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Multivariate statistical evaluation of ground water quality

Salar Khaiiatali[1], Arezoo Hassan Noori[2], Reza Masoudiaghdam mehrabad[3]

[1]Departmenr of Civil Engineering, Azarbaijan Shahid Madani University, Tabriz, Iran.

[2]Departmenr of Chemistry, Kerman Branch, Islamic Azad University, Kerman, Iran.

[3]Departmenr of Geosciences, Kerman Branch, Islamic Azad University, Science and Research Branch,Tehran, Iran.

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ABSTRACT

In this study, the statistical results for the underground water of Qaem Shahr plain were evaluated. This evaluation is particularly important due to the main concerns of drinking water, irrigation, and sustainable agriculture in the region. Farmers rely on underground water as a supplement to surface water for irrigating their fields. Given the significance of this issue, the primary objective of this research is to study the water quality in the case study. Multivariate statistical analysis has become increasingly popular for quantifying the relationship between water quality parameters and processes in groundwater aquifers. In this particular study, data were collected from water samples taken from 22 wells in the years 1999 and 2011. By analyzing these samples, we sought to identify the elements that have a significant impact on the quality of the unlimited coastal aquifer of Qaem Shahr plain. Our investigation focused on the wells in use and explored the influential processes that affect water quality in the aquifer.

The water samples were analyzed using multivariate statistical analysis, which involved measuring the concentration of cations and main anions, as well as parameters such as EC, T.D.S, pH, and hardness. For this study, we utilized multivariate statistical methods, including factor analysis (FA), and water quality indicators such as WHO and CCME classifications.

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1. Introduction

Water is indeed an essential resource for human existence and vital for the survival of all living creatures in the ecosystem. In its purest form, water is not readily available in nature and often contains varying amounts of suspended substances. It's important to note that certain salts in water are actually beneficial to our health, but an excess of these salts can pose risks to human well-being. Therefore, the availability of clean drinking water is crucial for maintaining a healthy society. As a result, water quality issues have become increasingly complex and diverse, warranting immediate global attention and action [1]. Over the past decade, the environment has been greatly affected by the unprecedented growth in population, rapid urbanization, and the expansion of agricultural activities. This has led to the gradual and continuous destruction of resources, especially surface water [2]. One of the most crucial factors in modern water management is the quality of underground water, given its sources. Different methods are used to evaluate water quality in each region. Include the hydrogeochemical methods [3] [4] [5], geophysical investigations [6], and remote sensing with GIS [7] [8] [9] [10]. Among all these, the hydrogeochemical method is one of the main uses.

Water quality standards are essential for safeguarding the various designated uses of water, each with its unique requirements. Take, for instance, the disparity between the standards for drinking water and agricultural use. Drinking water necessitates a higher standard compared to water used for agricultural purposes. To specify the quality of water, several organizations and indexes exist. The World Health Organization

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(WHO) is a specialized United Nations agency responsible for international public health with a team of 8,000 experts, including the world's leading public health experts. [11]. The water quality index (WQI) is similar to the trophic state index (TSI), both of which were developed for the national assessment of surface waters.

The Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) provides a flexible index template adaptable to the site specificity and treatment considerations of drinking source water. The CCME WQI is an objective-based index that compares measured water quality values with guidelines to create a score from 0, representing the worst quality, to 100, representing the best quality. [12]. The Bureau of Indian Standards (BIS) has specified drinking water quality standards in India to provide safe drinking water to the public. [13]. Also, underground water is a vital source of fresh water in urban and rural areas of the world. However, its indirect abstraction and rapidly increasing pollution pose a serious threat to sustainable water supply worldwide and need to be assessed. [14]. The summary of the indexed used in this work is shown in Table1.2.

Table 1. Water quality indexes used in this study

Parameters	Max value	Min value	WHO Median Value	CCME Median Value
Magnesium (mg/l)	1000	0.1	70	NA
Calcium (mg/l)	500	30	150	1000
Ph maximum	10.5	8	8.5	8.5
Ph minimum	7	5	6.5	6.8
Sodium (mg/l)	400	100	200	200
Sulfate (mg/l)	800	50	250	500
Potassium (mg/l)	50	0.2	12	NA
Total dissolved solids (tds)	2500	200	1000	500
Electrical conductivity	NA	NA	500	NA
Chlorine (mg/l)	5	0.1	1	100

*NA: the value is not available.

