Trend in river water quality: tracking the overall impacts of climate change and human activities on water quality in the Dez River Basin

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ABSTRACT

A perceptible degradation in water quality complicates safe water supply for drinking and irrigation purposes. Therefore, this study aims at monitoring water quality changes and effective factors in the Dez River Basin, which are required to manage water resources effectively. To this end, the common influence of flow rate changes on water quality was separated by implementing seasonal Mann–Kendall test on residuals resulting from the LOWESS test. The results show that after adjusting the effects of seasonality and streamflow fluctuations, significant positive trends in most water quality parameters are still observed. It emphasizes the role of other factors controlling river water quality in the basin. Comparison of the trends of modified quality parameter time series (residuals) in different subbasins having natural or mad-made conditions, with or without significant groundwater resources, shows almost the same presented trends in water quality. This supports that, overall, minor changes occurred in land use, groundwater table, and environmental and human factors with no important influences on presented trends in water quality. Our analyses show that overall reduction in precipitation as well as positive trends in temperature and evaporation led to intensified streamflow variations, explaining the main changes in the river water quality of the basin.

Key words | climate change, Dez River Basin, evaporation, seasonal Kendall, water quality

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HIGHLIGHTS

- Developing a new framework using non-parametric statistical tests to monitor changes in surface water quality.
- Assessing the effects of natural and anthropogenic factors on spatio-temporal variations of water quality.
- Providing valuable information on temporal change of water quality in arid and semi-arid regions of Iran.

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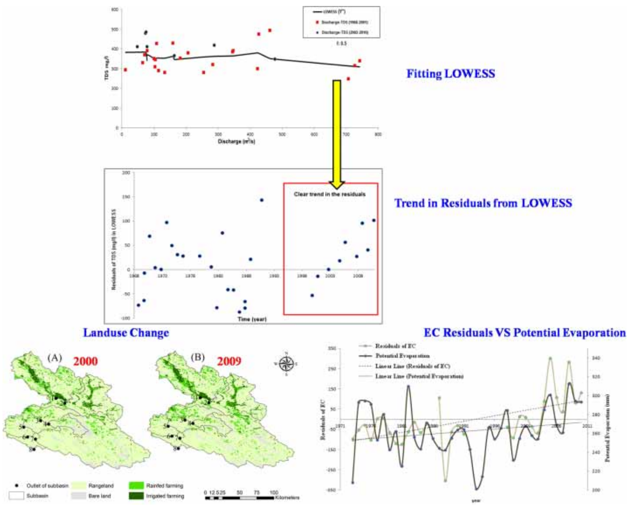
GRAPHICAL ABSTRACT



INTRODUCTION

The Dez River, as the second largest river in Iran and one of the major tributaries of the Karun River, is one of the main water resources in the Khuzestan province in order to provide fresh water needed for drinking, domestic uses, and agriculture purposes. Hence, besides water quantity, it is important to evaluate the water quality of the Dez River Basin. In arid and semi-arid climates, with considerable shortage of potable water, monitoring of river water quality and the influencing factors should receive great importance. Analysis of water quality as well as monitoring possible water quality changes are important tasks for better management of water resources. Therefore, many studies have considered these issues in different parts of the worlds (Luo *et al.* 2011; Ballantine & Davies-Colley 2014; Sayemuzzaman *et al.* 2018) and on a global scale (Jiang *et al.* 2014). Water quality can be affected by anthropogenic activities such as land use change (Soko & Ababio 2015; Shrestha *et al.* 2018; Wijesiri *et al.* 2018), chemical toxin discharge (Gevrey *et al.* 2010), as well as hydrometeorological changes of temperature (Crossman *et al.* 2013), evaporation (Abdel Wahed *et al.* 2014), rainfall and streamflow (Tabari *et al.* 2011; Xie *et al.* 2015; Murphy & Sprague 2019). Assessment of long-term trends in water quality parameters can be considered as an appropriate approach to determine any environmental changes over time, help to identify and analyze the most substantial factors affecting the water quality (Ballantine & Davies-Colley 2014; Goodrow *et al.* 2017), and clarify some new aspects of hydrological processes. There are various measures to determine the trend in water quality time series that can be named as time series analysis methods (Long *et al.* 2009) including parametric (Kundzewicz & Robson 2004; Yenilmez *et al.* 2011) and non-parametric tests (Bouza-Deano *et al.* 2008). Due to skewness, serial correlation, non-normal data, 'less-than' (censored) values, outliers, and missing values in hydrological data, it is recommended to use non-parametric methods to determine the trend of water quality parameters (Helsel & Hirsch 1992; Hamed & Rao 1998; Mozejko 2012). Hence, based on several studies, in different parts of the world, the non-parametric Mann–Kendall method and Sen's slope test (Yenilmez *et al.* 2011; Naddeo *et al.* 2013; Ballantine & Davies-Colley 2014; Entry & Gottlieb 2014; Niazi *et al.* 2014; Yevenes *et al.* 2018; Chen *et al.* 2019), seasonal Kendall (Helsel & Hirsch 2002; Ballantine & Davies-Colley 2014; Dabrowski *et al.* 2014; Entry & Gottlieb 2014; Hughes & Quinn 2014; Cloern 2019), and LOWESS (Helsel & Hirsch 2002; Hughes & Quinn 2014; Entry &

Gottlieb 2014; Ahn & Kim 2019; Biswas & Mosley 2019) have been chosen to assess the possible trend in water quality time series.

