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Assessment of Anthropogenic Activities on the Water Quality of Froumad Plain Based on Qualitative Indicators

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Abstract

Tested water samples taken from the ophiolite region of Forumad show that most of the concentrations of calcium, magnesium, sodium, sulfate, potassium, bicarbonate, and nitrate elements are in the standard range. Hydrogeochemical studies of the water samples show the existence of magnesium sulfate, chloromagnesium, and chlorosodium. Results of measuring the physical properties of the water shows that the above values were lower than the 1053 standard of Iran and water hardness is higher than the standard in only some cases. Water pH in the studied region is within the alkaline range. Assessing the distribution of heavy metals through statistical methods (Pearson coefficient and cluster graph), two different origins (anthropogenic and lithological origins) have been identified that are responsible for the entry of heavy metals into the water resources of the studied region. The anthropogenic origin of the distribution of heavy metals in the region is due to local mining of the chromite and ophiolitic rocks and the lithological origin is a result of local mining of conglomerate and volcanic rocks. Evaluating the metal index of MI and HPI shows the water contamination by heavy metals. The zoning map shows that the metallic contamination surrounding Forumad village is low and reaches its maximum amount around the chromite Forumad mine. The qualitative index of GQI (non-metallic cations and anions including calcium, sodium, chlorine, magnesium, sulfate, and dissolved solids in water) shows that the water quality is within the acceptable range. Based on the zoning map, the water quality GQI index is higher in the downstream around Forumad village.

Keywords: *Water resource contamination, metal index, GQI index, ophiolite, zoning map, Forumad*

1. Introduction

Water is a basic element and vital factor for human survival and important usages of water include agricultural activities, industrial activities, and drinking. Unfortunately, today different human activities are causing decreased water quality levels and subsequent contamination. Assessing the quality of underground water provides a clear vision for managers and experts to evaluate the quality process and the risk of water contamination [1]. The increase and accumulation of heavy metals in water resources are some of the factors that humans are facing today [2]. Also, the pollutions caused by the geological formations, mineral springs, and saline water resources can lead to the decrease of water quality levels and its contamination [3]. In the Forumad region, mining activities are being done on the ophiolitic and chromite rocks on a large scale. Ophiolitic rocks contain a large variety of heavy metals and mining activities on these rocks can be harmful for the region if they are not done according to environmental principles. Water and soil contamination and various diseases are examples of such harms. Chromium is a heavy metal that is abundantly present in these rocks [4] and if this element enters into the water sources of this region as chromium VI, it can cause diseases such as nose mucous membrane ulcers, bronchitis, dryness and sensitiveness of the skin, and skin and lung cancer [5]. Chromium is a heavy metal that is abundantly present in these rocks [4] and if this element enters into the water sources of this region as chromium VI, it can cause diseases such as nose mucous membrane ulcers, bronchitis, dryness and sensitiveness of the skin, and skin and lung cancer [5]. Genetic alterations and birth defects are other harmful effects of this element [6]. In the present study, the water quality in the ophiolite region of Forumad has been evaluated to determine possible contamination and the effects of mining activities on the water quality.

2. Geology

Ophiolites are a set of mafic and ultramafic rocks that are well-ordered or layer-by-layer and have been mixed through tectonic stresses [7]. In 1927, Stein Mein applied the term ophiolite for a set of periodite, gabbro, diabase, split and foraminifera sediments such as radiolarian, marine clays, and limestone for deep waters [8]. The studied area is located in the southwestern zone of the mélange ophiolite in the city of Sabzevar (northwest of Sabzevar). The Sabzevar ophiolitic set is located on the northern edge of the sub-continent in east-central Iran and its age is attributed to

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the Mesozoic period [9]. The Sabzevar ophiolitic zone's characteristic set is calc-alkaline magma [9]. Sabzevar ophiolites are formed in an area behind the arc and near a subduction trench [10]. Rock units of the area include serpentinite, harzburgite, dunite, chromite, layered gabbros, and basalt that have formed the ophiolitic units, and are pyroclastic units and quaternary sediments (Fig. 2). The Forumad Chromite mine is one of the largest and most important chromite mines of the country, which is more than 3 km long and 700 m wide. In the Forumad Chromite mine, chromite is in the form of discontinuous and lenses layers. The type of chromites found in this region is podiform chromitites [11] and in some cases, the thickness of these lenses is up to 5 meters. Extraction of minerals in this mine is done by open pit mining. Wastes from mining activities are seen in the mine range and are in a large scale (Fig. 1).