Table 2. Unit weightage of parameters based on the Indian drinking water standard (IS: 10500, 1993)

Parameters	Highest permitted Value for water (SI)	Unit weightage (WI)
PH	7.5	0.02808068
TURBIDITY	5	0.04212103
TDS	500	0.00042121
TOT. HARD	300	0.00070201
CHLORIDE	250	0.00084242
NITRATE	45	0.00468011
FLURIDE	1	0.21060514
FE	0.3	0.70201716
MG++	30	0.00702017
CA++	75	0.00280807

2. Study area

This studied area is limited to the Caspian Sea from the north and the Alborz mountain range from the south (Fig 1). The study area is located in a geographic location of 52°35'E to 52°23'E longitude and 35°44'N to 36°47'N latitude in Mazandaran province. The total area of the study area is approximately 3348.1 KM ^{2}, of which 935.5 KM ^{2} is plain and the rest (2412.6 KM ^{2}) is the northern slopes of the Alborz mountains [15]. According to the geomorphology and the state and type of geological formations, the watershed is also the subject of the state of the region and therefore the water level curves of the underground water level follow a certain order. Accordingly, unit hydrograph curves are influenced by surface morphology, recharge area (southern areas) and unconfined aquifer drainage (northern and coastal areas). Since the average level of the Caspian Sea is minus 27 meters lower than the level of the open sea, the figures of the underground water level curve in the studied area are between 60 and -25 meters and decrease from south to north. The general direction of underground water flow in the region is from south to north and northeast. The climatic conditions governing the Qaem Shahr plain are influenced by the sea humidity and the mountain climate. Based on this, the average annual rainfall in the studied area is about 730 mm, the maximum of which is in the months of November and December and the lowest in the months of June and July. The average annual air temperature of Qaem Shahr is 17.2 degrees Celsius, August and January are the hottest and coldest months of the year, respectively.

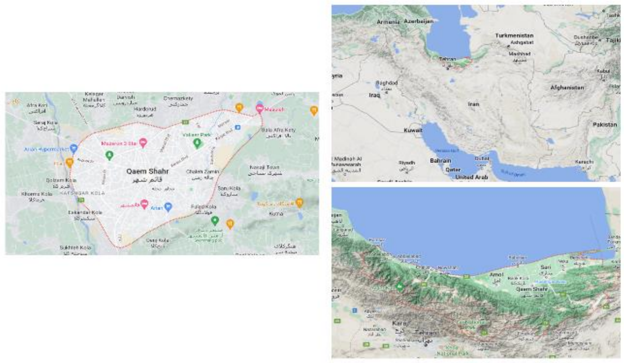

Fig 1. Location map of the study area.

3. Material and methods

A detailed field study was conducted in the coastal area of Qaem Shahr during the years 1999 to 2011. Samples were collected from 22 wells situated at this area [15]. The analysis of water samples was used for multivariate statistical analysis, which included the measurement of the concentration of cations and main anions and parameters such as EC, T.D.S, pH, and compared the results with water quality indicators in detail. Concentrations of sodium and potassium were calculated by Flame Photometer method concentrations of calcium, magnesium, bicarbonate, and chloride were calculated by volumetric method; and concentration of sulfate was calculated by spectrophotometer; conductivity and total dissolved solids were measured through a conductivity meter. The statistical hydro-geochemistry collected data of the analyzed parameters for 1999 and 2011 are presented in Table 3,4.