In river basin management, analysis of the relationship between water quality parameters and streamflow rate is a crucial step to distinguish changes in water quality (Assilis *et al.* 2001). Therefore, this case study considers the influence of common seasonal fluctuations and flow rate changes on water quality using a set of non-parametric statistical techniques, i.e., modified Kendall, LOWESS, and seasonal Kendall on residues resulting from the LOWESS test, to identify possible climate, environmental, and anthropogenic factors controlling water quality changes in the Dez River Basin.

MATERIALS AND METHODS

Study area and data set

The Dez River Basin, located in the western part of Iran between 48° 22′ 16″ to 50° 18′ 54″ E and 32° 33′ 48″ to 34° 06′ 52″ N, covers approximately 15,990 km^2. Elevation of the study site ranges from 292 to 4,049 meters above sea level (masl), and the length of the river is 415 km (Figure 1). The basin receives an average annual precipitation of 100 to 460 mm, mostly in winter (70–80%), especially during February and March. The average annual temperature and actual evaporation are 16 °C and 260 mm, respectively. The dominant land-use type in the Dez River Basin is rangeland. Land-use proportions were derived from satellite images – Landsat 4–5 Thematic Mapper (TM) images acquired in 2000 and 2009 (USGS 2019). To accurately identify the farming areas, the could-free images were selected as they are representative of the cropping season of the basin (Wilken *et al.* 2017). Land-use maps were provided using the Semi-Automatic Classification Plugin (SCP), version 6.4.2 in QGIS environment. The hydrochemical parameters of streamflow were monitored in a monthly time interval over 44 years (1967–2010) at 12 monitoring sites by the Ministry of Energy of Iran. These sites are scattered within the study area and covered the main river channel (the Dez River) and some important tributaries

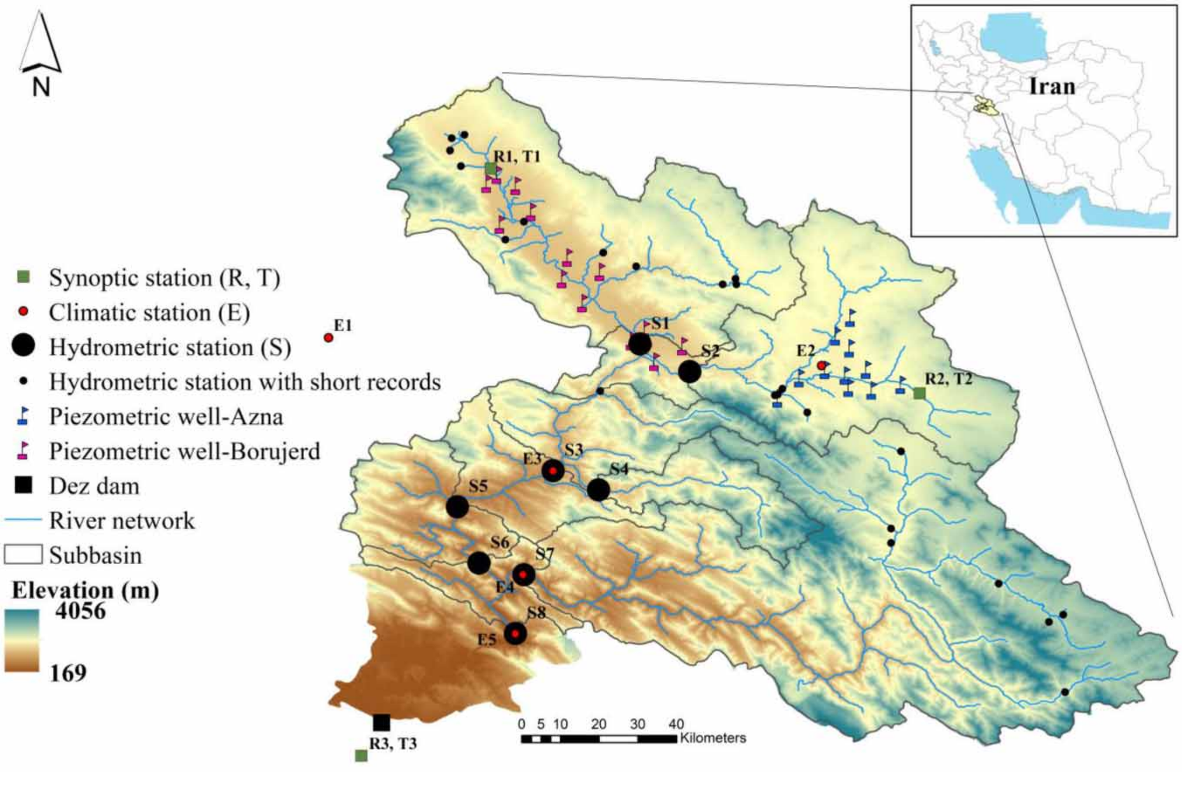


Figure 1 | Study area and location of monitoring sites.