Fig 1: A view of the minerals harvest site and waste dump of the Forumad Chromite Mine

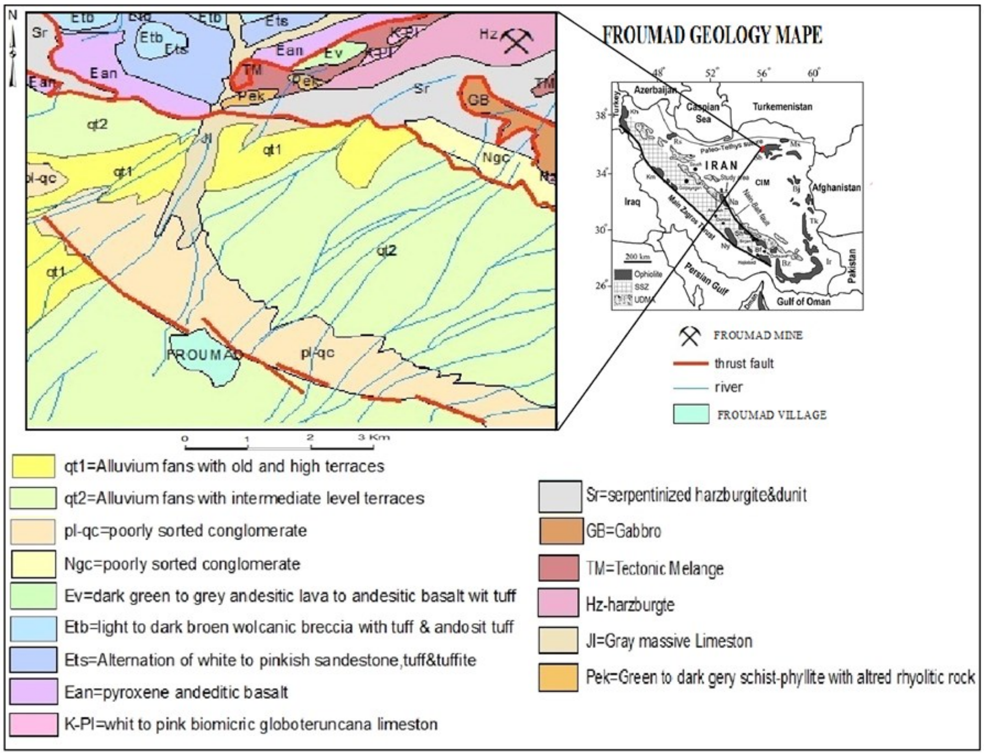

Fig 2: Forumad 1:100000 geological map (after [12])

3. Materials and Methods

The sampling process was done on May 2014 in order to assess the quality of underground water and to determine heavy metal contamination in the Forumad plain. The physical parameters such as total dissolved solids (TDS), electrical conductivity (Ec), and pH were measured at the site. To determine the cation amounts and heavy element concentrations, the samples were transferred to the Iran Mineral Processing Research Center to be analyzedby the inductively coupled plasma optical emission spectrometry (ICP-OES) method. The titration method was used to measure the hardness, alkalinity, and anions of the water. The HPI and MI index was used to process the data and evaluate the heavy metal contamination. The GQI index was used to determine the water quality and examine the area and zoning of the drinking water quality. Also, interpolation was applied in the GIS area to produce raster maps.

4. Discussion

4.1. Evaluation of the physical properties of water

The water quality can vary in different locations due to the traveled distance and dissolution of different materials [13]. In order to evaluate the characteristics of the water resources of the region in the Forumad plain, its physical characteristics were studied. According to the evaluations, pH amount is within the slightly alkaline range (8.06 to 9.7). Samples near the mine (for example sample F35) have a higher pH than other samples. The concentration of dissolved materials in the water (TDS) has changed from 343 to 650 ppm in the samples and this concentration amount is lower than the 1053 standard of Iran. Sample F49 has the highest amount of TDS due to the influence of limestone unites and waste dumps. Electrical conductivity is another important factor that indicates the mobility of the elements in the water and region lithology is one of the factors that impacts Ec. The range of electrical conductivity changes is varied in the studied samples (493 to 930 µSiemens/cm). The obtained values are directly related to the dissolved materials in the water, so the value of Ec in sample F49 is the highest because the region it was taken from contains the highest level of dissolved materials. The measured hardness values indicate the changing rate of hardness from 116 to 450 $CaCo_3$. According to the 1053 standard of Iran, the highest hardness amount is related to sample F35 (Fig. 3).

4.2. Examining the concentration amounts of cations and non-metallic anions

The comparison of calcium, magnesium, sodium, sulfate, potassium, nitrate, and bicarbonate values in the studied samples with WHO standards shows that the calcium amount varies from 7 to 43 mg per liter, magnesium amount from 29 to 97.3 mg/l, sodium amount from 27 to 75 mg/l, potassium amount from 2 to 13.9 mg/l, sulfate concentration amount from 15 to 80 mg/l, nitrate from 2 to 5 mg/l, bicarbonate from 90 to 280 mg/l, and chlorine concentration from 16 to 190 mg/l (Table 1).

