solubility in water respectively. As it can be viewed, unlike sulphates and chlorides which have a fixed procedure from upstream toward downstream, carbonates have a very diverse saturation. It is due to the fact that carbonates are very susceptive in pH alterations. As it is clear in figure 3, fluorite, except in resources w_{23} to w_{25} in which concentration of fluoride in water increases significantly, in other water resources it is under saturation. It means although solution of fluorite is less than the other mines containing fluoride (like phosphate mines), in most of the samples of water its amount is under saturation [11]. It shows the high ability of water in dissolving fluoride existing in fluorite.

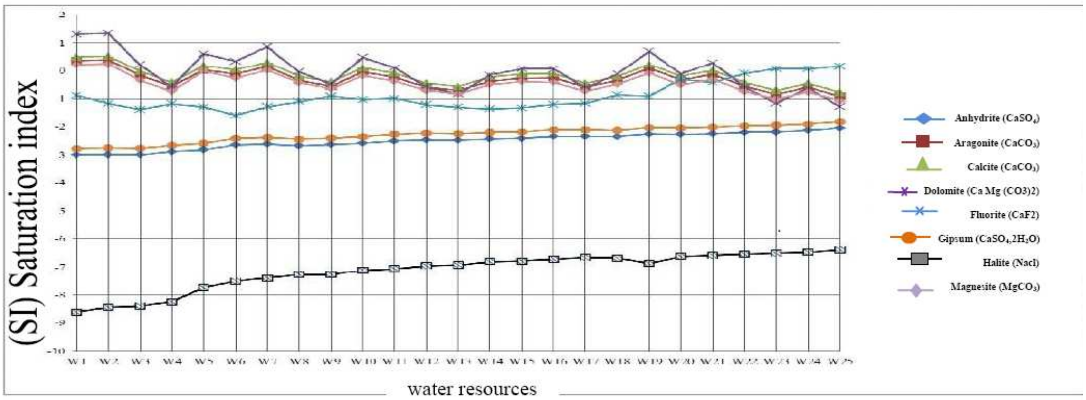


Figure 3- saturation index of different mines existing in Roumeshgan plain's ground water

Data correlation

Linear correlation between different variables is determined with coefficients between +1 and -1. When correlation coefficient of a number is near to +1 or -1, the relations of two parameters has a significant value. Positive correlation represents common features between two different elements like common evolution pattern from upstream to downstream. If the correlation coefficient is negative, it shows that an alteration of one parameter from upstream to downstream is against the other parameter. In the present research, correlation matrix is drowning with spearman method by software SPSS 19 which is represented in table 2. As it can be viewed in this table, Sodium, Chlorine, Sulphate, TDS, EC and Fluoride – lesser than the others – have a high correlation with each other. Due to this fact and co–concentration maps taken from surfer software, it can be said that the concentration of the mentioned parameters increases from the basin's upstream toward its downstream. On the other hand, Bicarbonate has a sever negative relation with the mentioned parameters and due to its concentration alterations it can be said that its amount is decreased from upstream toward downstream. The rather high correlation of Bicarbonate with pH on one hand, and on the other hand increasing of the amount of these two parameters in water resources near the Carbonate units make it too clear the effect of these units in increasing of Bicarbonate and pH. The cations of Calcium and Magnesium have just a high correlation with each other which reveals their high behavioral and chemical similarities from upstream to downstream and the same origin for both of these elements. As it mentioned before, fluoride with sodium, sulphate, chlorine, TDS and EC has a direct relation, while it has a reversal relation with Bicarbonate. Correlation of fluorine with calcium and sodium is positive, while the amount of the correlation of fluorine with sodium is more positive than fluorine with calcium which shows the tendency of fluorine to combine with sodium. While moving, more of sodium replaces calcium, than more sodium have reaction with fluorine and its correlation becomes more positive.

