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Investigation of the Trend of Groundwater Quality Changes in Dezful Aquifer

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Abstract

In this study, modified Mann-Kendall test by removing the effects of internal autocorrelation, slope of trend line test and Pettitt test were used to investigate the time and spatio-temporal changes of the quality parameters of the groundwater of Dezful aquifer in the period of 1999-2017. In this regard, the parameters of potassium, sodium, magnesium, calcium, sulfate, chlorine, bicarbonates, acidity, total dissolved solids and electrical conductivity were used in 30 wells in Dezful aquifer. The results of examining the trend of changes in the investigated values based on the modified Mann-Kendall statistic showed that on average, 74% of the investigated wells experienced an increasing trend in the mentioned qualitative values. While the trend of changes in pH values in the entire studied range was decreasing, the trend of increasing changes in potassium, sodium, magnesium, calcium, sulfate, chlorine, bicarbonates, total dissolved solids and electrical conductivity was in 4, 10, 10, 0, 14, 37, 37, 27 and 27% of the wells are significant at the 5% level, respectively. According to the investigation of the time of changing point of trend in the studied qualitative values, the results showed that the time of changing of the trend in qualitative variables started from 2000 in potassium, sulfate and chlorine variables and included other variables until 2001. The decreasing changes of pH values at the level of the studied area also started in 2005. The increase in the changes of the investigated qualitative values, especially in the central and southeastern regions, has caused a decrease in the usefulness of groundwater in the studied region, and this issue affects its use in different sectors. Investigating the changes in the qualitative values of groundwater is one of the important methods in monitoring the quality of groundwater, and using the obtained results, restrictions can be applied regarding its use in different sectors.

Keywords: Autocorrelation effect, Changing time, Mann-Kendall, Pettitt test.

1. Introduction

Iran is one of the countries whose largest area is located in the hot and dry region, and its average rainfall is about 250 mm, which is considered one of the dry and scarce countries in the world. About 90% of the available water in the country is consumed in the agricultural sector, more than 80% of which is supplied from groundwater sources. Poor water management has caused excessive withdrawals from groundwater through digging new wells and additional pumping of the groundwater level, which has caused the groundwater resources to be under stress. Recently, with the decrease of 0.5 to 1.5 meters in the water level, the fertility of many agricultural plains has been endangered and many wells have lost their use. Also, the indiscriminate construction of factories and industrial centers in the past years, as well as the disposal of sewage and waste and garbage from these centers, as well as urban sewage, have had a negative impact on the amount and quality of groundwater (Daneshvar Vousoughi and Dinpashoh, 2013)

The series of these events has caused damage to aquifers, soil, and the quality and quantity of water resources. In the analysis of the long-term hydrological effects of groundwater extraction on groundwater quality, it is necessary to examine the trend of changes in groundwater quality values as a monitoring system. Determining the temporal and spatial trends of the qualitative values of groundwater is necessary for better management of groundwater resources in each basin in order to manage the water resources of aquifers. One of the most important tests in determining the trend of changes in qualitative and quantitative values is the non-parametric Mann-Kendall test (Ahmadi et al., 2022; Kendall, 1957; Nazeri Tahroudi et al., 2019; Rostami et al., 2022).

Frapporti (1994) evaluated the time trends in water quality variables. He showed a significant increase in nitrate concentration in the type of polluted water, which is generally rich in nitrate. Bronswijk and Prins (2001) used an alternative method to show temporal changes in nitrate concentration. They used groundwater age dating to interpret the nitrate concentrations of agricultural wells and sandy soils in the Netherlands and found a relationship between the year of infiltration and the proportion of nitrate-contaminated groundwater. Their results showed a good agreement with the estimated agricultural nitrogen inputs, which indicated an increase in nitrate concentration in the last 30 years. Broers and Grift (2004) studied the trend of groundwater quality through non-parametric Mann-Kendall test at certain depths and time-depth concentration profiles due to changes caused by human activities in agricultural practices in Nord-Brabant province, Netherlands.

Almedeij and Al-Ruwaih (2006) investigated the fluctuations of the groundwater level in the residential areas of Kuwait. They found that the groundwater level has a negative correlation with temperature and a positive correlation with precipitation. Bouza-Deaño et al. (2008) investigated surface water quality trends for thirty-four physico-chemical and chemical variables along the Spanish Ebro River surface water using Mann-Kendall seasonal test and Sen’s slope estimation. The results showed that the parameter changes over time are mainly due to the decrease in phosphate concentration and the increase in pH level in Ebro basin from 1981 to 2004. Using data collected from 9 wells during the period 1995 to 2003, Ketata et al. (2011) investigated the hydrochemical analysis of groundwater in the South Gabes Deep Aquifer and Deep Aquifer (Southeastern Tunisia). Water samples were checked for salinity and pH. The results showed that the salinity and concentration of the main elements remained more or less constant.

Chow et al. (2017) used the Mann-Kendall seasonal test to identify trends in dissolved organic carbon (DOC), sulfate, nitrate, calcium, magnesium, pH, and acidification index over a 16-year period. A statistically decreasing trend was detected for all water quality parameters, except DOC. Sakizadeh and Chua (2020) investigated the impact of the construction of the Karkheh dam in 2010 (as the time of changing of trend) on the quality of groundwater. Time series of total dissolved solids (TDS) and other water quality data including potassium (K), sodium (Na), magnesium (Mg), calcium (Ca), bicarbonate (HCO3), sulfate (SO4), and chloride selected for the period between 1996 and 2012. The magnitude of the trend was estimated by Sen's slope estimator for HCO3, SO4, and TDS to be 0.005, -0.02, and -3.04, respectively, where showed the decrease for SO4 and TDS, while for HCO3, it shows an increasing trend.

Ha et al. (2022) investigated the trend of changes in water quality and organic matter indicators in the Seomjin River in South Korea. The results of their research showed that during the study period, biochemical oxygen demand decreased, while chemical oxygen demand and total organic carbon decreased in one basin and increased in other basin. They also stated that the study of changes in river quality values can be used as a reference to facilitate continuous water management. Gu et al. (2023) investigated the water quality of seven major basins in China in the 2008 to 2019. Their research results showed that in recent years, the overall water quality in China is improving, but it is still not optimistic. This issue makes it important to take measures to protect water resources and control pollution in China.

Due to the existence of self-autocorrelation, time series do not present the trend of real changes using different models and methods. In fact, the existence of self-autocorrelation causes the trend of data changes to not be displayed correctly. In this study, it has been tried to use modified Mann-Kendall test by removing the effects of self-autocorrelation and Pettit's test to monitor the temporal and spatial quality variables of groundwater in the Andimeshk plain aquifer, as well as the time of their trend change. In addition to examining the temporal and spatial changes of groundwater quality variables in the study area, in this research, the slope of the trend line has also been tried to estimate the rate of changing of quality parameters on an annual scale. In fact, the main goal of this study is to monitor the quality variables of groundwater such as potassium, sodium, magnesium, calcium, sulfate, chlorine, bicarbonates, acidity, total dissolved solids and electrical conductivity in 30 wells in the aquifer area.