(Figure 1). For water quality analysis, eight stations including Dorud Tireh (S1), Marbareh (S2), Sepid Dasht Cezar (S3), Sepid Dasht Zar (S4), Keshvar Sorkhab (S5), Tangeh Panj Cezar (S6), Tangeh panj Bakhtiar (S7), and Taleh Zang (S8), were selected based on their time series length and quality of data (Table 1). Human activities such as dam construction do not effect these monitoring sites. In addition, there are no main industrial companies in the upstream of the Dez River, where cities are located in the downstream of the Dez dam. The Dez dam is located in the downstream of the outlet of the study area (Figure 1).

Ten hydro-chemical parameters including electrical conductivity (EC), pH value (pH), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), total dissolved solids (TDS), and sodium adsorption ratio (SAR), were monitored and analyzed by Iran Water Resources Management Company (IWRMC) at monthly intervals. EC and pH were measured in the field by portable multi-parameter water quality meter. TDS were determined by gravimetric analysis. The dissolved water samples were shipped to the laboratories of IWRMC for analysis of Ca^{2+} and Mg^{2+} (by EDTA titration), Na^+ (by flame photometer), SO_4^{2-} (by barium chloride titration), HCO_3^- (by sulfuric acid titration), and Cl^- (by silver nitrate titration). SAR, generally used to assess water suitability for irrigation, was calculated using Na^+, Ca^{2+}, and Mg^{2+} concentrations. It should be noted that time series were entirely checked by graphical and statistical methods for outliers and any possible errors. However, missing values in time series (no sampling dates or deleted data as results of our data quality check) were not estimated because of possible uncertainty in reconstruction of water quality data.

In order to consider the effect of seasonal patterns on water quality, temporal trend in water quality is assessed by seasonal Kendall test, after preparing water quality time series. The Mann–Kendall method is the most common non-parametric test (Kendall 1975) for assessing trends in water quality parameters and hydrological components (Cloern 2019). For the detection of trends in precipitation, temperature, evaporation, and discharge time series, the modified Mann–Kendall test (Hamed & Rao 1998) is used. Serial correlation is considered following the methodology used by Kumar *et al.* (2009). Further information about the modified Mann–Kendall test is available in Mahmoodi *et al.* (under review). In the next step, the LOWESS test is applied to distinguish the effects of discharge, as an exogenous variable, on water quality variations. Then, seasonal Kendall test is performed on the residuals from LOWESS to assess trend in water quality time series when the main exogenous effect (effects of discharge) is considered and removed. Residuals from LOWESS test were considered to search another possible controller of water quality in the Dez River Basin. The slope of the trend line is estimated by Theil–Sen method.

Seasonal Kendall test (SK)

Obviously, most parameters of the surface water quality show a strong seasonal pattern (Helsel & Hirsch 1992). In order to identify trends in surface water quality over time, like other exogenous effects, the seasonal effects should be

Table 1 | Physiographic characteristics of the selected stations

River name	Station name	Code	Longitude (degrees east)	Latitude (degrees north)	Elevation (masl)	Drainage area (km^2)	Available records
Tireh	Dorud Tireh	S_1	49.03	33.28	1,450	3,400	1955–2010
Marbareh	Marbareh	S_2	49.04	33.28	1,450	2,655	1955–2010
Cezar	Sepid Dasht Cezar	S_3	48.53	33.13	970	7,170	1955–2010
Zar	Sepid Dasht Zar	S_4	48.53	33.13	970	680	1955–2010
Sorkhab	Keshvar Sorkhab	S_5	48.37	33.08	770	336	1962–2010
Cezar	Tangeh Panj Cezar	S_6	48.45	32.56	600	9,410	1967–2010
Bakhtiar	Tangeh panj Bakhtiar	S_7	48.46	32.56	600	6,432	1955–2010
Dez	Taleh Zang	S_8	48.46	32.49	480	16,213	1955–2010

Data source: Ministry of Energy (MOE), Iran.

eliminated (Helsel & Hirsch 1992). In seasonal Kendall method, seasons should be defined (Helsel & Hirsch 1992). Since the Dez River Basin records were collected at monthly intervals, seasons are considered according to 12 months or 12 seasons. Seasonal Kendall test is performed according to separate calculation of Mann–Kendall on M season or month and then statistical test is measured by combination of results. The water quality data for each season (in this study, for each month) compare to the data of other years in the same season (in this study, in the same month) (Helsel & Hirsch 1992; Ballantine & Davies-Colley 2014). By summing the S Kendal data for each season (S_i), the overall statistics of seasonal Kendal S_k is calculated as follows:

$$S_k = \sum_{i=1}^{m} S_i$$

The null hypothesis in this test is defined as the absence of trend in the time series. In the absence of trend, S_k will have a normal distribution and its average ($\mu_{sk} = 0$), and variance (σ_{sk}) can be calculated as follows:

$$\mu_{sk} = 0,$$

$$\sigma_{sk} = \sqrt{\sum_{i=1}^{m} \left(\frac{n_i}{18}\right) * (n_i - 1) * (2n_i + 5)}$$

where (n_i) is the number of data in the i^{th} season.