Table 2- Spearman's correlation coefficients in different physicochemical parameters in ground water resources

	Ca	Mg	Na	K	HCO3	SO4	Cl	F	TDS	EC	pH
Ca	1.00	0.82**	0.12	-0.11	-0.09	0.19	0.11	0.37	0.21	0.21	0.05
Mg	0.82**	1.00	-0.08	-0.26	0.13	-0.02	-0.09	0.31	0.01	0.01	0.06
Na	0.12	-0.08	1.00	0.35	-0.99**	0.99**	0.99**	0.68**	0.98**	0.98**	-0.47*
K	-0.11	-0.26	0.35	1.00	-0.40	0.33	0.36	0.048	0.31	0.31	-0.30
HCO3	-0.09	0.13	-0.99**	-0.40	1.00	-0.97**	-0.99**	-0.66**	-0.96**	-0.96**	0.50*
SO4	0.19	-0.02	0.99**	0.33	-0.97**	1.00	0.98**	0.71**	0.99**	0.99**	-0.42*
Cl	0.11	-0.09	0.99**	0.36	-0.99**	0.98**	1.00	0.68**	0.97**	0.97**	-0.48*
F	0.37	0.31	0.68**	0.05	-0.66**	0.71**	0.68**	1.00	0.71**	0.71**	-0.33
TDS	0.21	0.01	0.98**	0.31	-0.96**	0.99**	0.97**	0.71**	1.00	1.00**	-0.37
EC	0.21	0.01	0.98**	0.31	-0.96**	0.99**	0.97**	0.71**	1.00**	1.00	-0.37
pH	0.05	0.06	-0.47*	-0.30	0.50*	-0.42*	-0.48*	-0.33	-0.37	-0.37	1.00

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

The high correlation of fluoride with Sodium helps fluoride to be more resistant and be unwilling to combine with the other ions existing in water and finally it causes increasing of fluoride solubility with sodium in the water [27]. Positive correlation of fluorine with sulphate also reveals the increasing of fluorine with increasing of sulphate [28].

The amount of correlation of fluoride with mentioned parameters and also its concentration distribution in water resources shows the fact its amount is increasing from upstream toward downstream, and it is up to a point that its amount in the exit of the basin is higher than the determined standard amount by the universal health organization.

Principal component analysis (PCA)

Principal component analysis was done to better understand the relation among physicochemical parameters in ground water resources and also the decreasing of variables. A certain amount and a special vector can be taken from the matrix of the covariance of primary variables in this way. Each of the principal variables is a collection of independent variables which is showed by multiplication of dependent variables in each other with a special vector. The special amounts of each principal component are a unit of aggregative variance and the presence of primary variables in principal components are determined with loading the numbers and studying alteration of each variable, which generally called ranking. First the variables with high correlation are determined and classified. In this method, to evaluate eligibility kervit Bartlett test (Bartlett's sphericity) is done on the matrix of data correlation. According to cattle & Jasper's standards, the principal components which their special amount is higher than 1 (Eigen Value >1) are remained and the rest are deleted [2, 5, 12, 20, 24]. In table 5 principal components and aggregation variance of physicochemical parameters are shown. Special amounts in two components is higher than 1. These two components consist of 83.94% of all data which is an acceptable number. As it is seen, in the first component which is 64.98% of all data, sodium, sulphate, chlorine, TDS and EC and also fluoride are in one section and pH and Bicarbonate are in the other section. Existing Sodium, Sulphare, Chlorine, TDS and EC shows weathering and dissolving evaporative mines in underground layers and also existing Fluoride in this group shows that the main ground – made origin of this element is in centralized evaporated mines. There are cations of Calcium and Magnesium in the second component. In the diagram taken from principal–component analysis the mentioned explanations are very obvious and as it is shown pH and Bicarbonate are in one group, and Calcium and Magnesium are in the other group, and in the third group, Chlorine, Sodium, EC and TDS along with Fluoride are located.