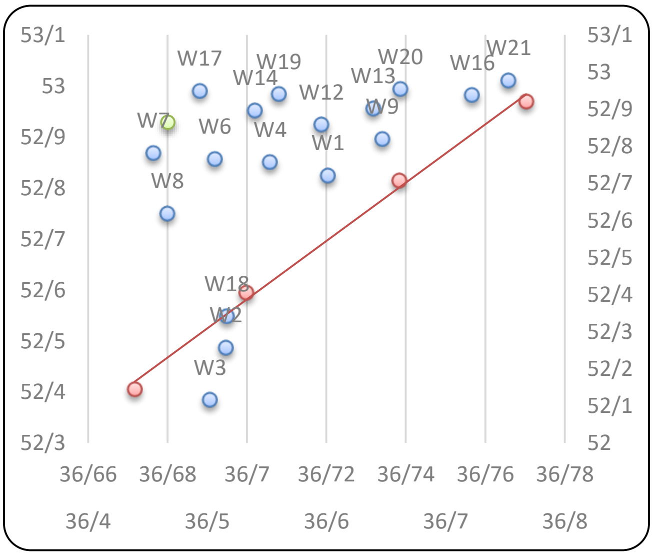

Fig 2. Location of the main and rechecked wells in the area.

Table 3. Statistical collected data of the hydro-chemical parameters for 1999

W number	Ec	T.D.S	PH	Ca	Mg	Na
W8	1300.00	845.00	7.50	110.00	52.80	55.20
W7	830.00	539.00	7.50	82.00	28.80	39.10
W17	720.00	475.00	7.50	68.00	36.00	20.70
W22	1700.00	1139.00	7.80	130.00	42.00	147.20
W6	1500.00	900.00	8.10	138.00	44.40	87.40
W14	1900.00	1216.00	7.80	130.00	64.80	149.50
W19	1700.00	1020.00	8.20	122.00	40.80	181.70
W4	1500.00	1005.00	7.70	82.00	39.60	158.70
W5	2700.00	1728.00	7.70	230.00	106.80	133.40
W1	2500.00	1600.00	7.80	82.00	43.20	379.50
W12	1600.00	960.00	7.80	142.00	51.60	96.60
W15	2400.00	1536.00	7.80	102.00	46.80	326.60
W13	1800.00	1152.00	7.70	138.00	82.80	80.50
W18	3700.00	2368.00	8.00	209.00	93.60	437.00
W9	950.00	618.00	7.90	90.00	39.60	43.70
W20	1100.00	715.00	8.10	107.80	40.80	48.30
W10	3200.00	2048.00	7.90	162.00	74.40	388.70
W2	1800.00	1150.00	7.60	130.00	48.00	163.30
W3	2400.00	1536.00	7.80	142.00	52.80	266.80
W16	3600.00	2304.00	7.60	178.00	103.20	400.20
W11	1600.00	960.00	7.70	90.00	63.60	133.40
W21	3100.00	1984.00	7.50	136.00	46.80	448.50

W number	K	HCO_3	Cl	SO_4	GW-Depth
W8	6.00	500.20	71.00	110.40	42
W7	3.20	353.80	42.60	72.00	32
W17	2.00	250.10	31.95	110.40	35
W22	3.60	256.20	216.55	297.60	22
W6	3.60	555.10	81.65	148.80	18
W14	3.60	701.50	145.55	144.00	2
W19	3.20	457.50	244.95	148.80	-5
W4	4.40	289.90	198.80	206.40	-8
W5	10.00	719.80	142.00	513.60	-12.75
W1	6.40	457.50	408.25	264.00	-15
W12	3.60	597.80	106.50	129.60	-11.8
W15	6.00	561.20	404.70	139.20	-10.8
W13	6.00	579.50	99.40	254.40	-15
W18	6.80	518.50	550.25	595.20	-13
W9	2.40	427.00	42.60	67.20	-16.5
W20	3.60	396.50	53.25	120.00	-15.5
W10	7.20	732.00	443.75	321.60	-18
W2	3.60	762.50	99.40	105.60	-23
W3	6.00	884.50	213.00	148.80	-22
W16	8.00	988.20	443.75	316.80	-21.5
W11	3.60	305.00	149.10	302.40	-25.2
W21	6.00	353.80	507.65	484.80	-22