The Z_{sk} seasonal Kendall statistic can be calculated as follows:

$$Z_{sk} = \begin{cases} \dfrac{S_k - 1}{\sigma_{sk}} & if \quad S_k > 0 \\ 0 & if \quad S_k = 0 \\ \dfrac{S_k + 1}{\sigma_{sk}} & if \quad S_k < 0 \end{cases}$$

Positive values of S_k indicate a positive trend, and vice versa. The test statistic Z_{sk} gives the significance level of rejecting the null hypothesis (Kumar *et al.* 2009). Therefore, if the test statistic is smaller than the Z_{crit} statistical value of the considered significance level (such as ±1.645 for a confidence level of 90%), then the identified trend is not significant (Carmona & Poveda 2014).

Sen's slope estimator

The slope of the trend line can be calculated by Theil–Sen method as follows:

$$Q = \text{median} \frac{X_j - X_k}{j - k}$$

where Q is the slope of the trend line between consecutive data X_j and X_k, at times j and k, respectively, and J is always greater than K. Positive values indicate increasing trends and negative values indicate decreasing trends.

LOWESS (locally weighted scatter plot smoothing)

After elimination of seasonal variations, other variables can affect water quality parameters where the river discharge is the main variable. For a more detailed analysis of trend in water quality and separating the effect of discharge, LOWESS test was applied to all time series. As well as LOWESS test separating the effect of discharge, studying the residuals is an appropriate approach to determine the role of other possible environmental factors affecting water quality, such as changes in groundwater–surface water interaction, temperature, evaporation, etc. After obtaining water quality parameter values (Y'') using LOWESS curve, residuals (R) can be calculated as follows:

$$R = Y - Y''$$

where Y and Y'' are observed and estimated (by LOWESS) water quality parameter values, respectively. The smoothing technique, LOWESS, will define the relationship between water quality parameters and river discharge without assuming the normality of residuals or linear relationship (Helsel & Hirsch 1992). In this regard, an example is presented in Figure 2 where LOWESS is fitted on TDS versus discharge data at station S_8. Using such fitting curve, the residual values were calculated for all quality parameters at all monitoring sites. For example, in Figure 3, the residuals from the last nine years are plotted mainly above the smoothed fitted line, means higher TDS values for the same discharge values in the last nine years. This increasing trend in the given

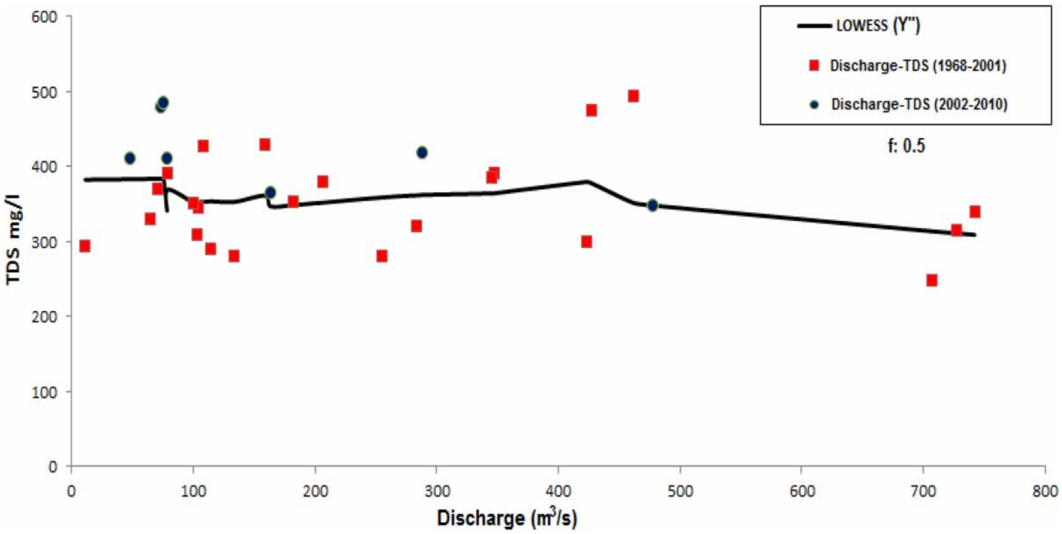


Figure 2 | Fitting LOWESS to TDS data at S_8.