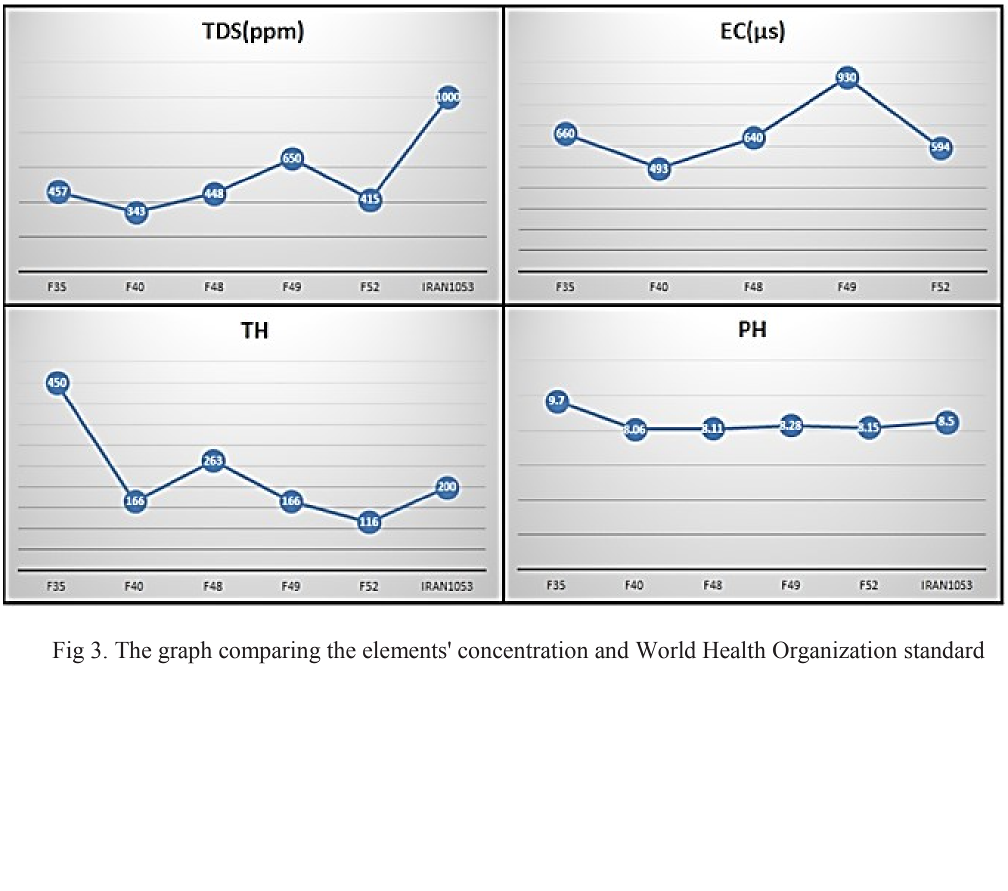

Fig 3. The graph comparing the elements' concentration and World Health Organization standard

These amounts and when compared with WHO standards indicate the low concentrations of anions and cations in the area. Although the concentration of magnesium in sample F35 is higher than the standard level of WHO due to the effects of harzburgite unites (Fig. 4). Further evaluation of cations and anions and their comparison in the Piper diagram showed that the majority of the samples are in the range of sulfate magnesium type (Fig. 5). Ophiolitic units lead to the enrichment of sulfate magnesium values in the samples and to be within this range. Sample F35 is drawn to the chloromagnesium range due to the high amounts of magnesium and chlorine. Also, sample F52 is determined by the chlorosodium type. This is probably because of water recharge from conglomerate units (Fig. 5). Evaluating the samples in the Stephan graph also confirms that the studied samples are in the sulfate magnesium, chloromagnesium, and chlorosodium groups due to the type and facies of the water (Fig. 6).

Studying the development cycle of the studied water of the region through the Durov diagram indicates that these samples go through a hydrochemical development cycle from chloromagnesium to sulfate magnesium (Fig. 7).

4.3 studying the concentration of heavy elements

Comparing the heavy metal values in the taken samples with WHO standards indicates that the concentration of most of the above elements is lower than the WHO standard concentration range. The concentrations of aluminum, iron, chromium, and nickel elements in sample F49,the concentration of iron in sample F35, and the concentration of chromium in sample F52 are higher than the standard and have been enriched (Table 2).

Table 1. Concentration value of the non-metallic cations and anions in the water (values are according to ppm)

Sample	Ca	Mg	Na	K	NO3	So4	Cl	Hco3
F35	7.6	97.3	29	13.9	4	15	190	90
F40	14	29.7	49	4.6	5	75	39	150
F48	43	44.6	75	2.3	2	80	44	280
F49	35	33.1	27	6.8	<5	31	16	150
F52	9	24.9	102	1.2	<5	57	60	150
WHO	100	50	200	*	45	450	250	*