Table 4. Statistical collected data of the hydro-chemical parameters for 2011

W number	Ec	T.D.S	PH	Ca	Mg	Na
W8	1328.00	850.00	7.10	134.00	46.80	52.90
W7	1387.00	888.00	6.90	134.00	45.60	71.30
W17	1018.00	851.00	7.30	94.00	38.40	46.00
W22	950.00	609.00	7.20	104.00	26.40	41.40
W6	868.00	543.00	7.20	94.00	34.80	20.70
W14	1762.00	1127.00	6.90	162.00	64.80	89.70
W19	1404.00	898.00	7.50	136.00	50.40	64.40
W4	1058.00	670.00	7.30	96.00	40.80	48.30
W5	1201.00	769.00	7.10	102.00	44.40	66.70
W1	2040.00	1294.00	7.40	150.00	60.00	174.80
W12	2210.00	1414.00	7.50	130.00	54.00	250.70
W15	1765.00	1129.00	6.90	84.00	46.80	167.90
W13	2620.00	1676.00	7.20	164.00	69.60	271.40
W18	2420.00	1548.00	7.90	178.00	78.00	193.20
W9	789.00	504.00	7.40	68.00	32.40	36.80
W20	1576.00	1008.00	7.50	108.00	54.00	128.80
W10	1190.00	754.00	7.60	106.00	43.20	62.10
W2	1390.00	883.00	7.30	128.00	55.20	57.50
W3	897.00	559.00	7.40	86.00	37.20	29.90
W16	6680.00	4275.00	7.40	338.00	136.80	876.30
W11	3260.00	2063.00	7.50	216.00	88.80	322.00
W21	1810.00	1149.00	7.40	160.00	58.80	110.40

W number	K	HCO3	Cl	SO4	GW-Depth
W8	3.90	475.80	95.85	115.20	69
W7	4.29	451.40	127.80	120.00	50
W17	3.51	347.70	81.65	91.20	25.1
W22	3.51	335.50	71.00	81.60	18.5
W6	3.12	408.70	28.40	43.20	26
W14	3.51	585.60	159.75	153.60	2
W19	3.51	579.50	88.75	86.40	-4.9
W4	3.12	402.60	78.10	67.20	-5.7
W5	3.51	414.80	113.60	81.60	-11.3
W1	3.90	576.30	291.10	76.80	-14.2
W12	4.68	323.30	521.85	86.40	-10.1
W15	3.51	542.90	255.60	57.60	-8.7
W13	4.68	738.10	386.95	134.40	-8.8
W18	4.68	634.40	340.80	182.40	-12.6
W9	3.12	231.80	49.70	115.20	-15.5
W20	3.51	433.10	188.15	144.00	-14.7
W10	4.68	488.00	85.20	57.60	-15.4
W2	3.51	530.70	113.60	81.60	-21.5
W3	3.12	359.90	46.15	62.40	-23.2
W16	5.46	847.90	1494.55	499.20	-22.5
W11	5.07	976.00	443.75	177.60	-24.5
W21	3.90	664.90	152.65	120.00	-24.8

4. Results and discussion

The physical parameters measured in this study are EC, T.D.S and also PH. The T.D.S of samples, average value from 1999 to 2011 changed from 1263.55 to 1157.32 and the median value changed from 114.5 to 893. Also, the average value of EC changed from 1981.82 to 1801.05 and the median value changed from 1750 to 1397. The value of PH is around the standards in the period of this study (Fig 3). The highest EC is recorded in w18, 10,16 and 21 because of the proximity to the sea. T.D.S is one of the parameters used to understand the amount of contaminant present in the groundwater which is directly proportional to EC. The high concentration of T.D.S is in w18,10,16 and 21 as the EC. Due to over-exploitation by urbanization, this area has the possibility of salt enrichment from sea water. The PH of the samples ranged from about 7 to 8.2, indicating an alkaline nature. The major cation is sodium and the major anion is *chloride. The maximum amount of the Na and Cl in this study is recorded around the sea level.* High sodium in underground water can be a concern for people on a low sodium diet. High chloride levels can cause plumbing corrosion problems, which could shorten the life of plumbing, hot water heaters and appliances, and increase the metal content of the water.