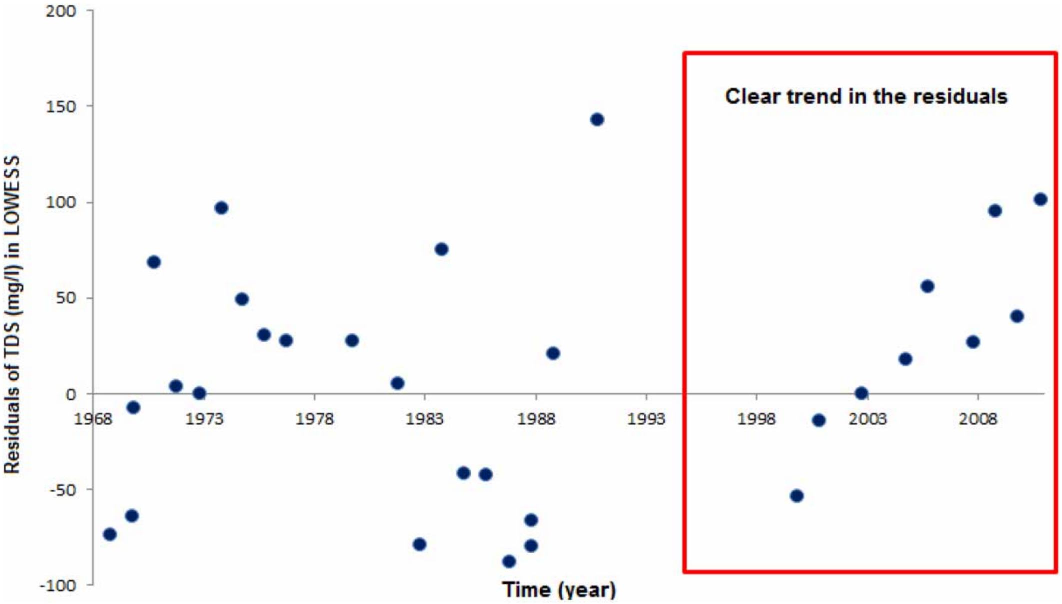


Figure 3 | Residual from LOWESS test for TDS records at S_8 (residuals were derived from Figure 2).

residual time series may illustrate changes in some other variables than discharge, affecting TDS values.

Moreover, besides searching for possible correlation of different variables with the residuals' time series from LOWESS test, seasonal Kendall test on residuals of LOWESS test is performed, to search any possible trend in controller of river water quality beyond discharge effects. Smoothing factor (f) in the LOWESS test should be selected rationally and reasonably based upon the target of smoothing factor (Helsel & Hirsch 1992), that $f \approx 0.5$ in most cases of this study was found to be ideal (the same value is reported by Dabrowski *et al.* 2014).

Serial correlation

The lack of internal correlation between the data is required for using non-parametric tests. It is because such correlations can have an effect on data analysis and significance of trend statistics (Kumar *et al.* 2009). Therefore, the effects of autocorrelation were considered in trend analysis of whole time series data.

Categorization of trends

The significance levels were considered at confidence levels of 90, 95, and 99%. Z_{crit} statistical values of these considered significance levels are ±1.645, ±1.96, and ±2.575, respectively.

Trend test results are categorized as being significant or non-significant as follows:

1. No significant change: the null hypothesis for the modified Mann–Kendall test or seasonal Kendall test was not rejected (If $-Z_{crit} < Z\ (Z_{sk}) <+ Z_{crit}$).
2. Significant increase/decrease: the null hypothesis for the modified Mann–Kendall test or seasonal Kendall test was rejected (If $-Z_{crit} > Z\ (Z_{sk})$ or $Z\ (Z_{sk}) >+ Z_{crit}$).

RESULTS

Seasonal Kendall test (SK) and removing the effect of seasonal variations

Due to a strong seasonal pattern in surface water quality, the elimination of the seasonal effects can help to have more detailed trend analysis. Therefore, by using the seasonal Kendall test, the trend of water quality parameter without the seasonal effects was determined (Table 2). It shows the general trend of water quality after adjustment for seasonal variations. Ca^{2+}, HCO_3^-, and Mg^{2+} at all stations show rising trends at confidence level of 95% and increasing trends in EC and TDS were significant for most sites. The slopes of the trend lines are calculated by Theil–Sen method in Table 3. Considering the seasonal variations, there are still many significant changes in water quality which corroborate the role of other factors in water quality changes. In the next section, the effects of the main controllers of water quality, i.e., streamflow, are also removed by LOWESS test and then seasonal Kendall test is performed on the residuals of LOWESS test to explore the effects of other water quality controllers in the study area. Temporal trends in streamflow discharge of the Dez River Basin for given stations is reported by Mahmoodi *et al.* (under review).

LOWESS test and removing the effect of discharge variations

After eliminating seasonal variations, the second major external variable affecting water quality is discharge and its temporal changes. For elimination of discharge effect and more detailed trend analysis of water quality, the LOWESS test is executed. Therefore, water quality data (Y) against discharge were plotted, then a smooth fitted line defined by LOWESS test and residuals (the differences between observed values (Y) and the y-value on the fitted line (Y'')) were calculated. In the next step, to identify trends, seasonal Kendall test was applied on the residuals' time series. The results of trend analyses on the residuals are presented in Table 4. As the results demonstrate, most of the water quality parameters show positive significant changes. For all monitored stations, increasing trends in Mg^{2+}, HCO_3^- are observed at confidence level of 95% and for Ca^{2+} at confidence level of 90%. TDS and EC also carry inclining significant trends in confidence level of 95%, at all stations except S_5. pH is the only parameter showing no significant trend for all the stations except S_5, when discharge effect is eliminated. There were some declining trends of SO_4^{2-}, Na^+, and SAR in some sites. The slopes of the trend lines calculated by Theil–Sen method are presented in Table 5. After elimination of the two major exogenous variables, i.e., discharge and seasonal patterns, any possible effects on water quality can be clarified by searching the relevance between environmental and anthropogenic activities and the residuals from LOWESS. In other words, these analyses reveal the possible effects of some other environmental factors on surface water quality, such as change in surface water–groundwater interaction, precipitation, temperature, evaporation, and any other human activities (such as land-use changes). Also, it