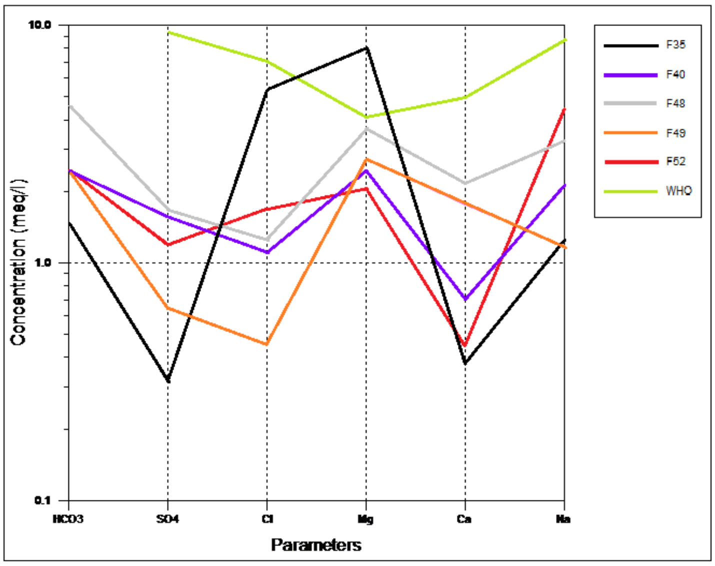

Fig 4. Schoeller diagram for classification of water in Froumad plain

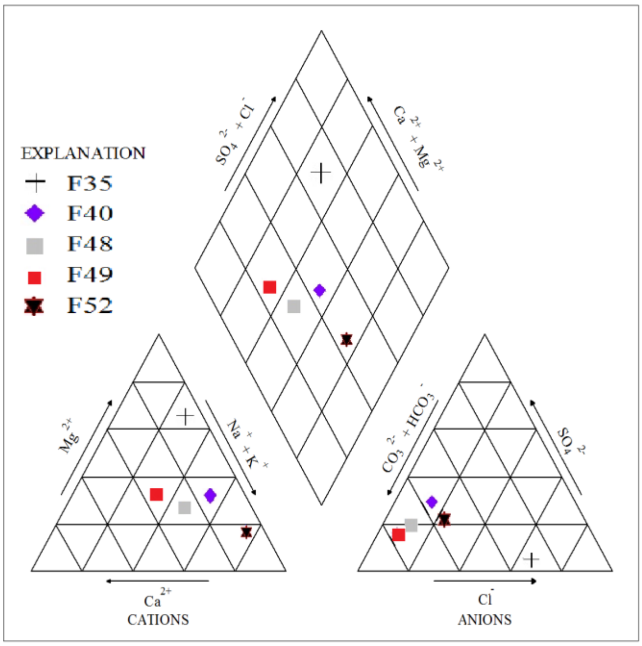

Fig 5. Piper diagram indicating the type and facies of the taken samples

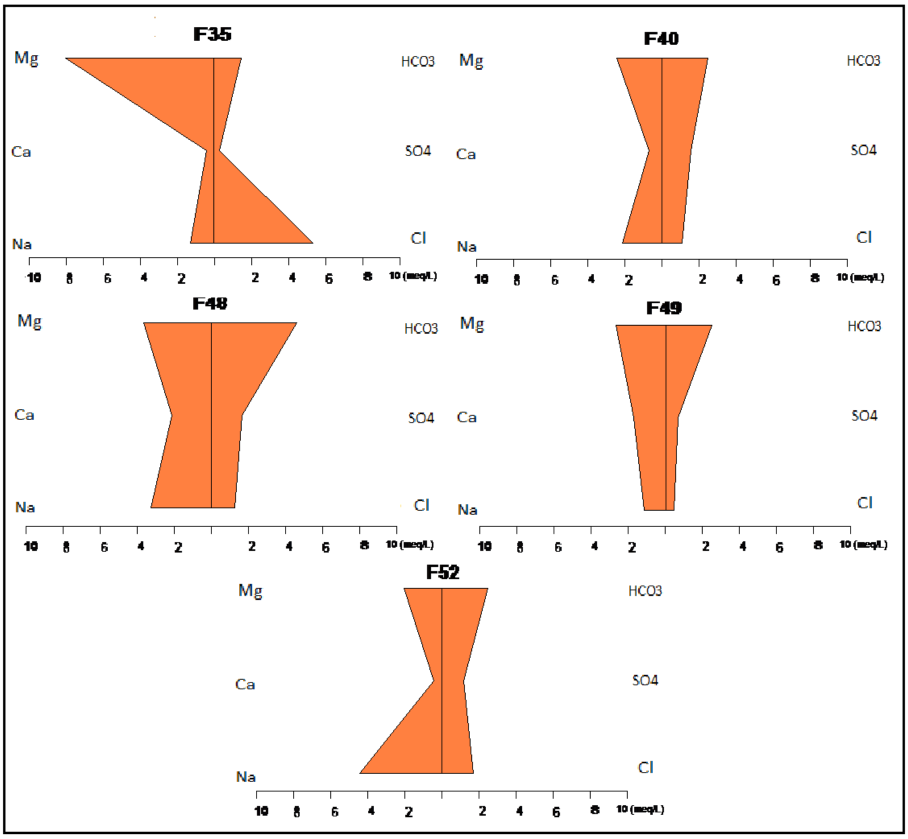

Fig 6. Stiff diagram indicating the type and facies of the taken samples

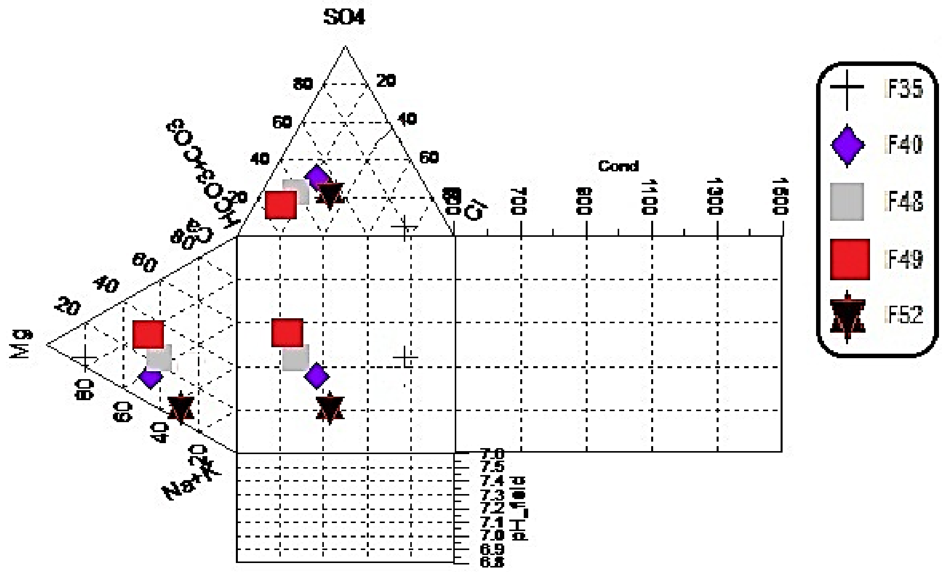

Fig 7. Durov diagram of the water samples of the studied area

Table 2. The values of the samples' elements (values are according to the ppm)

sample	Al	B	Ba	Cd	Cr	Fe	Mn	Ni	Pb	Sr	Zn
F35	0.15	<0.05	0.06	<0.02	0.02	0.5	<0.02	<0.02	<0.05	0.03	<0.02
F40	0.06	0.14	0.04	<0.02	0.06	0.12	<0.02	<0.02	<0.05	0.48	<0.02
F48	<0.05	0.23	0.1	<0.02	0.03	<0.05	<0.02	<0.02	<0.05	0.41	<0.02
F49	3.42	0.16	0.03	<0.02	0.1	5.89	0.2	0.14	<0.05	0.24	<0.02
F52	<0.05	0.11	0.03	<0.02	0.11	<0.05	<0.02	<0.02	<0.05	0.2	<0.02
WHO	0.2	0.3	0.3	0.0003	0.005	0.3	0.4	0.07	0.01	*	3

5. Studying the concentration of heavy elements

5.1. Pearson coefficient

The relation and correlation of heavy metals in the studied samples was studied by calculating the Pearson coefficient (Table 3). According to the conducted examinations and obtained values from the Pearson table, there is a clear and positive correlation between aluminum with: iron ($r=0.99$, $p<0.01$), manganese ($r=1.000$, $p<0.01$) and nickel ($r=1.000$, $p<0.01$). Also, there is a positive correlation between iron with nickel and manganese elements. Chemically, iron is very active and has a similar chemical behavior with that of nickel [14]. There is also a relation between chromium with iron, aluminum, manganese, and nickel elements on a weaker level. This suggests a common and identical