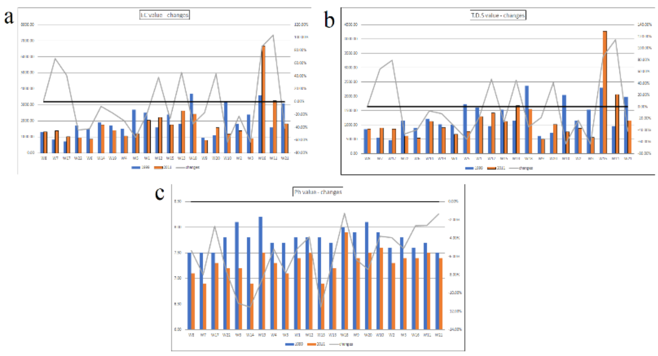

Fig 3. Changes in 1999 to 2011 for (a) EC values (b) T.D.S vlues (c) PH values.

The sodium ion is ubiquitous in water. Most water supplies contain less than 20 mg of sodium per litre, but in some countries levels can exceed 250 mg/litre. Salt infiltration, mineral deposits, seawater spray, sewage effluent, and salt used in road deicing can all contribute significant amounts of sodium to water. In addition, water-treatment chemicals, such as sodium fluoride, sodium bicarbonate, and sodium hypochlorite, can together result in sodium levels as high as 30 mg/litre. Domestic water softeners can give levels of over 300 mg/litre, but much lower ones are usually found [18]. Chloride in surface and underground water from natural and human sources, such as runoff containing de-icing salts from roads, use of mineral fertilizers, landfill leachates, septic tank effluents, animal feed, industrial effluents, irrigation drains and Intrusion of sea water occurs in coastal areas. [19]. Chloride in water may be significantly increased by treatment processes that use chlorine or chlorides. For example, treatment with 40 g of chlorine per m3 and 0.6 mol of iron chloride per litre, required for the purification of groundwater containing large amounts of iron, or surface water polluted with colloids, has been reported to result in chloride concentrations of 40 and 63 mg/litre, respectively, in the finished water [20]. As water moves through soil and rock, it dissolves very small amounts of minerals and holds them in solution. Dissolved calcium and magnesium are the two most common minerals that make water “hard” [21]. The calcium amount of the study wells varies from 70 to 230 mg/l. One of the main reasons for the abundance of calcium in water is its natural presence in the earth's crust. Also, the maximum concentration of magnesium was recorded near the sea level, as well as the calcium. Because in the coastal areas due to salt infiltration, the magnesium content is higher in the groundwater. The collected data shows the range between 2 to 10 mg/l for the amount of potassium. All of the samples show the potassium concentration to be less than 10 mg/l. Bicarbonates get into water when it passes through a calcium carbonate or magnesium carbonate.

Water above pH 7.5 is usually associated with high bicarbonates. The maximum concentration of Co4 and Hco3 are found along the coastal side of the region.

4.1 Ground water level changes

The depth of underground water in the area has been studied. According to the data, the GWL around the center of the study area (Qaem Shahr) increased by about 50% during the study period (Table 5, Fig 4). The wireframe and the contour for GWL in 1999 and 2011 shown in Figures 4 and 5, respectively.

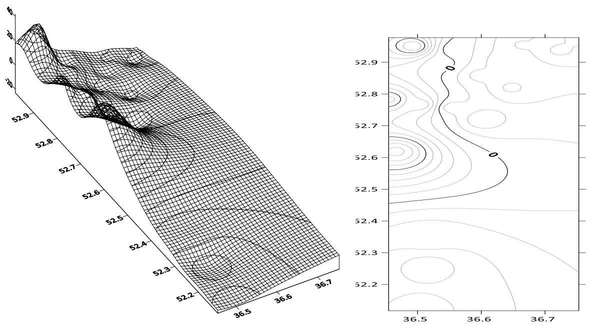

Fig 4. 3D wireframe and contour for GWL in 1999 (Surfer plot).