Table 2 | Values of Z_{sk} for hydrochemical time series at eight monitoring sites; values higher than +1.645 indicate significant positive trends and values lower than −1.645 signify significant negative trends (for a confidence level of 90%)

	Z_{sk}-seasonal Kendall									
Station	**Ca^{2+}**	**Cl^-**	**EC**	**HCO_3^-**	**Mg^{2+}**	**Na^+**	**pH**	**SAR**	**SO_4^{2-}**	**TDS**
S_1	7.05*	– 0.79^{ns}	No data	4.916*	3.017*	– 6.463*	– 1.469^{ns}	– 7.599*	– 0.94^{ns}	4.267*
S_2	8.015*	5.773*	8.458*	7.137*	3.132*	– 2.813*	– 1.395^{ns}	– 4.696*	0.129^{ns}	8.533*
S_3	9.595*	7.556*	8.457*	7.266*	4.897*	3.477*	1.588^{ns}	– 8.184*	0.821^{ns}	6.114*
S_4	6.995*	6.685*	4.124*	4.21*	2.919*	No data	0.628^{ns}	– 0.41^{ns}	– 2.67*	4.055*
S_5	7.275*	– 0.02^{ns}	0.996^{ns}	5.714*	2.679*	– 7.049*	– 3.387*	– 8.164*	– 4.69*	0.996^{ns}
S_6	2.082*	8.726*	4.232*	2.33*	4.337*	3.986*	– 1.198^{ns}	2.576	– 2.78*	4.927*
S_7	3.105*	2.748*	0.952^{ns}	4.576*	4.594*	– 0.518^{ns}	0.819^{ns}	– 2.079*	– 4.82*	2.515*
S_8	5.185*	4.147*	3.056*	6.012*	3.658*	1.337^{ns}	0.871^{ns}	– 0.57^{ns}	– 3.95*	3.485*

^{ns}Indicates no significant trend at the 90% confidence level.

*Indicates significant trend at the 90% confidence level.

Table 3 | Slope of significant trend (according to Table 2) in hydrochemical time series by Sen's slope estimator

	Slope of trend by Sen's slope estimator-seasonal Kendall									
Station	**Ca^{2+} mg/L/year**	**Cl^- mg/L/year**	**EC μS/cm/year**	**HCO_3^- mg/L/year**	**Mg^{2+} mg/L/year**	**Na^+ mg/L/year**	**pH per year**	**SAR Per year**	**SO_4^{2-} mg/L/year**	**TDS mg/L/year**
S_1	0.044	–	No data	0.042	0.096	– 0.025	–	– 0.021	–	2.755
S_2	0.036	0.065	4.991	0.032	0.093	– 0.031	–	– 0.044	–	3.19
S_3	0.021	0.009	2.64	0.019	0.067	0.038	–	– 0.007	–	1.706
S_4	0.013	0.005	0.882	0.009	0.003	No data	–	–	– 0.002	0.513
S_5	0.032	–	–	0.018	0.007	– 0.048	– 0.011	– 0.038	– 0.022	–
S_6	0.004	0.013	1.630	0.006	0.009	0.005	–	0.002	– 0.006	1.043
S_7	0.009	0.010	–	0.009	0.006	–	–	– 0.002	– 0.005	0.840
S_8	0.010	0.009	1.249	0.012	0.005	–	–	–	– 0.005	0.799

Table 4 | Values of Z_{sk} for the residuals from LOWESS test at eight monitoring sites; values higher than +1.645 indicate significant positive trends and values lower than −1.645 signify significant negative trends (for a confidence level of 90%)

	Z_{sk} in LOWESS									
Station	**Ca^{2+}**	**Cl^-**	**EC**	**HCO_3^-**	**Mg^{2+}**	**Na^+**	**pH**	**SAR**	**SO_4^{2-}**	**TDS**
S_1	7.315*	– 2.2*	No data	5.187*	2.003*	– 6.96*	– 1.61^{ns}	– 8.66*	– 1.22^{ns}	4.149*
S_2	7.862*	5.947*	8.202*	7.145*	3.011*	– 2.93*	– 1.09^{ns}	– 4.67*	0.727^{ns}	8.353*
S_3	9.762*	7.007*	8.103*	7.159*	4.48*	1.911*	1.325^{ns}	– 1.99*	0.753^{ns}	7.48*
S_4	7.689*	6.041*	4.8*	5.27*	3.239*	No data	0.575^{ns}	– 3.79*	– 2.06*	4.264*
S_5	6.977*	– 0.81^{ns}	0.619^{ns}	5.014*	2.07*	– 5.97*	– 3.41*	– 6.81*	– 3.35*	0.811^{ns}
S_6	1.829*	7.745*	3.65*	2.223*	4.11*	2.273*	– 1.64^{ns}	0.459^{ns}	– 2.83*	4.359*
S_7	3.849*	3.471*	2.336*	4.464*	4.776*	1.352^{ns}	0.804^{ns}	– 0.14^{ns}	– 3.03*	3.424*
S_8	5.352*	4.469*	3.424*	5.919*	4.09*	2.455*	1.324^{ns}	0.892^{ns}	– 2.8*	3.829*

^{ns}Indicates no significant trend at the 90% confidence level.