Table 1- The chemical analysis results of Roumeshgan region's ground waters

Abbreviation	Ca	Mg	Na	K	HCO3	SO4	Cl	F	TDS	EC	pH
	mg/L									µS/cm	
W1	53.7	49.1	12.7	0.8	389.3	26.9	9.9	1.34	543	699	8.40
W2	52.1	47.1	14.9	1.2	386.2	27.9	8.7	0.97	542	697	8.43
W3	54.2	43.9	14.9	1.2	361.8	26.9	9.9	0.75	520	669	7.90
W4	51.7	45.9	29.0	1.3	361.2	41.8	23.0	0.85	557	721	8.10
W5	51.9	44.9	15.9	1.6	370.4	34.1	13.1	0.94	535	684	7.50
W6	49.9	44.8	38.9	1.6	347.2	64.9	26.9	0.61	581	749	8.00
W7	51.6	46.9	43.9	1.2	353.9	68.7	33.0	0.87	603	772	8.24
W8	39.9	42.9	50.8	0.9	339.3	71.0	35.1	1.20	589	757	7.87
W9	42.9	44.8	52.9	0.8	338	75.89	36.9	1.45	597	763	7.64
W10	47.9	43.9	58.8	1.6	331.3	78.8	45.1	1.20	613	784	8.11
W11	46.9	42.9	65.8	1.9	319.1	96.5	46.8	1.27	626	801	7.95
W12	45.9	43.9	70.8	2.7	309.4	108.6	56.7	1.00	643	824	7.63
W13	42.9	41.9	73.8	2.4	304.5	111.0	58.7	0.93	647	834	7.54
W14	42.8	41.1	88.7	2	295.3	123.9	64.9	0.87	663	861	7.89
W15	43.1	41.7	90.8	1.9	289.2	128.7	67.0	0.91	668	876	8.00
W16	46.7	42.9	95.9	0.8	286.2	142.7	74.8	1.00	695	918	7.98
W17	45.4	42.6	100.7	0.9	283.1	147.5	80.8	1.08	706	927	7.67
W18	43.9	41.0	98.9	1.6	282.5	147.5	78.7	1.53	699	926	7.93
W19	55.9	46.8	86.9	1.1	320.9	152.7	56.7	1.32	726	976	8.21
W20	51.1	43.8	105.8	2.0	278.2	163.8	84.7	2.78	734	998	7.90
W21	51.9	44.8	108.7	2.4	273.4	170.5	90.8	2.41	748	1056	8.10
W22	52.9	44.7	113.8	1.6	271.5	186.4	94.7	3.42	773	1078	7.67
W23	54.9	47.8	116.8	2.2	264.2	193.6	98.9	4.18	786	1103	7.40
W24	58.9	51.9	120.7	1.3	260.5	207.5	105.6	4.05	815	1148	7.63
W25	63.1	55.8	128.7	1.4	252.6	238.2	124.8	4.36	879	1219	7.30

Table 3- the amounts of each component, special amounts, the percentage of variance and aggregative variance

		Ca	Mg	Na	K	HCO3	SO4	Cl	TDS	EC	pH	F	E.V	Var %
Comp	1	0.40	0.39	0.95	0.31	-0.94	0.98	0.98	0.99	0.99	-0.59	0.87	7.15	64.98
	2	0.84	0.87	-0.26	-0.51	0.32	-0.09	-0.15	0.01	0.06	0.16	0.35	2.08	18.96