2. Materials and Methods:

2.1. Case study

The studied area in this research is Dezful-Andimeshk plain. Dezful-Andimshek plain is located about 130 km from Ahvaz city, downstream of Dez Dam. This plain has an area of more than 2070 square kilometers, which includes the mountainous regions to the low altitude of the province. In this study, the quality data of groundwater in the study area including electrical conductivity (EC) in mmhos/cm, total dissolved solids (TDS) in mg/l, acidity (pH), potassium (K), sodium (Na), magnesium (Mg), calcium (Ca), sulfate (SO4), chlorine (Cl) and bicarbonates (HCO3) in terms of mg/l in the aquifer of the studied area in the period of 1999-2017 was used on an annual scale. The studied data were selected from 30 sampling sites in the studied area. The location of the studied stations is presented in Figure 1. Table 1 presents the statistical characteristics of the studied data along with the code of the studied station.

2.2. Trend analysis

In this study, changes in the time series of groundwater quality in Dezful Plain are investigated with the modified Mann-Kendall non-parametric test. The modified non-parametric Mann-Kendall test has been widely used in various meteorological and hydrological studies (Ahmadi et al., 2022 and 2018; Khalili et al., 2016; Nazeri Tahroudi et al., 2019; Rostami et al., 2022). This test examines the absence of autocorrelation in time-series, so the effect of autocorrelation must be removed first to be able to use the modified Mann-Kendall test.

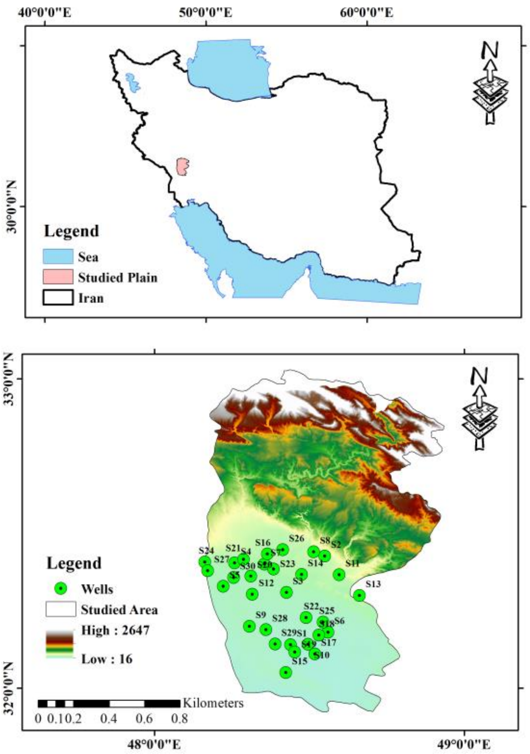

Fig. 1. Location of the studied area along with the studied stations

2.3. Conventional Mann-Kendall

In the conventional Mann-Kendall test, each value in the time series is continuously compared with other values in the time series. The statistics of this test are estimated as follows (Hamed and Rao, 1998; Khaliq et al., 2009):

$$S = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} sgn\left(x_j - x_i\right) \tag{1}$$

Where x_j is the consecutive values, n is the length of the time series, and $sgn(\theta)$ is the sign function, which is estimated as described below:

$$sgn(\theta) = \begin{cases} 1 & if \quad \theta > \circ \\ \circ & if \quad \theta = \circ \\ -1 & if \quad \theta < \circ \end{cases} \tag{2}$$

In $n \geq 8$ case, the statistic S is almost normally distributed and its mean and variance are as follow (Kendall, 1957; Mann, 1945):

$$E(S) = 0 \quad (3)$$

$$V(S) = \frac{n(n-1)(2n+5) - \sum_{i=1}^{n} t_i (t_i - 1)(2t_i + 5)}{18} \quad (4)$$

where t_i is the number of identical data in i[th] category.

Table 1- Statistical characteristics of the studied data

Code	Mean values									
	K	Na	Mg	Ca	SO4	Cl	HCO3	pH	TDS	EC
	mg/l								mg/l	mmhos/cm
S1	0.04	2.7	2.5	3.8	7.8	2.3	4.8	7.7	546.3	840.4
S2	0.02	0.3	1.2	1.8	0.2	0.5	2.4	7.7	195.6	301.0
S3	0.03	1.8	2.3	4.2	1.5	1.9	4.6	7.6	498.3	766.4
S4	0.04	1.7	1.2	3.7	2.0	1.6	3.8	7.7	454.1	698.6
S5	0.06	5.1	1.4	4.9	4.5	4.9	4.5	7.7	871.1	1340.0
S6	0.07	6.9	2.8	3.7	2.5	6.5	4.1	7.7	835.9	1286.1
S7	0.04	1.7	2.5	3.4	2.5	1.8	4.0	7.6	515.4	792.9
S8	0.03	0.8	1.5	2.0	0.6	0.9	2.6	7.9	256.5	394.5
S9	0.03	0.7	1.4	2.0	0.4	0.9	2.6	7.9	249.5	383.7
S10	0.3	3.2	2.4	3.2	1.5	2.6	4.4	7.8	541.5	833.1
S11	0.1	9.45	3.1	5.3	4.6	4.6	2.9	7.8	353.6	5436.1
S12	0.03	1.4	1.7	3.3	1.1	1.6	3.5	7.8	389.1	598.7
S13	0.05	2.3	3.1	4.5	4.9	1.6	3.2	7.7	581.6	894.6
S14	0.04	2.6	2.6	3.7	1.8	2.5	4.5	7.7	541.6	833.2
S15	0.05	6.4	2.2	2.5	4.0	1.4	2.8	7.9	713.1	1097.3
S16	0.07	1.4	2.2	3.7	1.7	1.6	3.7	7.8	437.2	661.6
S17	0.05	3.2	2.4	3.9	3.1	2.4	3.9	7.7	547.2	897.2
S18	0.05	3.8	2.8	3.6	2.3	3.1	4.5	7.8	610.6	939.5
S19	0.04	1.8	1.2	2.9	1.6	1.9	3.2	7.8	407.3	626.6
S20	0.05	1.7	2.0	3.9	1.5	1.9	4.0	7.7	471.8	725.6
S21	0.05	1.2	3.1	5.3	5.3	1.3	2.8	7.8	575.3	885.1
S22	0.03	2.3	2.3	3.3	1.5	2.0	3.4	7.8	487.5	751.2
S23	0.05	1.8	2.2	4.6	3.0	1.8	3.7	7.8	517.1	795.6
S24	0.04	4.2	3.4	6.3	5.5	5.0	3.4	7.8	860.2	1287.6
S25	0.08	4.5	2.3	2.8	2.3	3.0	4.2	7.9	578.9	890.7
S26	0.03	1.4	1.8	3.2	1.6	1.6	3.1	7.7	385.0	592.2
S27	0.03	1.7	1.2	2.9	1.4	1.8	3.4	8.0	402.1	618.5
S28	0.03	1.3	1.8	2.5	1.1	1.5	2.9	7.8	235.1	515.3
S29	0.03	2.3	2.2	3.1	1.8	1.9	3.6	7.7	462.4	714.1
S30	0.06	2.3	3.0	3.7	2.2	2.1	4.6	7.9	536.4	825.1

The standardized Z test score is estimated as follows:

$$Z = \begin{cases} \frac{S-1}{\sqrt{Var(S)}} & S > 0 \\ 0 & S = 0 \\ \frac{S+1}{\sqrt{Var(S)}} & S < 0 \end{cases} \quad (5)$$

In this study, a significance level of 5% was used to check the significance of the trend. If the values of Z are more than 1.96 and less than -1.96, the trend of calculated changes is significant increasing and decreasing significant respectively.