origin for these elements. On the other hand, examining the relation and correlation of heavy metals between: chromium with magnesium, iron with aluminum, and potassium and chromium show a negative correlation between these elements. This indicates different origins for magnesium and potassium elements in the water resources of the region. Moreover, this correlation between Ec with aluminum, iron, manganese and nickel is positive and strong, which is not unexpected with respect to the area lithology.

5.2. Diagram of cluster analysis (CA)

Cluster analysis classifies the elements based on their similarity or difference. It also better shows the correlation between the elements. According to the obtained diagram from cluster analysis, two main clusters exist. The first main cluster has been divided into two sub-clusters based on the dependence level of the metals. The first subcluster contains elements such as manganese, nickel, aluminum, and iron where manganese, nickel, aluminum and iron show a strong dependence. The second subcluster also contains the element chromium. The second main cluster is also divided into two-sub clusters. The first sub-cluster contains magnesium and potassium, and the second one contains the element cadmium.

Table 3. Matrix of correlation values (r) for chemical parameters and heavy metals in the water samples of the Forumad plain

Correlations

	Al	Cr	Fe	Mg	Mn	Ni	PH	Ec	k
Al	1								
Cr	.484	1							
Fe	.999**	.460	1						
Mg	-.216	-.748	-.174	1					
Mn	1.000**	.498	.997**	-.242	1				
Ni	1.000**	.498	.997**	-.242	1.000**	1			
PH	-.117	-.548	-.073	.961**	-.144	-.144	1		
Ec	.923*	.306	.928*	.034	.918*	.918*	.101	1	
k	.143	-.502	.187	.878	.115	.115	.924*	.258	1