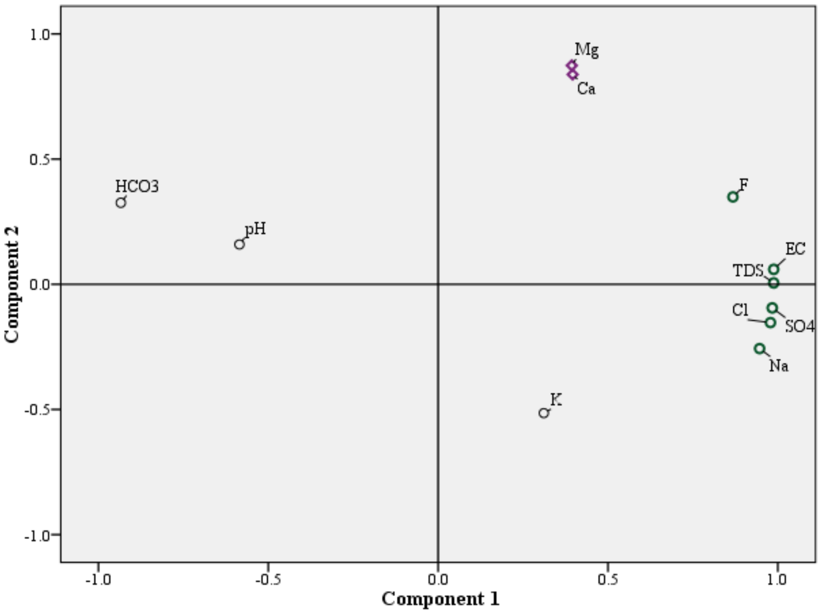
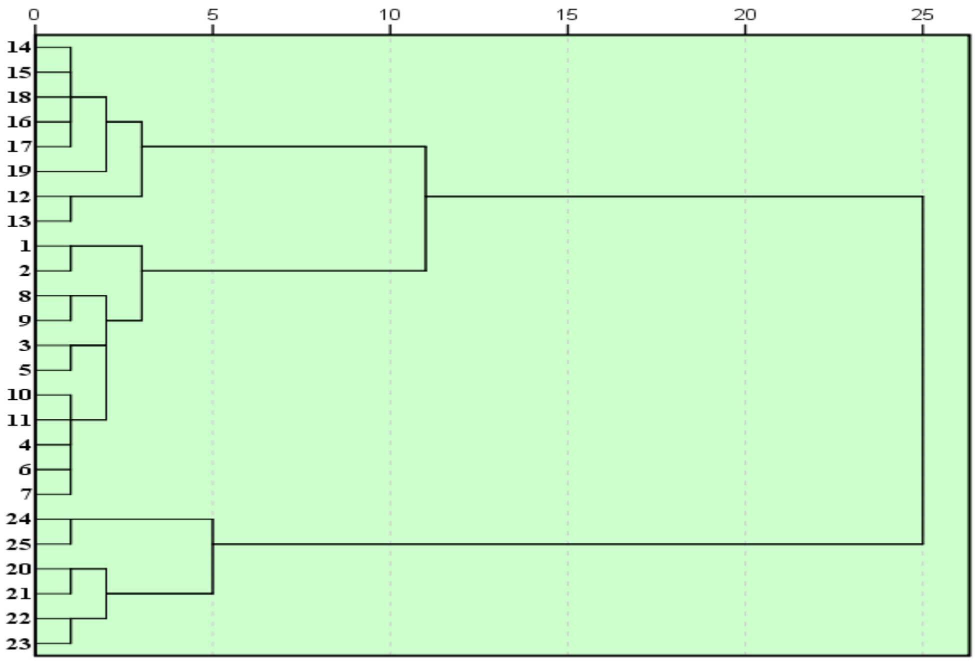


Figure 4- Principal component analysis diagram



Picture 5- The dendogram of water resources (whit ward's method and Euclidian square distances)

Cluster analysis

Cluster analysis is a powerful means to identify and select homogeneous group from crude hydrochemical data. This method encompasses different algorithm and with it the crude data can be categorized based on the level of their relation to each other. With this method, different parameters based on the maximum relation with each other can be categorized. Hence, the collection of data taken from this method has a less relation with the other collections. The results taken from–cluster analysis depend on specific measure of similarity and linking methods [17]. In the present research and based on cluster analysis usage, agglomerative hierarchical clustering with ward's linkage method, clustering algorithm and Euclidian distance were done to determine the amount of similarity. It should be noted that ward's method is a famous method which by considering data variance, evaluates the distance between clusters. Euclidian distance is also a geometrical distance in a multi dimensional space. The result of this analysis is a diagram which is called dendogram. In figure 5, the dendogram of water resources is represented. According to this dendogram, which is drowning with SPSS 19 software, the water resources are divided in to 3 main groups. In first group the resources from W_1 to W_{11}, in the second group resources from W_{11} to W_{19} and in the third group resources from W_{20} to W_{25} (Wells 20 to 25 get the most effect from Gachsaran formation) are located. Moreover, it is seen that the third has a little relation with the first and the second group. The reason for this can be mentioned in much variety in mineralogy, difference in the constructions of the existing formations in the region and over interpreting of man–made activities. The other fact which is significant is that the highest concentration of Fluoride is seen in the third, second, and the first group of water resources respectively. Due to increasing in agriculture activities and using different chemical fertilizers, the high concentration of Fluoride in the third group shows that probably the man–made activities have a special effect in increasing the concentration of Fluoride.