2.4. Sen's slope estimator

This index shows the magnitude of the uniform trend. The value of the slope of the trend is estimated as follows (Sen, 1968; Thiel, 1950):

$$\beta = Median\left(\frac{x_j - x_i}{j - i}\right) \quad \forall i < j \tag{6}$$

where β is the estimator of the slope of the trend line and X_i, X_j are the i-th and j-th observation values, respectively. Positive values indicate an increasing trend and negative values indicate a decreasing trend.

2.5. Mann-Kendall test by removing the self-autocorrelation coefficient

This method was presented by Kumar et al. (2009). In this method, the effect of the autocorrelation coefficient (r_k) is calculated and if it is significant, it is removed from the data series as follows:

$$r_k = \frac{\frac{1}{n-k}\sum_{i=1}^{n-k}(x_i - \bar{x})(x_{i+k} - \bar{x})}{\frac{1}{n}\sum_{i=1}^{n}(x_i - \bar{x})^2} \tag{7}$$

In the next step, the autocorrelation between the data is removed from the main series if it is significant. In this way, at first, the slope of the trend line or β is calculated using equation (6), and the new series will be as follows without slope:

$$x'_i = x_i - (\beta \times i) \tag{8}$$

In the next step, the autocorrelation coefficient component (for example, the first order) is removed from the new series and the residual series (y'_i) is estimated from the following equation:

$$y'_i = x'_i - r_1 \times x'_{i-1} \tag{9}$$

And finally, the slope of the trend line $(\beta \times i)$ is added to the last series and the final series (y_i) will be as follows:

$$y_i = y'_i + (\beta \times i) \tag{10}$$

Now, by applying the Mann-Kendall test, the existence of a trend in them is examined (Bandyopadhyay et al., 2009; Burn and Elnur, 2002; Hamed and Rao, 1998; Khaliq et al., 2009; Luo et al., 2008).

2.6. Changing Point Test (Pettitt test)

This method is a non-parametric test that was presented by Pettitt in 1979. This method is used to find turning points in a time series. Pettitt's test is a rank test without distribution to detect significant changes in the mean of time series. The statistics of this test are as follows (Pettitt, 1979):

In the first step, the time series $U_{t,n}$ is estimated as follows:

$$U_{t,n} = \sum_{i=1}^{t}\sum_{j=i+1}^{n} sgn(x_j - x_i) \tag{11}$$

where *t* is equal to the length of the period and *n* is the number of data. The value of *k* is calculated in the form of equation (12) and replaced in equation (13) and the *P* statistic is obtained:

$$k = \max\left[U_{t,n}\right] \tag{12}$$

$$P = 2 \times e^{-\frac{6k^2}{n^3 + n^2}} \tag{13}$$

If the calculated *P* value is smaller than the significance level of α, this changing point in the series can be considered statistically significant.

In this study, the spatial changes of Z-statistics of Mann-Kendall test are zoned using GIS software and Spline interpolation method.

3. Results and Discussion

In this study, at first, the trend of time changes of the studied qualitative variables was investigated using the modified Mann-Kendall test. The trend of changes in quality parameters was investigated on an annual scale in the period of 1999-2017.

3.1. The results of examining the trend of changes in the studied values

The results of examining the trend of changes in the studied qualitative values using the modified Mann-Kendall test were presented in Figure 2. According to Figure 2-a, it can be seen that the trend of changes in calcium values during the studied period on an annual scale in stations S5 (Shahrek Bahram), S11 (Sarbisheh), S27 (Chichali) and S29 (Hor Riyahi 2) has been decreasing and in other stations there has been an increasing trend. Among the decreasing trends, the trend of calcium changes is significant in stations S11 and S29 and decreasing and insignificant in two other stations (S5 and S27).

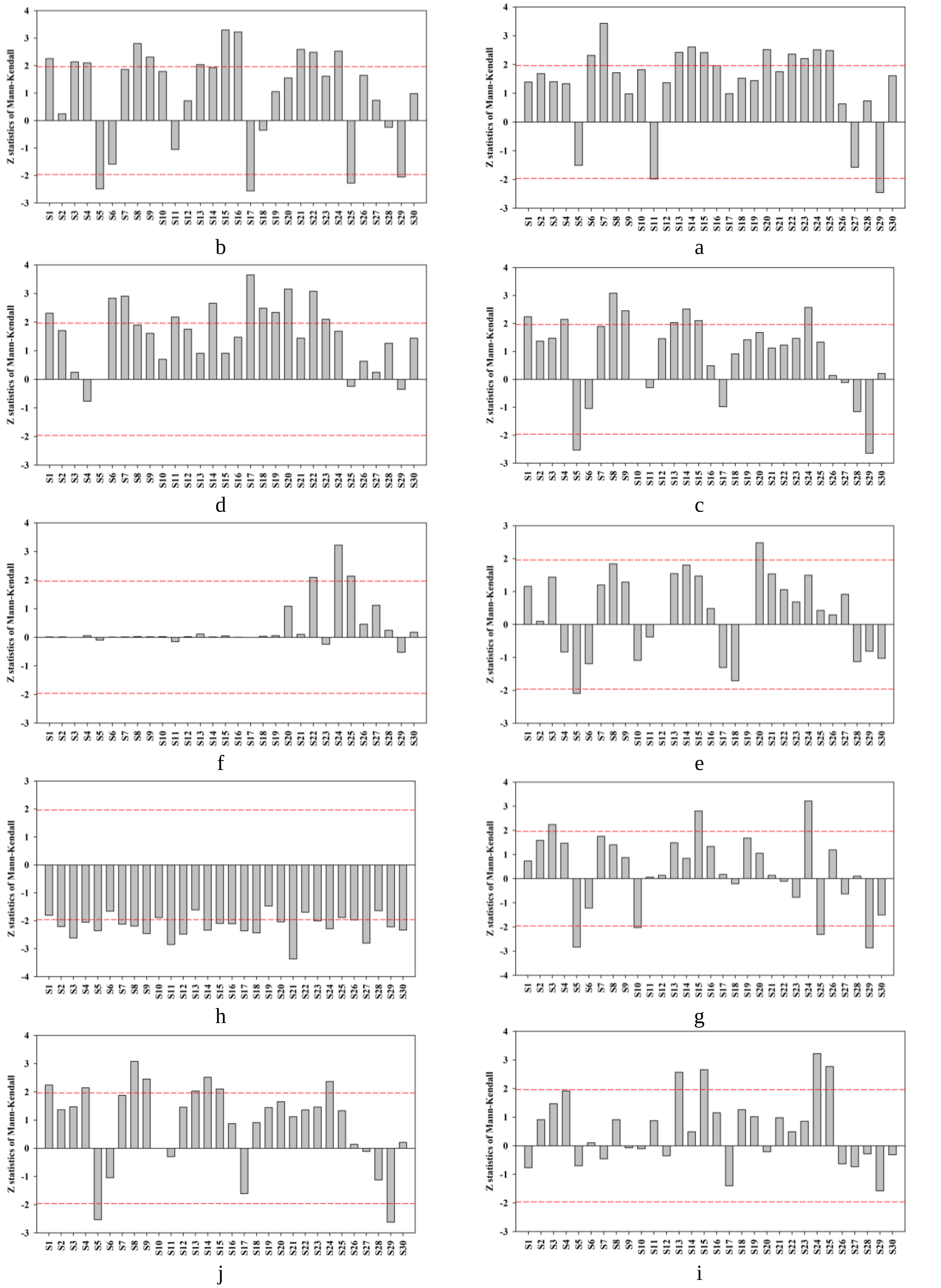

Fig. 2. The results of the Mann-Kendall statistic in examining the changes in qualitative parameters (a: Ca, b: Cl, c: EC, d: HCO3, e: K, f: Mg, g: Na, h: pH, i: SO4 and j: TDS)