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

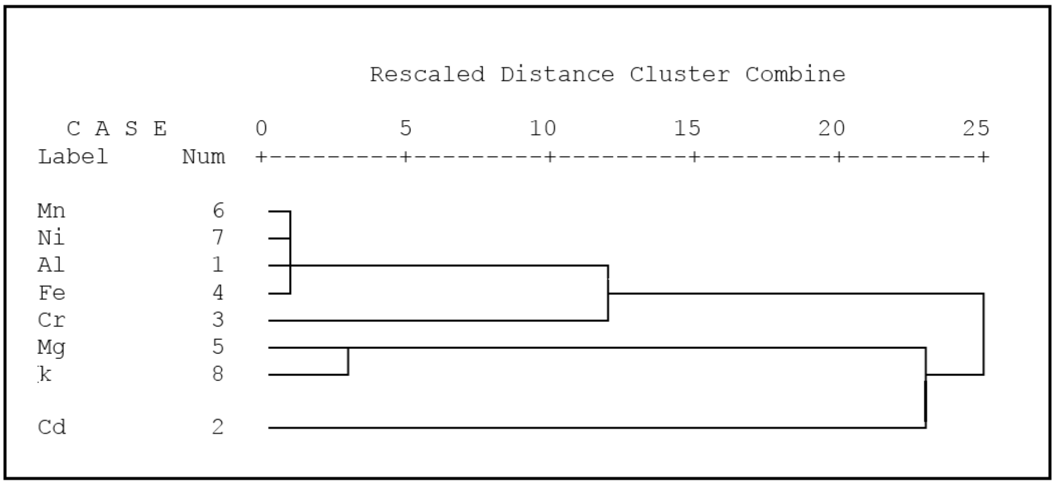

Fig 8. Hierarchical cluster diagram obtained from the cluster analysis of heavy metals in the water samples of the studied area

The obtained results from the cluster analysis diagram are consistent with the obtained results from the Pearson coefficient. According to the above diagram, at least two different origins of entry of these elements into the water resources of the studied region are suggested: 1) an anthropogenic origin that is associated with ophiolitic rocks and mining activities of chromite rocks for elements such as chromium, manganese, nickel, aluminum, and iron, and 2) a lithological origin that is associated with the conglomerate and volcanic rocks for elements such as magnesium, potassium, and cadmium (Fig. 8).

6. Examining the drinking water quality of the studied area

In order to assess the water quality level of the studied area, the GQI index and two metal indexes of MI and HPI have been used. To do this, the WHO standard has been applied.

6.1. Water quality assessment using the GQI index and GIS (Geographical Information System)

In order to investigate the spatial distribution and zoning of the drinking water quality, the GQI index has been used [15]. To do this, chemical parameters of calcium, magnesium, sodium, chloride, sulfate, and total amount of dissolved solid materials have been used. The numerical values of these parameters can be linked to WHO standards. To calculate the GQI index, first the point dataset of the arithmetic average of the above said six chemical parameters was interpolation in the ArcGIS 10 environment through Inverse Distance Weighting (IDW), and then the raster map of concentration was prepared. Then, so that the different data could have a common scale and criteria, using equation 1, concentrations of each pixel (Ci) in the raster maps that were created in the previous step were correlated with the WHO standard of that variable (CWHO).

Equation (1) $C = \frac{Ci - C_{WHO}}{Ci + C_{WHO}}$

The result of this scale unification is the production of six new maps in which their pixels' value have changed between (-1) and (1) Next, the ranking map was determined. In the above map, concentrations were graded from 1 to 10 and to do so, equation 2 was used [15].

Equation (2) $r = (0.5 \times (C * C) + 4.5 \times C + 5$

In the above ranking map, rank 1 indicates good quality of underground water, and rank 10 indicates low quality of water. In addition, in order to show the overall quality of the region's underground water according to the WHO standard, the GQI water quality index was used. To do so, equation 3 was used and the ranked map of GQI was drawn.

Equation (3) $GQI = 100 - [\frac{r_1 w_1 + r_2 w_2 + \cdots + r_6 w_6}{6}]$

In this equation, r is the rank of each pixel and w is the relative weight of each of the parameters. To calculate WQI, the weighted average of different parameters has been computed where in the parameters with greater values (higher difference with standard value) have a relative weight, and thus are more effective [16]. The relative weight of each parameter depends on their average ranking (r) and the relative weight was obtained from equation 4.

Equation (4) $w = \text{mean } r + 2$

Based on the zoning maps for each variable, the concentration of chloride and magnesium was low around the Froumad village and increased towards the chromite mine. This can be probably due to the impact of ophiolitic units and mining on the chromite rocks of the region. The sulfate and sodium concentrations were the lowest in the upstream area (around the chromite mine of Forumad) and its concentration increases towards Forumad village. Travelling by water and the influence of lithological units has led to the existence of sulfate and sodium concentrations. The calcium element is low near the chromite mine and Forumad village. Proximity to the carbonate sedimentary units and its impact on the water resources have resulted in the high value of calcium and hardness in this part of the region (northwest region). Moreover, the influence of these units has also led to the high concentration of TDS in this part compared to around Forumad village and the chromite mine of Forumad (Fig. 9). According to the calculations, the value of the GQI quality index in the Forumad ophiolite region varies from 78.62 to 86.76 in these samples. According to Table 4, the underground water of the studied region is in the acceptable quality rank according to the drinking water standards. The zoning map of the water quality for the studied region shows that the water quality has increased around the Forumad village in the downstream of the region (Fig. 10).

6.2. Examining the water quality using the Metal Index

Metal index (MI) is a measure for showing the effects of heavy metal contamination on water quality and human health [17]. This index was expressed through equation 5.