Types and faces of Roumeshgan plain's ground waters

Piper's triangular diagram, which is used for showing the chemical combination, is composed of two parallelogram triangles and one rhombus. The right triangle represents the percentage of equivalent anions and the left triangle represents the percentage of equivalent cations. To determine types and faces of Roumeshgan region's ground water samples exactly, these sources could be divided in to 3 zones: Zone 1 (the upstream region), zone 2 (the middle–plain region) and zone 3 (the downstream region). The type of ground water in the feeding area of this region is Bicarbonate and then during its flow, in penetrable layers based on the existing mines on the stream of movement specially gypsies formations, becomes Sulphate and in the exit of the plain and evaporative areas it becomes a kind of Chlorine. Generally, according to Piper's diagram for Roumeshgan plain's ground waters the following results have been taken:

1- The general type of this region's water is Bicarbonate, Calcic and Magnesia (Mg, Ca–HCo_3), that is, these waters have a temporary hardness.

2- In most of the cases, the cations of Calcium and Magnesium are more than Sodium and Potassium.

3- In all of the samples existing in zone 1 and some of the samples existing in zone 2. The following conditions are governing: Mg^{2+}> Na^+ + K^+> Ca^{+2}, while in samples existing in zone there this condition is governing: Na^++ K^+ > Mg^{2+}>Ca^{2+}.

4- In all of the taken samples except the two last samples the following condition is governing: Hco_3^-> $So4^{2-}$>$C1^-$ and in the two last samples the amount of Sulphate becomes more than the amount of Bicarbonate. Based on what mentioned before we come to this point that types of samples in zone 1 and 2 are Bicarbonate, Magnesia, Calcic and Sodic and in samples of zone 3 Sulphate Sodium is outstanding.