*Indicates significant trend at the 90% confidence level.

Table 5 | Slope of significant trend (Table 4) in hydrochemical time series by Sen's slope estimator

	Slope of trend by Sen's slope estimator-seasonal Kendall									
Station	**Ca^{2+} mg/L/year**	**Cl^{-} mg/L/year**	**EC μS/cm/year**	**HCO_3^- mg/L/year**	**Mg^{2+} mg/L/year**	**Na^{+} mg/L/year**	**pH Per year**	**SAR Per year**	**SO_4^{2-} mg/L/year**	**TDS mg/L/year**
S_1	0.040	– 0.007	No data	0.034	0.012	– 0.026	–	– 0.021	–	2.692
S_2	0.034	0.005	5.000	0.030	0.009	– 0.004	–	– 0.005	–	3.364
S_3	0.021	0.008	2.456	0.019	0.006	0.003	–	– 0.010	–	1.364
S_4	0.013	0.004	0.923	0.009	0.003	No data	–	– 0.006	– 0.003	0.625
S_5	0.030	–	–	0.018	0.010	– 0.045	– 0.009	– 0.035	– 0.027	–
S_6	0.006	0.012	1.375	0.005	0.008	0.005	–	–	– 0.005	1.277
S_7	0.007	0.006	0.380	0.008	0.006	–	–	–	– 0.008	0.714
S_8	0.010	0.007	1.062	0.012	0.005	0.002	–	–	– 0.006	0.881

might help for better understanding the changes in river water quality and identifying any possible controller.

Other possible controllers of water quality in the Dez River Basin

Land-use change and human influence

Due to the non-industrialized condition of the district, the most important human activity that might affect water quality is land-use change (Shrestha *et al.* 2018). The different pattern of sediment production in response to land-use change could result in water quality degradation (Bussi *et al.* 2016). Sediment loadings transported from the basin into the river results mainly from agriculture intensification (Taniwaki *et al.* 2017). The spatial distribution of the major land-use classes in 2000 and 2009 are shown in Figure 4. The available could-free Landsat images that cover the whole basin in the mosaic manner within the same season, to accurately represent land uses, limit our analysis of land-use change for the years 2000 and 2009. In the year 2000, the Dez River Basin catchment is dominated by rangeland (77.1%). Bare land covers 7.1% and is mostly found at the middle part of the basin (subbasins 4 and 7). Rainfed and irrigated farming areas accounted for 8.8% and 6.9% of the study area and are mainly found in the northern part of the basin (subbasins 1 and 2). Comparing the land-use map of the years 2000 and 2009, the most

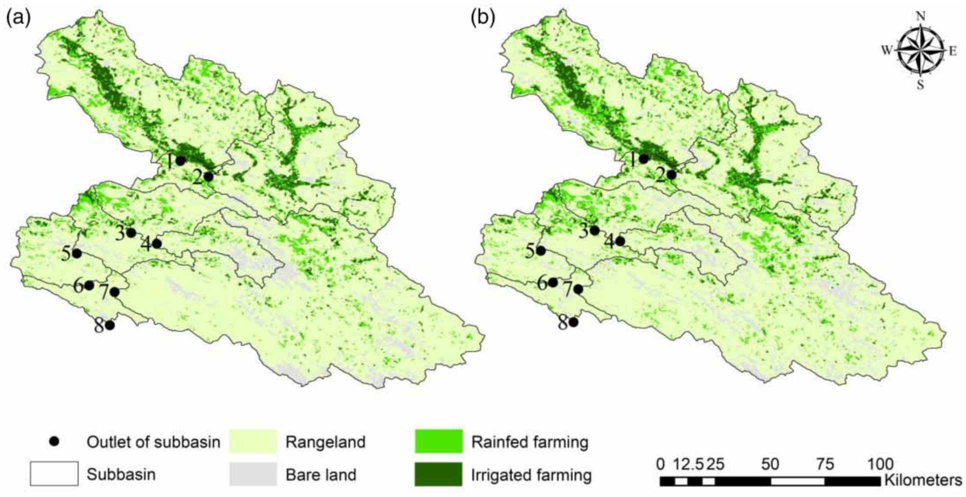


Figure 4 | Land-use map of study area in 2000 (a) and 2009 (b).

obvious changes occurred in the rangeland areas, about +3.9% (Table 6). From 2000 to 2009, the areal coverage of bare land and irrigated farming decreased by −2% and −1.7%, respectively, while the percentage of change for rainfed farming is almost null (0.2%). This shows that those reductions in bare land and agricultural areas could lead to decreasing sediment production in the whole basin and improve the water quality. However, despite this fact, water quality parameters mainly experienced an increasing trend (Table 4, S_8). This means, although the change in land use could have an impact on water quality of the Dez River Basin; it is not the main driver over the study period. Moreover, this could be supported by the results in the smaller scale, comparing subbasin 2, where the main reduction occurred in the area of rainfed farming (−2%), irrigated farming (−4.8%), and bare land (−9.7%), with other subbasins. A trend pattern of river water quality at this station is quite similar to others.