Among the increasing trends, the changing trend of stations S6, S7, S13, S14, S15, S20, S22, S23, S24 and S25 has an increasing and significant trend at the level of 5% and the changing trend of other stations is non-significant at level of 5%. Figure 2-b also shows the changes in chlorine values during the studied period. According to this figure, it is possible to see incremental changes in the chlorine levels of groundwater in most of the stations. Apart from stations S5, S6, S11, S17, S18, S25, S28 and S29, which witnessed the decreasing trend of chlorine in the groundwater, the other investigated stations experienced an increasing trend. The decreasing trend of chlorine values in stations S5, S17, S25 and S29 is significant and the decreasing trend in stations S6, S11, S18 and S28 is non-significant at the level of 5%. The trend of incremental changes in chlorine values in stations S1, S3, S4, S8, S9, S13, S15, S16, S21, S22 and S24 is significant at the level of 5% and other incremental trends are non-significant at the level of 5%. According to Figure 2-c, it is possible to see the changes of EC values during the period of 1999-2017 in the groundwater of the study area. As in Figure 2-b, the changes of EC values in stations S5 and S29 are decreasing and significant and in stations S6, S11, S17, S27 and S28 are decreasing and non-significant at the level of 5%.

The changes of other existing stations regarding electrical conductivity values in the studied area are incremental. According to Figure 2-c, it is possible to see significant increasing changes in electrical conductivity values at the level of 5% in stations S1, S4, S8, S9, S13, S14, S15 and S24. Increasing changes in EC values can quickly changing water quality, and increasing salinity causes a decrease in water quality in terms of agriculture, drinking, and even industry. Other investigated stations have experienced an increasing trend regarding electrical conductivity values.

Regarding the changes in the amount of bicarbonates during the period under investigation, the results of Figure 2-d showed that there was no significant decrease in this parameter, but the decreasing changes of bicarbonates in stations S4, S25 and S29 are non-significant during the period of 1999-2017. Apart from the three mentioned stations, the trend of changes in bicarbonates in the studied period is increasing in other stations. The increasing changes of bicarbonates in stations S1, S6, S7, S11, S14, S17-S20, S22 and S23 are significant at the level of 5% and the incremental changes of other stations are non-significant. According to Figure 2-e, the increasing changes of potassium values are only significant at the level of 5% at S20 station.

Significant decreasing changes at the level of 5% were observed only in S5 station. Other investigated stations have also experienced non-significant increase and decrease in potassium values. Changes in potassium values in stations S4, S6, S10, S11, S17, S18 and S28-S30 are decreasing and non-significant and in other stations increasing and non-significant at the level of 5%. The changes of magnesium values in the groundwater of the studied area are evident in Figure 2-f. The changes of this parameter in three stations S22, S24 and S25 are incremental and significant. The decreasing changes of magnesium values were non-significant and were observed only at four stations S5, S11, S23 and S29. Other stations have also experienced an increasing and non-significant trend in the changes of magnesium values.

Figure 2-g shows the changes of sodium values during the period of 1999-2017 in the groundwater of Dezful plain. Like other investigated parameters, in station S5, annual sodium changes have been decreasing and significant. In addition to station S5, stations S10, S25 and S29 have also experienced significant decreasing changes regarding annual sodium. The changes in sodium values of groundwater in three stations S3, S15 and S24 in the studied area have been increasing and significant. Other investigated stations have also experienced a combination of insignificant decreasing and increasing trends. But in Figure 2-h, you can see the decreasing changes of pH values in all the studied stations in the period of 1999-2017.

The decreasing trend of pH values in stations S1, S6, S10, S13, S19, S22, S25 and S28 is non-significant and significant in other stations. If this factor is less than 6, it will indicate the acidity of the water. Consumption of acidic water will have very adverse effects on the body. Figure 2-i shows the changes of SO4 values in the studied area in 30 studied stations. Increasing and decreasing changes are observed in all studied stations. The decreasing changes of SO4 values in all stations are decreasing and non-significant. The increasing trend of SO4 values is also significant only in stations S13, S15, S24 and S25 at the level of 5%. The trend of changes in TDS values on an annual scale in the study area using the modified Mann-Kendall statistic is also presented in Figure 2-j. The changes of this parameter are in accordance with the changes of EC and Figure 2-c.

3.2. The results of the Sen’s slope estimator

The slope of trend changes is also an index to examine the periodic changes of the studied variables, and in this study, using this index, it is possible to estimate the annual changes of the quality parameters of groundwater. The results of the slope of the trend line of the investigated qualitative parameters in the period of 1999-2017 were presented in Figure 3. Figure 3-a shows the slope of the trend line of calcium in the studied stations. According to this figure, it can be seen that the largest decrease in the changes of calcium values is related to station S11 with a decrease of about -0.19 mg/liter every year and the largest increase is related to stations S13 and S24 with an increase about 0.22 mg/liter, which according to the period of 19 years, the changes of calcium values will be about 4.3 and 4.27 mg/liter, respectively.

The changes in the slope of the trend line of chlorine values can also be seen in Figure 3-b, the largest amount of changes in chlorine values is related to station S24 with an annual increase of about 0.23 mg/liter during the period under investigation. Stations S6 and S11 also show the greatest decrease in the amount of annual chlorine, which is about -0.40 mg/liter, which according to the length of the studied period, show the changes of -7.7 mg/liter. The electrical conductivity values, like the chlorine values, according to Figure 3-c, have the largest decrease during the period under investigation, and these changes are on average about 44 mmhos/cm every year, which during the 19-year period is a decrease of about 841 mmhos/cm.

Station S13 also had the highest increase in EC in the studied area during the studied period. According to Figure 3-d, the highest amount of increase in the bicarbonates, like other parameters, occurred in station S6, which shows an increase of about 0.14 mg/liter per year. The highest decrease of bicarbonates in each year is equal to -0.012 mg/liter and is related to station S4. The slope of changes in potassium values in the study area in most stations is around zero, which does not show any special changes.