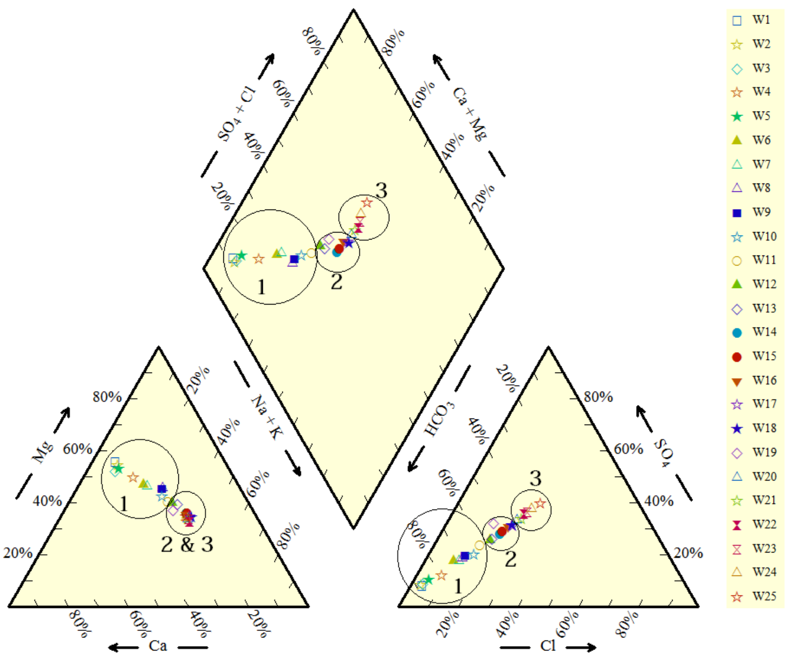


Figure 6- The Piper diagram of Roumeshgan plain's ground waters

In figure 7 scattering of anion and cation sequence in the plain is shown. In cationic sequence, three kinds of cations sequence and two kinds of anionic sequence in the plain can be viewed. In the plain's upstream regions, because of lime dolomites of Kashkan formation, it can be seen the increasing of concentration of Magnesium, Calcium and Sodium respectively. In the second kind of cationic sequence, as it closes to Gachsaran's evaporative formation the concentration of Sodium increases and this element replaces Calcium in the second rank. Finally in the third ground the increasing of durability in downstream parts of the plain and the more than before effect of Gachsaran's formation increases the concentration of Sodium again and, among the other cations, the mentioned element take the highest concentration for itself. In anionic sequence, because of the wide spreading of Carbonate formation in the basin, in most of the plain's water resources, the concentration of Bicarbonate ion is higher than the other anions. Gradually by gradual movement of water stream for upstream to downstream and sedimentation of Bicarbonate mines and also the high effect of Gachsaran's formation, the Sulphate ion replaces Bicarbonate in downstream parts of the basin. It should be noted that concentration of fluoride in downstream parts of the basin, in which type and faces of water is Sulphate Sodium , is more than the other parts of the plain significantly.

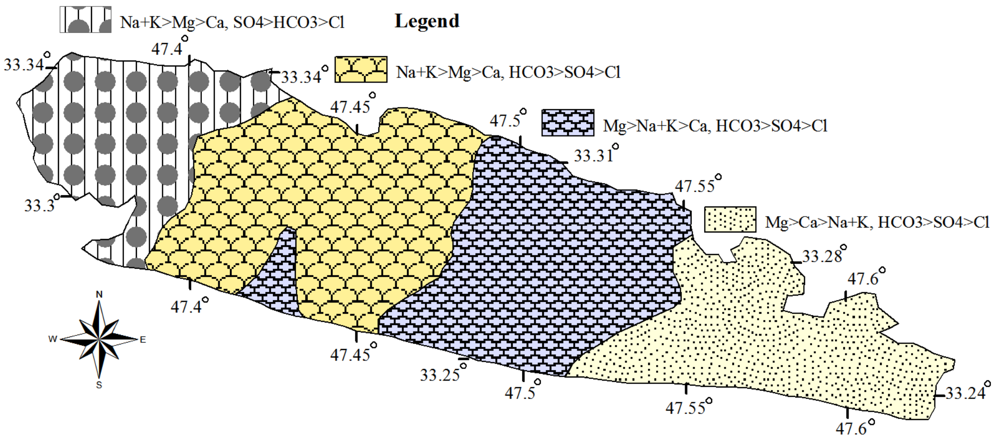


Figure 7- Special scattering of anionic and cationic sequence in Roumeshgan plain

CONCLUSION

This research is done to study Fluoride hydrochemically and also the main elements existing in water resources of Roumeshgan plain, Lorestan province. Thus, 25 samples of the region's water resources were gathered and studied. The results taken from the analysis of ground water samples shows that as we move forward from the region's upstream toward downstream, the concentration of Fluorine in the region's ground water increases.

In order to have better results and explanations, statistical methods such as correlation matrix, principal component analysis, and cluster analysis with the software SPSS were done. For better explanation of the behaviors of the dissolved elements in underground water resources, these elements were divided in to two principal components. Existing fluoride, sodium, chloride and sulphat in one group shows their close chemical behavior. The correlation coefficient of the ions existing in these waters shows that the correlation of Fluorine with Calcium, Sodium and Sulphate is positive and it is negative with Bicarbonate and pH.

The cluster analysis divided the water resources in to 3 classes and it also showed that the water resources in downstream are quite different from the rest of water resources of the region about their combinations. This is due to the high geological varieties (the existence of Carbonate and Sulphate formation in this region) and also agriculture and man–made activities in this basin. Piper's diagram also shows that type and faces of the upstream samples are bicarbonate, magnesium, calcic and soguicand the downstream samples are sulphate sodic.