Equation (5) $MI = \sum_{I}^{N} \frac{ci}{(MAC)i}$

Ci is the concentration of each element in the water, and i (MAC) is the number of the metal element. The maximum allowable limit of concentration for the intended element in the above equation is 1, and if MI>1 , then the water is not suitable for drinking. Based on the evaluation of the MI, the above examples (Fig. 11) show that the water in the studied region is contaminated with heavy metals. The highest level of contamination is found in sample F49. Water resources of the studied area with the total high value of the MI (MI= 34.01) are in the contaminated area. In the zoning map, the metal contamination of the MI is visible in various places (Fig. 13). According to the zoning map, metal contamination has the highest value in the northern part of the area and near the chromite mine.

6.3. Examining the water quality using the heavy metal pollution index

The heavy metal pollution index (HPI) was referred to by by Mohan, et al. [18]. This index, which is based on the concentration of heavy metals is calculated by equation 6.

Equation (6) $HPI = \frac{\sum W i q_i}{\sum W i}$

The weight ratio of Wi is the i-th component and is calculated with the standard inverse: is Wi=1/Si and qi is the quality rate of the i-th component that is calculated by equation 7.

Equation (7) $qi = \Sigma(Mi(-))/(Si) \times 100$

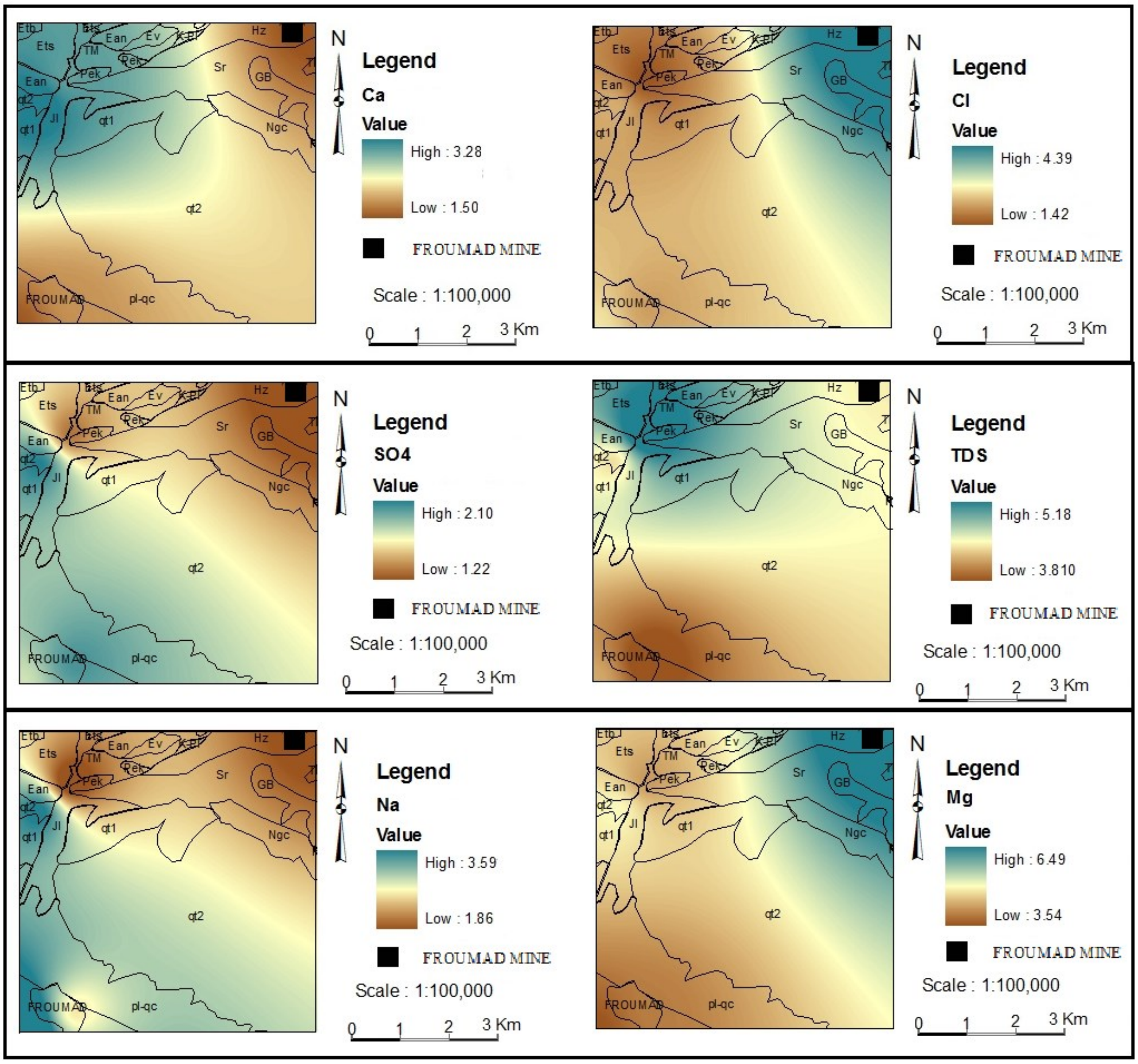

Fig 9. The zoning map for the evaluated variables (the map units are according to Figure 2)

Table 4: Water quality based on the GQI [15]

low	Weak	Average	Acceptable	reasonable	Water quality
0-25	26-50	51-70	71-90	91-100	GQI