The most decreasing changes in potassium are related to station S5 and the most are related to station S24. According to Figure 3-f, the decreasing changes of magnesium can be seen in two stations S11 and S5 with a decrease of -3.01 and -1.75 respectively, which includes the largest decrease in magnesium in the studied area. In the studied area, the largest decrease in sodium levels according to Figure 3-g is similar to other quality parameters investigated in S6 station with an annual decrease of -0.4 mg/liter. The most sodium changes are related to station S24. The pH values also decreased in all studied stations, and the largest decrease is related to the S23 station with an annual decrease of about -0.067 units per year. The average decreasing changes of pH values in the study area is about -0.048 units per year. The major changes in the amount of sulfates in the study area were increases, and as shown in Figure 3-i, the highest increase of sulfates occurred at station S13 and about 0.34 mg/liter per year. The highest (lowest) amount of TDS according to Figure 3-j occurred in station S24 (S6) with the amount of 28.7 (-7.28) mg/liter.

3.3. The results of the investigation of the time of changing point

The time of changing point of the investigated qualitative values in this study was estimated using Pettitt's test and the results were presented in Table 2. According to Table 2, it can be seen that the major changes in the potassium levels occurred between 2006 and 2011. The first failure in the potassium time series occurred in 2000 at station S19. Changes in sodium time series also started from 2002 at S7 station and finally in 2014 it experienced the last failure in the studied series at S28 station.

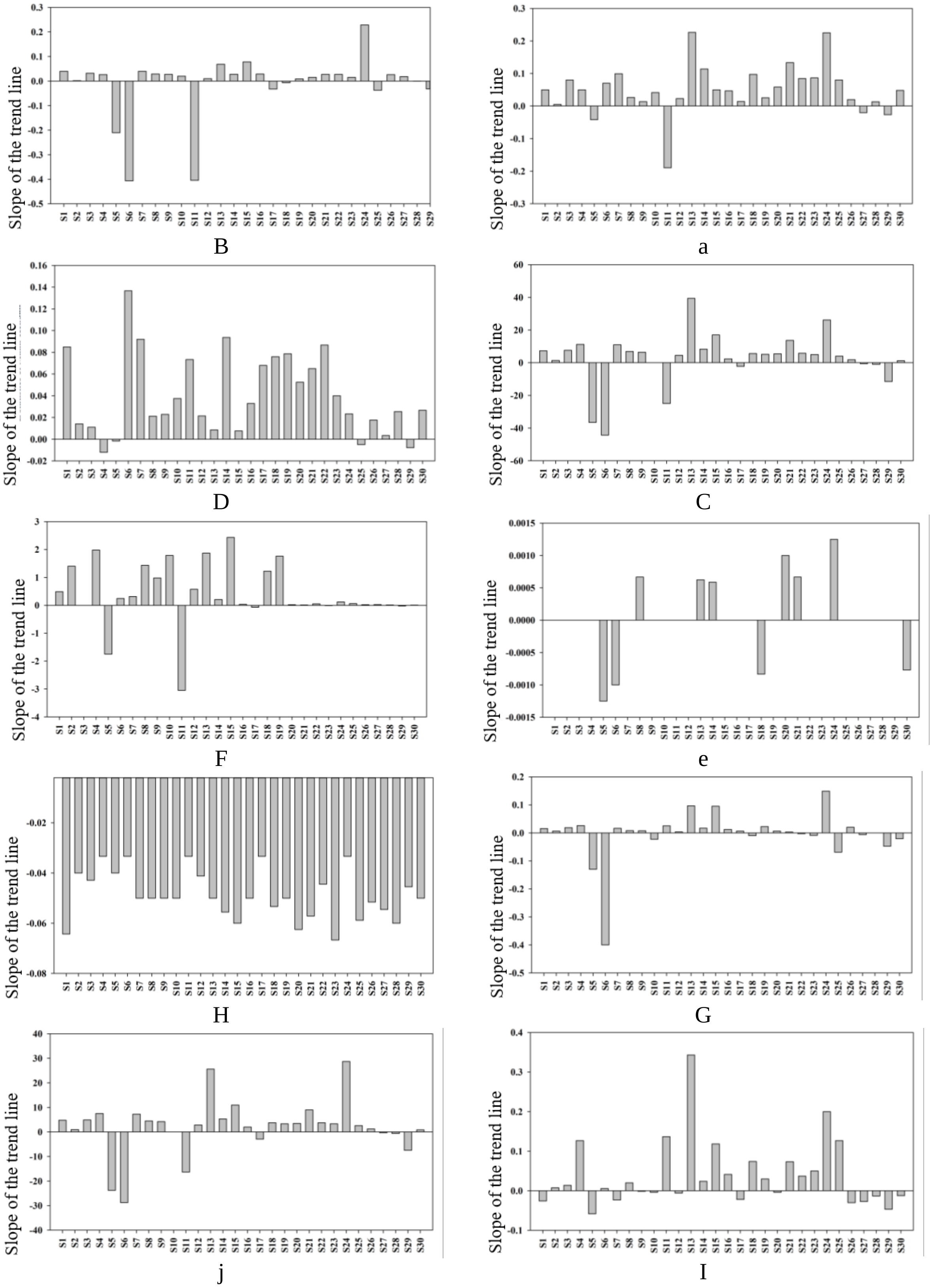

Fig. 3. Results of slope of the trend line statistics of qualitative parameters in examining the changes in qualitative parameters (a: Ca, b: Cl, c: EC, d: HCO3, e: K, f: Mg, g: Na, h: pH, i: SO4 and j: TDS)

The changes of sodium values in the study area occurred between 2006 and 2009, which have almost the same range of changes as chlorine values in the study area. However, according to Table 2, it can be seen that the major changes in sulfate values in the study area started earlier than other quality parameters and the failure of these quality values has been occurred in the period from 2003 to 2009.

Changes in the time series of magnesium in the study area started almost from 2001 at station S9 and finally, the last changing in the time series of magnesium was observed in the 2013 at station S5. The major changes in calcium time series in the study area are in the period from 2006 to 2011, but the failure in the series of observations such as magnesium values started in 2006 at station S2 and the last failure was related to station S9 in 2011.

Table 2- The results of the investigation of the time of changing point of the qualitative values

Station	K	Na	Mg	Ca	SO4	Cl	HCO3	pH	TDS	EC
S1	2006	2007	2004	2010	2014	2006	2010	2010	2009	2009
S2	2010	2006	2004	2001	2006	2003	2004	2008	2005	2005
S3	2006	2006	2003	2009	2011	2008	2006	2010	2006	2006
S4	2002	2002	2010	2007	2011	2007	2012	2009	2007	2007
S5	2011	2010	2013	2002	2001	2009	2013	2007	2009	2009
S6	2006	2006	2007	2012	2015	2006	2008	2005	2006	2006
S7	2004	2002	2004	2005	2004	2009	2009	2006	2003	2003
S8	2011	2012	2010	2012	2000	2011	2010	2010	2011	2011
S9	2011	2013	2001	2013	2000	2011	2004	2010	2013	2013
S10	2008	2008	2009	2004	2003	2010	2001	2007	2007	2007
S11	2010	2005	2010	2009	2005	2009	2009	2005	2005	2005
S12	2013	2007	2006	2006	2006	2007	2007	2008	2007	2007
S13	2004	2007	2008	2005	2006	2005	2008	2006	2007	2007
S14	2004	2007	2004	2010	2010	2008	2010	2009	2009	2009
S15	2012	2006	2008	2011	2009	2005	2005	2008	2006	2006
S16	2014	2005	2008	2008	2006	2007	2006	2010	2014	2007
S17	2011	2009	2011	2013	2007	2010	2006	2010	2010	2010
S18	2010	2010	2004	2007	2006	2000	2009	2010	2012	2012
S19	2000	2006	2010	2009	2005	2008	2009	2009	2006	2006
S20	2009	2007	2008	2011	2013	2008	2010	2009	2006	2006
S21	2010	2011	2004	2011	2005	2011	2011	2008	2011	2011
S22	2008	2005	2005	2011	2000	2007	2007	2008	2006	2006
S23	2007	2009	2004	2003	2004	2005	2007	2010	2005	2005
S24	2013	2009	2004	2009	2004	2008	2002	2009	2009	2004
S25	2000	2006	2004	2008	2004	2004	2007	2010	2010	2010
S26	2007	2007	2005	2007	2001	2007	2012	2007	2001	2001
S27	2003	2004	2006	2006	2008	2007	2003	2007	2009	2009
S28	2010	2014	2007	2012	2002	2010	2005	2008	2001	2001
S29	2010	2007	2002	2008	2003	2011	2013	2008	2010	2010
S30	2008	2008	2004	2011	2009	2005	2009	2008	2004	2004