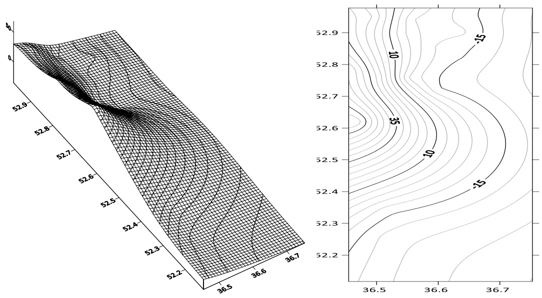

Fig 5. 3D wireframe and contour for GWL in 2011 (Surfer plot).

Table 5. GWL changes in percent from 1999 to 2011

Well	W8	W7	W17	W22	W6	W14	W19	W4
Percent	**64%**	**56%**	-28%	-16%	**44%**	0%	-2%	-29%
Well	W5	W1	W12	W15	W13	W18	W9	W20
Percent	-11%	-5%	-14%	-19%	-41%	-3%	-6%	-5%
Well	W10	W2	W3	W16	W11	W21		
Percent	-14%	-7%	5%	5%	-3%	13%		

Water resource management in the study area requires much more attention due to the precious value of water as the most important element of a sustainable environment. As the contours show, the groundwater level around the city increased during the study due to the government's policy to find and block illegal wells, as well as the reduction of farms due to water quality, economic issues and urbanization.

4.2 Multivariate statistical summaries

The multivariate statistical summaries and pearson correlation values of the data are presented in Table 6,7 and 8, respectively.

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Table 6. Multivariate Statistical summary of the hydro-chemical parameters for 1999

	Min	Max	Ave	STD	Median	Skew	CV	Kurt	Quartile
Ec(µS/cm)	720.00	3700.00	1981.82	863.34	1750.00	0.58	0.44	-0.50	1450.00
T.D.S(mg/l)	475.00	2368.00	1263.55	553.75	1144.50	0.61	0.44	-0.53	886.25
PH	7.50	8.20	7.77	0.20	7.80	0.45	0.03	-0.35	7.60
Ca	1263.55	553.75	0.61	0.44	-0.53	0.89	0.32	0.80	90.00
Mg	28.80	106.80	56.51	22.16	47.40	1.19	0.39	0.41	40.80
Na	20.70	448.50	190.27	142.42	148.35	0.70	0.75	-0.98	74.18
K	2.00	10.00	4.95	2.02	4.00	0.73	0.41	0.16	3.60
HCO3	250.10	988.20	529.46	203.33	**147.33**	0.58	0.38	-0.26	353.80
Cl	31.95	550.25	213.48	167.30	147.33	0.81	0.78	-0.77	78.99
SO4	67.20	595.20	227.35	147.96	148.80	1.21	0.65	0.74	117.60

Table 7. Multivariate Statistical summary of the hydro-chemical parameters for 2011

	Min	Max	Ave	STD	Median	Skew	CV	Kurt	Quartile
Ec(µS/cm)	720.00	6680.00	1801.05	1259.65	1397.00	3.02	0.70	11.02	1048.00
T.D.S(mg/l)	504.00	4275.00	1157.32	801.42	893.00	3.05	0.69	11.26	733.00
PH	6.90	7.90	7.31	0.24	7.35	0.07	0.03	0.53	7.18
Ca	1157.32	801.42	3.05	0.69	11.26	2.22	0.43	6.69	95.50
Mg	26.40	136.80	54.87	23.64	48.60	2.16	0.43	6.27	40.20
Na	20.70	876.30	144.69	184.25	69.00	3.26	1.27	12.42	47.73
K	3.12	5.46	3.90	0.69	3.51	0.79	0.18	-0.44	3.51
HCO3	231.80	976.00	515.86	178.88	120.70	0.93	0.35	0.91	391.93
Cl	28.40	1494.55	237.04	312.94	120.70	3.37	1.32	13.17	80.76
SO4	43.20	499.20	119.78	93.13	88.80	3.47	0.78	14.09	74.40

Table 8. Pearson's correlation coefficient values between 1999 to 2011

Parameter	r Value	Parameter	r Value
Ec	0.478560085	Na	0.353383
T.D.S	0.452755833	K	0.330536
PH	0.403140573	HCO3	0.156984
Ca	0.271295573	Cl	0.343506
Mg	0.606970757	SO4	0.233316

4.3 CWQI results and discussion

Multivariate statistical method (FA) were used in this study. The detailed formulation of WQI, as described in the Canadian Water Quality index is as follow [12]:

F1. Shows the percentage of variables that do not meet their guideline value at least once during the investigated time period, relative to the total number of measured variables.