In the above equation, Mi is the concentration of the i-th component and Si is the standard value of the i-th component. The (-) sign indicates the difference numerical value of two quantities that can be overlooking this algebra sign [19]. If the HPI>100, the water is contaminated with heavy metals, if the HPI=100 the water is on the verge of being polluted with heavy metals, and if the HPI<100 the water is not contaminated with heavy metals. Based on the evaluation of the HPI, all the samples have been contaminated with heavy metals (Fiq. 12). The highest range of pollution is related to sample F49. Calculating the total HPI (HPI=3401) for the studied region, the water resources are contaminated according to the metal pollution index of the HPI. Metal pollution of the HPI can be seen in various places of the zoning map. Based on the zoning map, the HPI pollution also has the highest enrichment in the northern part of the region and near the chromite mine (Fig. 13).

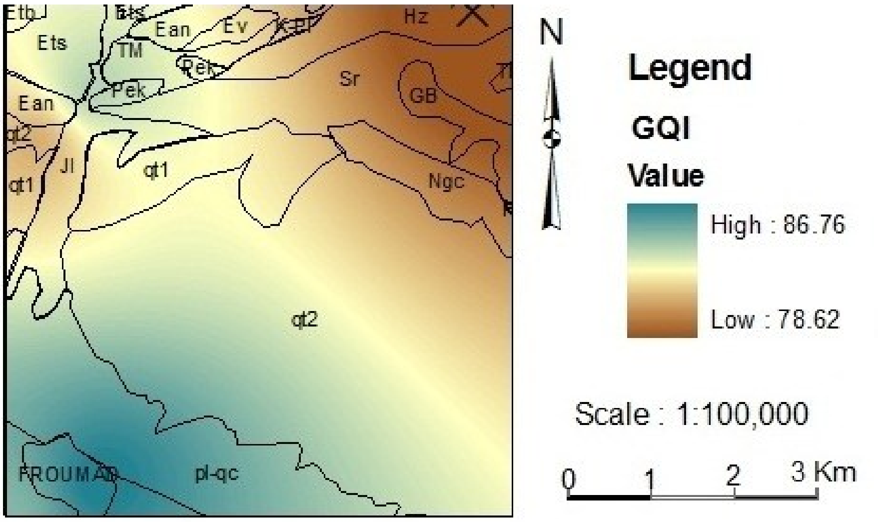

Fig 10. Zoning map of the GQI index (the map units are according to Figure 2)

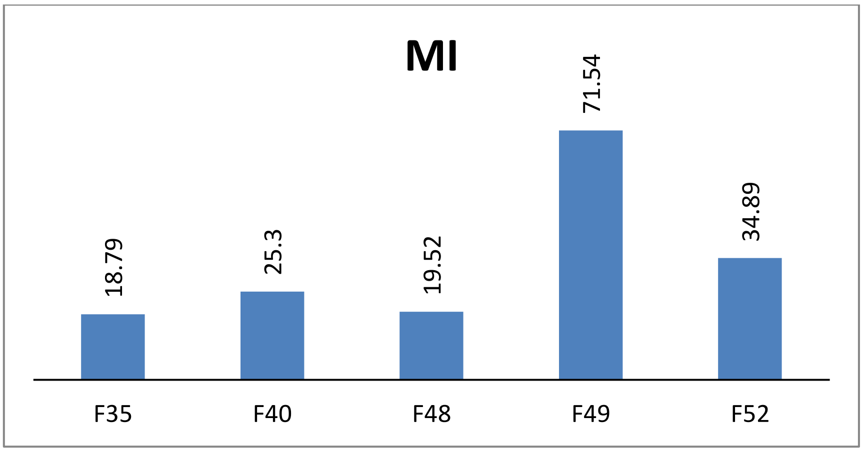

Fig 11. The diagram of calculated metal index for water samples from Forumad plain

7. Conclusion

Studying the physical properties of water shows that pH is at the slightly alkaline range. Soluble solid amounts and hardness in the studied waters are below the standard of Iran. The concentrations of calcium, magnesium, sodium, sulfate, potassium, nitrate, and bicarbonate show the depletion of samples compared to the WHO standard in most of the samples. According to the Piper and Stiff classifications, the samples fall within three classification types: sulfate magnesium, chloromagnesium and chlorosodium. The Durov diagram shows that the hydrogeochemical development cycle of water resources in the studied area is from chloromagnesium to sulfate magnesium facies. Investigating the correlation relations between heavy metals in the region shows that the concentration of chromium, manganese, nickel, aluminum, and iron elements are related to anthropogenic origins (ophiolite rocks and mining activities on the chromite rocks) of the region and the concentrations of magnesium, potassium, and cadmium are related to lithological origins (conglomerate and volcanic rocks). Comparing the concentrations of heavy metal with the WHO standard shows that the concentrations of elements such as iron, chromium, and nickel are higher than the standard in some samples and are contaminated. Evaluating the MI and HPI metal indexes shows that water resources are contaminated with heavy metals in the region. The GQI index, which is calculated on the basis of non-metallic anions and cations, shows that the water quality with values from 78.62 to 86.76 is within the acceptable range in the region.

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