The beginning of the changing point of the time series of bicarbonates in the studied area, such as the amounts of calcium, magnesium, electrical conductivity and total solids dissolved in groundwater, occurred in 2006 and continued until 2013. The major failure in the time series of bicarbonates also occurred in the studied area between 2003 and 2010. According to Table 2, the decreasing changes in pH values in the study area started from 2005 at S11 station and continued until 2010 at S16 station. The EC and TDS values also had a failure in the time series in 2001, which continued until 2013.

3.4. The results of examining the spatial changes of the studied variables

In order to investigate changes in the time series from a spatial point of view, the modified Z-statistics of Mann-Kendall test was used in the studied plain aquifer. The results of zoning values of Z-statistics of Mann-Kendall test regarding the changes of the groundwater quality data of the studied area were presented in figures 4 to 13. The red areas in the presented figures show a significant increasing trend at the level of 5% and the green areas also show a significant decreasing trend of the analyzed variables at the level of 5%. Non-significant decreasing and increasing changes can be seen with green and orange colors respectively. According to Figure 4, we can see the spatial changes of calcium values in the period of 1999-2017 in the studied area.

According to Figure 4, it can be seen that the western areas of the studied area and a part of the northern region of it are facing a decreasing trend of annual calcium amounts, and a non-significant increasing trend and a significant increasing trend in the eastern and southeastern areas as well as the center of the aquifer. The dominant trend of the studied area in terms of spatial changes of chlorine according to Figure 5 is increasing, and parts of the eastern and southeastern areas of the aquifer have faced a decrease in chlorine values. The central areas, southwest, north and northeast border of the studied area include an increasing trend in chlorine changes. According to Figure 6 and 14, the focus of decreasing changes in electrical conductivity values and TDS values of the studied aquifer is in the southeast areas, around station S28 and S29, as well as parts of the northeast, and most of the areas are facing an increase in this parameter. The central areas of the studied aquifer faced an increase in electrical conductivity during the period of 1999-2017, and these changes could be due to the reduction of the aquifer's nutrition and the drop in the water level in the studied aquifer. The increase in EC values in the central areas and the southwestern and northwestern border areas of the aquifer can threaten the water quality of this aquifer in terms of drinking, industry and agriculture.

During the studied period, increasing changes in HCO3 values can be observed in most of the studied aquifers as shown in Figure 7. Apart from the southwestern part and the northern boundary of the aquifer, other areas have faced an increasing trend in bicarbonates. The increase of bicarbonate in the groundwater and its use for agriculture causes the sedimentation of significant amounts of calcium and magnesium in the soil. According to Figure 8, we can see the trend of decreasing potassium levels in the central and northwestern areas of the aquifer. In the aquifer of the studied area, the changes in potassium levels are increasing in most areas.

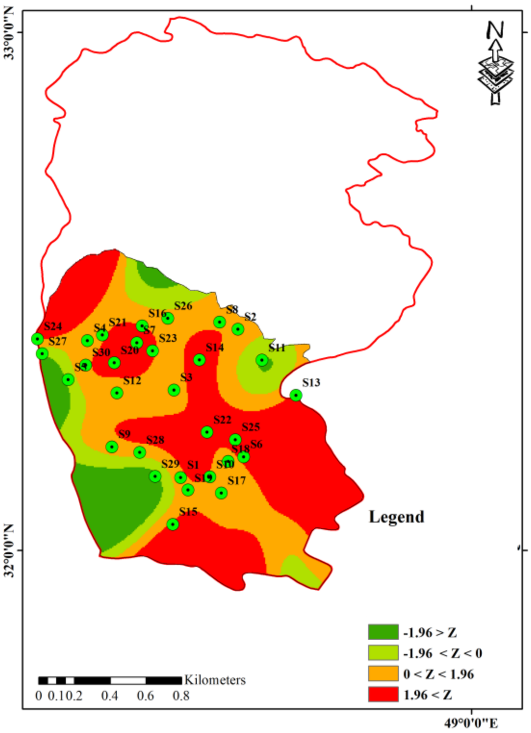

Fig. 4. The results of spatial changes of Ca values in the period of 2007-2017

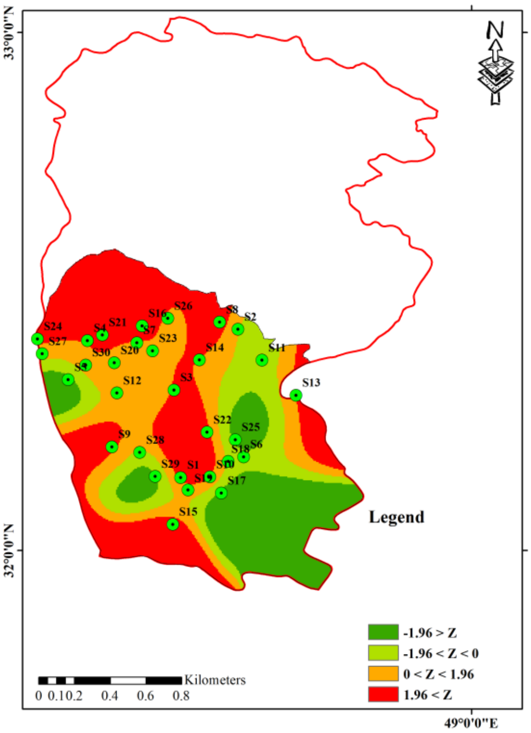

Fig. 5. The results of spatial changes of Cl values in the period of 2007-2017

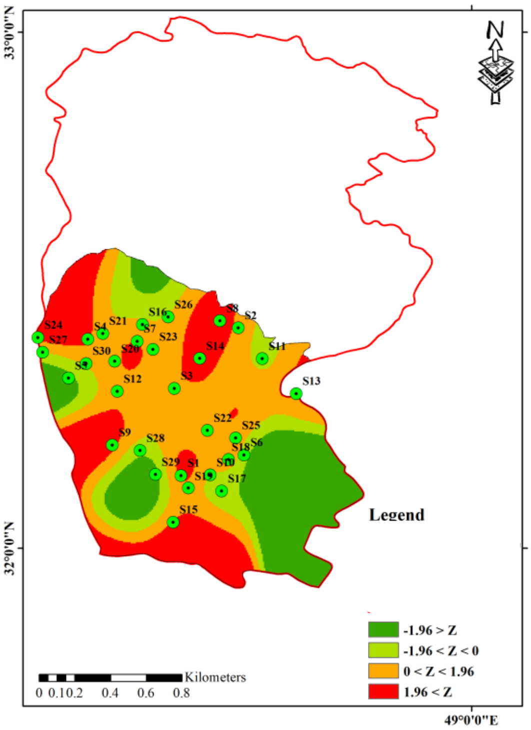

Fig. 6. The results of spatial changes of EC values in the statistical period of 2007-2017