In addition to, results showed that flouride concentration in the region's water (2 to 8-fold) more than normal range in in the region's water the level found in the water with fluoride concentration normal range (0.5 mg /L). These findings provide a basis for further studies. Therefore, further study is recommended for future; 1-Evaluation of serum and urine fluoride concentration of animals and humans that use in the region's water. 2-The relationship between flouride concentration and diseases related to elevation of flouride concentration such as fluorosis in animals and humans.

REFERENCES

[1] M Shams; R Nabizadeh Nodehi; M Alimohammadi; AH Mahvi, *World Appl Sci J*, **2009**; 7(12): 1516-20.
[2[MC Undu; B Mandal; GC Hazra, *Sci Total Environ*, **2009**; 407(8): 2771-82.
[3] M Jalai; Z Khanlari, *Environ Geology*, **2008**; 54: 87-93.
[4] M Jalai, *Environ Geology*, **2005**; 47: 763-72.
[5] MN Tijani, *Appl Geochem*, **2004**; 19: 1355-65.
[6] M Jalali, *Environ Geology*, **2009**; 56: 1479-88.
[7] R Anders; GO Mendez; K Futa; WR Danskin, *Ground Water*, **2014**; 52(5): 756-68.
[8] EA Murphy; GB Post; BT Buckley; RL Lippincott; MG Robson, *Annu Rev Public Health*, **2012**; 33: 209-24.
[9] L Kirkeskov; E Kristiansen; H Bøggild; F von Platen-Hallermund; H Sckerl; A Carlsen A. et al,. Community *Dent Oral Epidemiol*, **2010**; 38(3): 206-12.
[10] MM Jingarwar; A Pathak; NK Bajwa; HS Sidhu, *J Clin Diagn Res*, **2014**; 8(12): ZC31-4.
[11] K Luo; Y Liu; H Li H; *Environ Geochem Health*, **2014**; 34(1): 89-101.
[12] Z Meng; B Zhang, *Mutat Res* **1997**; 393(3): 283-8.
[13] KG Rawson; MM Ditmyer, *J Investig Clin Dent*, **2013**; 4(1): 49-53.
[14] OY Gou; T Wang; R Ma, *Northern ChinaJ Geochem Explor*, **2007**; 93: 1-12.
[15] SH Frisbie; EJ Mitchell; H Dustin; DM Maynard; B Sarkar, *Environ Health Perspect*,.**2012**; 120(6): 775-8.
[16] I Matiatos; A Alexopoulos; A Godelitsas, *Sci Total Environ*, **2014**; 1: 476-7.
[17] AE De Andrade; H Araujo; IH Palacio; R Souza; LMJ Guerreiro LMJ, *Environ Res*, **2008**; 106: 170-7.
[18] F El Yaouti; A El Manduor; D Khattaj; J Benavente; O Kaofmann, *Appl Geochem*, **2009**; 24: 16-31.
[19] A Salifu; B Petrusevski; K Ghebremichael; R Buamah; G Amy, *J Contam Hydrol*, **2012**; 140-141: 34-44.
[20] MC Sarraguça; AV Cruz; HR Amaral; PC Costa; JA Lopes, *Anal Bioanal Chem*, **2011**; 399(6): 2137-47.
[21] CR Paltineanu; N Tanasescu; E Chitu; F Mihailescu F. Int Agro, **2007**; 21: 81-93
[22] I Mohamad; F Othman; F Othman; AI Ibrahim; ME Alaa-Eldin; RM Yunus, *Environ Monit Assess*, **2015**; 187(1): 4182
[23] S Chaudhuri; S Ale, *J Environ Qual* **2014**; 43(4): 1404-16.
[24] CE Moya; M Raiber; M Taulis; ME Cox ME, *Sci Total Environ* **2015**; 508: 411-26.
[25] V Gvozdić; L Cačić; J Brana; D Puntarić; D Vidosavljević, Medicinski glasnik (Zenica), **2012**; 9(1): 91-6.
[26] DL Parkhurst; CAJ Appelo, *Water Resour Invest Rep*, **1999**; 99-4259.
[27] MAN Armienta; N Segovia, *Environ Geochem Health*, **2008**; 30: 345-53.
[28] A Joshi; G Seth, *J Environ Sci Eng*, **2011**; 53(2): 151-6.