F2. Indicates the frequency of individual test that does not meet the guideline value.

F3. Indicates the value by which the failed test value does not match its guide value in three steps.

- The number of times by which an indicidual concentration is greater than (or less than, when the objective is a minimum) the objective is called a " excursion" and is expressed as follow. When the test value must not exceed the value:

$$excursion\ (i) = \left(\frac{Failed\ Test\ Value\ i}{Objective\ i}\right) - 1 \quad (1)$$

For the cases in where the test value should not be less than the objective:

$$excursion\ (i) = \left(\frac{Objective\ i}{Failed\ Test\ Value\ i}\right) - 1 \quad (2)$$

- The cumulative amount by which individual tests are out of compliance is calculated by summing the excursions of individual tests from their objectives and dividing by the total number of tests (both thoses meeting objectives and thoses not meeting objective). This variables, which are called the normalized sum of excursions, or nse, are calculated as:

$$nse = \left(\frac{\sum_{i=1}^{n} excursion\ i}{\#\ of\ tests}\right) - 1 \qquad (3)$$

➢ F3 is then computed by an asymptotic function that scaled the normalized sum of the excursions from objective (nse) to yield a range between 0 and 100.

$$F3 = \left(\frac{nse}{0.01nse+0.01}\right) \qquad (4)$$

Once the factors have been obtained, the index itself can be calculated by summing the three factors as if they were vectors. The sum of the squares of each factor is therefore equal to the square of the index. This approach comsiders the index as a three-dimensional space defined by each factor along one axis. With this model, the index changes in direct proportion to changes in all three factors.

The CCME Water Quality Index (CCME WQI):

$$CCMEWQI = 100 - \left(\frac{\sqrt{F_1^2+F_2^2+F_3^2}}{1.732}\right) \qquad (5)$$

The divisor 1.732 normalises the resultant values to a range between 0 and 100, where 0 represents the "worse" water quality and 100 represents the "best" water quality. So, due to the median values for the studied wells, the results represent the ranges between 50 to 70 for this area.

4.4 WHOI results and discussion

The Guidelines for Drinking Water Quality (GDWQ) is one of the longest normative publications of the World Health Organization (WHO), with the first edition published in 1958 [16]. In this study, the WHO standard classification was used to calculate the WQI in stages as below (Table 7).

Table 7. Classification of WQI by WHO standard

Parameter used	Median Standard	Assigned weight	Relative weight	1999 Median	qi	Sii	2011 Median	qi	Sii
Sulfate (mg/l)	250	5	0.1724	148.80	59.52	10.26207	88.80	35.52	6.124138
Sodium (mg/l)	200	5	0.1724	148.35	74.175	12.78879	69.00	34.5	5.948276
PH	8	1	0.0345	7.80	97.5	3.362069	7.35	91.875	3.168103
Calcium (mg/l)	150	3	0.1034	147.33	98.21667	10.16034	120.70	80.46667	8.324138
Magnesium (mg/l)	70	3	0.1034	47.40	67.71429	7.004926	48.60	69.42857	7.182266
Chlorine (mg/l)	250	5	0.1724	147.33	58.93	10.16034	120.70	48.28	8.324138
Electrical Conductivity	500		0.0000	1750.00	350	0	1397.00	279.4	0
Total Dissolved Solids (TDS)	1000	5	0.1724	1144.50	114.45	19.73276	893.00	89.3	15.39655
Potassium (mg/l)	12	2	0.0690	4.00	33.33333	2.298851	3.51	29.25	2.017241

This paper presents the groundwater quality assessment carried out for the coastal area of Iran. Results show that the water quality index due to the WHOI, decreased in this area between 1999 and 2011. However, due to the WHOI, the results between 50-70 are in medium range and 70-90 are acceptable.

Conflict of interest

There is not conflict of interest.

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