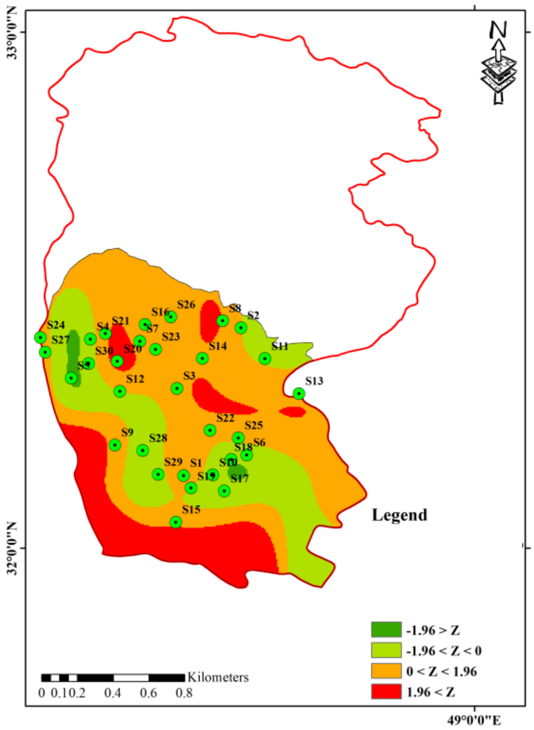

Fig. 8. The results of spatial changes of K values in the statistical period of 2007-2017

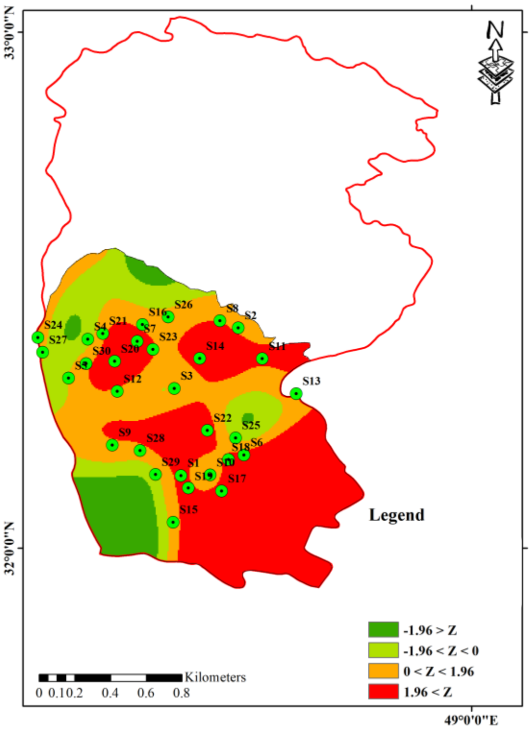

Fig. 7. The results of spatial changes of HCO3 values in the statistical period of 2007-2017

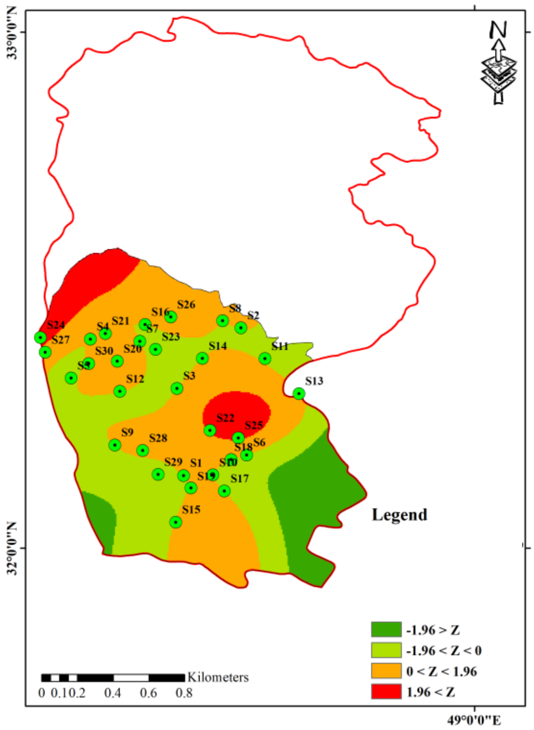

Fig. 9. The results of spatial changes of Mg values in the statistical period of 2007-2017

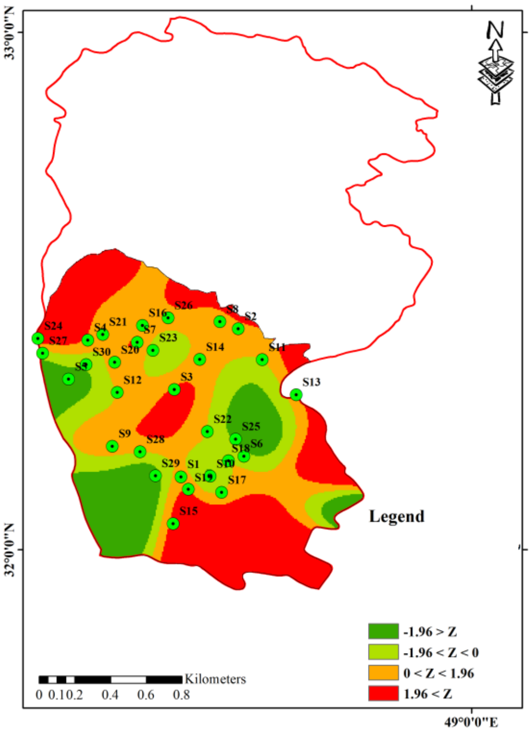

Fig. 10. The results of spatial changes of Na values in the period of 2007-2017

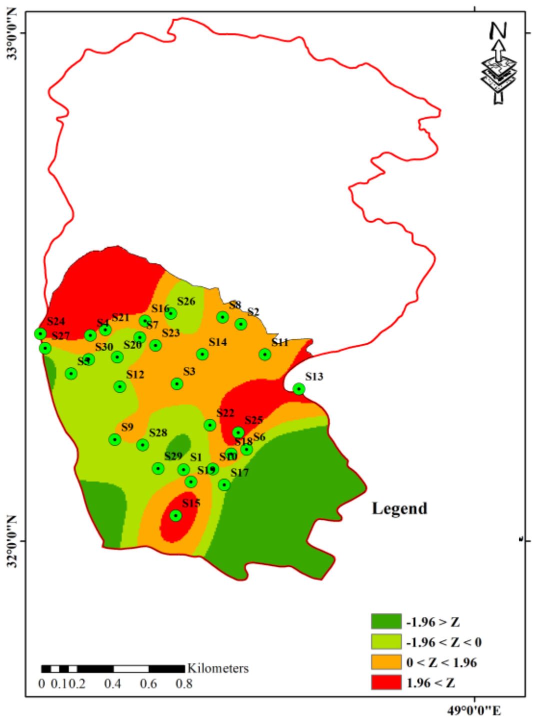

Fig. 12. The results of spatial changes of SO4 values in the statistical period of 2007-2017

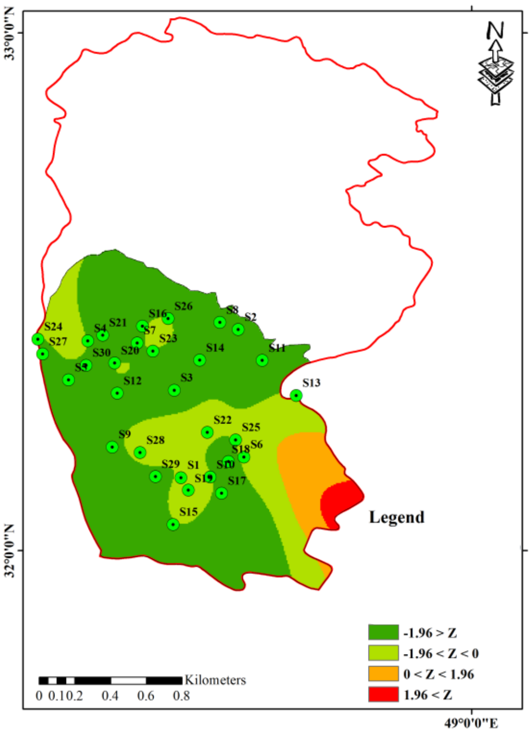

Fig. 11. The results of spatial changes of pH values in the period of 2007-2017

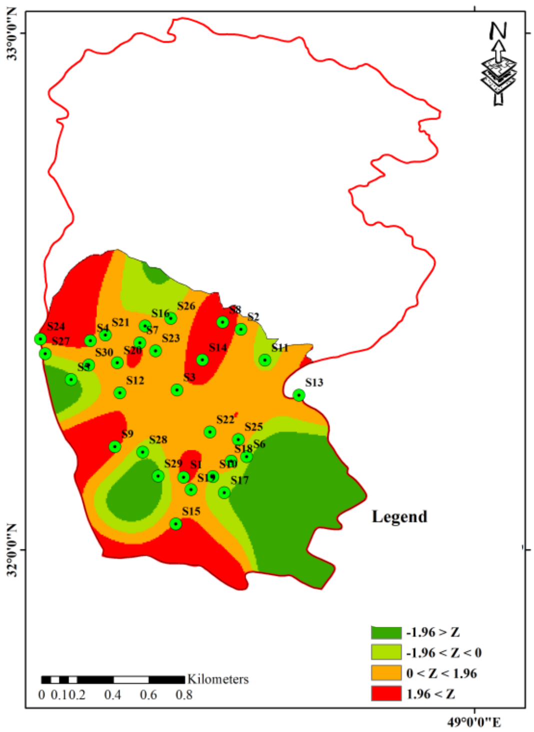

Fig. 13. The results of spatial changes of TDS values in the statistical period of 2007-2017

According to Figure 9, the trend of spatial changes of magnesium values is increasing in the center of the aquifer, the southern and northern areas of the aquifer, and this increase in the northern and central border of the aquifer is significant at the level of 5%.

According to Figure 10, the predominant changes in the amount of sodium in the studied aquifer are increasing, and this increase in annual sodium amounts in the southern, southeastern border, northeastern, parts of the center and also the northern areas of the aquifer is significant at the level of 5%. Unlike the other qualitative studied parameters, and according to Figure 11, it can be seen that almost all the studied area is decreasing in terms of pH changes, and most of the decreasing changes are significant in the studied aquifer at the level of 5%.

According to Figure 12, we can see the decreasing changes in the amount of sulfate dissolved in groundwater in the southeast, western areas and areas of the center of the aquifer. The trend of sulfate changes in the studied aquifer in the stations S15, S13, S22 and the northern and northeastern regions of the aquifer is increasing and significant. The increase in the qualitative values of the investigated area and the aquifer of the studied area during the studied period has caused a decrease in the quality of groundwater in the area, which affects the use of groundwater in the area for drinking. Taj et al. (2018) also stated in their research in Dezful Plain that due to the low quality index of groundwater in the region, digging wells for drinking should be avoided even if possible. Abdi and Zamani (2015) in their research regarding the spatial changes of the quality indicators of groundwater in Dezful plain using geostatistics stated that the zoning maps of the studied geometers indicate the unfavorable condition of the quality of groundwater resources in the southeastern and eastern parts are the plain. The only parameter investigated in this research, whose changing trend was decreasing in all stations, was the pH parameter of groundwater. This parameter has decreased in all stations and on average every year it has decreased by -0.05 units in the whole aquifer.

4. Conclusion

In this study, the modified Mann-Kendall test by removing the effects of internal autocorrelation was used to investigate the temporal and spatial changes of groundwater quality variables in the Dezful-Andimeshk plain in the period of 1999-2017 on an annual scale. The results of the investigation of the changes in the qualitative values showed that among the 30 investigated wells, the changes in the values of potassium, sodium, magnesium, calcium, sulfate, chlorine, bicarbonates, total dissolved solids and electrical conductivity were observed in 60, 67, 80, 87, 57, 74, 87, 74 and 74% respectively in the studied wells were increasing. The only time changes in the acidity values during the investigated period in all the wells was a decrease.

Since the investigation of changes in the quality of groundwater is the first step in monitoring the quality of groundwater in any region, incremental changes in the qualitative values of groundwater in the study area can be an alarm of the increase in groundwater pollutants. Increasing the quality of groundwater limits its use for various purposes. Examining the changes in the slope of the trend line in the studied area showed that the changes in the parameters of potassium, sodium, magnesium, calcium, sulfate, chlorine, bicarbonates, total dissolved solids and electrical conductivity are about 0.00004, 0.027, 0.40, 0.95, 0.04, 0.01, 0.04, 2.02 mg/liter and 2.54 (mmhos/cm) respectively have increased on average each year. Acidity values also decreased on average in the studied aquifer every year by about -0.05.

From a spatial point of view, the changes in calcium, bicarbonate, potassium, magnesium, and sulfate values are increasing in the central and southeastern regions, and this increase covers a larger area of the studied area than the decreasing trend. The trend of increasing changes in EC, TDS and Cl values compared to other parameters has covered a larger area of the studied area. The results of the investigation of the changing point in the time series of the investigated qualitative values showed that the changing point in the time series of potassium, sulfate and chlorine in the groundwater in the studied area occurred earlier than other parameters and in 2000. After that, in 2001, there was a break in the time series of magnesium, calcium, bicarbonates, electrical conductivity and total dissolved solids.

The last parameter that has changed in the study area in the annual time series was the pH parameter in 2005, which behaved differently from other parameters. Since the modified Mann-Kendall statistic removes the effects of internal autocorrelation, it presents the trend of changes and its slope of trend line in real form, which can be the best method for monitoring the quality of groundwater in any region.

5. Disclosure statement

No potential conflict of interest was reported by the authors.

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