Possible changes in groundwater levels (an environmental factor resulted from natural and man-made change)

The relationship between surface water and groundwater is inevitable, as in most arid and semi-arid basins in Iran such as central wadis, the base flow is supplied by shallow aquifer (Mahmoodi *et al.* 2020a, 2020b). In a particular area, a large difference between surface water and groundwater quality is common. In the Dez Basin, EC of groundwater is greater than the EC of surface water. Therefore, the different contribution of groundwater in streamflow can alter streamflow quality where there is an important interaction. Temporal trend in groundwater levels is monitored at 11 piezometric wells in Azna-Aligudarz plain and 13 piezometers in Doroud-Borujerd from 2001 to 2010. The modified Mann–Kendall test is applied to these available short time series (Table 7). The geographical positions of piezometers are presented in Figure 1. The results of the test show mostly declining trends in groundwater level of both aquifers, but these negative trends are significant only in P_2 and P_4 in Azna-Aligudarz plain and in P_1, P_8, P_{11}, and P_{12} in Doroud-Borujerd plain at a confidence level of 90%. Obviously, because of higher EC of groundwater rather than that of surface water, declining trends in groundwater levels can improve surface water quality in rivers which are affected by groundwater depletion and result in negative trends of EC values of surface water. While EC of surface water has positive significant trends in many cases, especially for station S_2, it can be interpreted that the minor declining trends in groundwater table cannot explain the observed positive trends in surface water quality constituents.

Table 6 | Percentage (%) of land-use changes for subbasins from 2000 to 2009

		Subbasin							
Land-use classes	**Year**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Bare land	2000	1.5	5.8	3.5	15.9	6.1	5.6	11.1	7.1
	2009	2.4	3.3	3.7	6.2	4.8	4.9	10.1	5.1
	Change (%)	**0.9**	**− 2.5**	**0.2**	**− 9.7**	**− 1.3**	**− 0.7**	**− 1.0**	**− 2.0**
Rangeland	2000	73.4	75.9	74.7	81	74.5	77.7	82.9	77.1
	2009	76.5	85.2	76.5	90.9	77.1	78	83.1	81
	Change (%)	**3.1**	**9.3**	**1.8**	**9.9**	**2.6**	**0.3**	**0.2**	**3.9**
Irrigated farming	2000	11.1	10.9	9.4	0.8	8.1	6.9	1.3	6.9
	2009	8.7	6.1	7.6	0.6	6.7	6.1	1.2	5.3
	Change (%)	**− 2.4**	**− 4.8**	**− 1.8**	**− 0.2**	**− 1.4**	**− 0.8**	**− 0.1**	**− 1.7**
Rainfed farming	2000	14.0	7.5	12.4	2.3	11.2	9.8	4.6	8.8
	2009	12.4	5.5	12.2	2.3	11.3	11.0	5.6	8.6
	Change (%)	**− 1.6**	**− 2.0**	**− 0.2**	**0.0**	**0.1**	**1.2**	**1.0**	**− 0.2**
Total area (km^2)		**3,340**	**2,508**	**7,099**	**640**	**8,499**	**9,288**	**6,276**	**15,990**

+, Increasing; −, decreasing.

Table 7 | Z values of modified Mann–Kendall test for groundwater table records in Azna-Aligudarz and Doroud-Borujerd plains

Azna-Aligudarz Plain	P	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}	P_{11}		
	Z	0.00^{ns}	-1.85^{*}	-1.60^{ns}	-1.85^{*}	0.10^{ns}	-1.36^{ns}	-0.37^{ns}	-0.31^{ns}	-0.94^{ns}	-1.11^{ns}	-1.35^{ns}		
Doroud-Borujerd Plain	P	P_1''	P_2''	P_3''	P_4''	P_5''	P_6''	P_7''	P_8''	P_9''	P_{10}''	P_{11}''	P_{12}''	P_{13}''
	Z	-2.35^{*}	-0.74^{ns}	-1.36^{ns}	-1.36^{ns}	0.93^{ns}	-0.12^{ns}	-1.11^{ns}	-2.35^{*}	0.49^{ns}	0.37^{ns}	-2.10^{*}	1.85^{*}	0.61^{ns}

P, piezometer.

^{ns}Indicates no significant trend at the 90% confidence level.

*Indicates significant trend at the 90% confidence level.

Precipitation and streamflow discharge variations

One of the climate factors affecting streamflow is precipitation, which can change water quality by change in river discharge. As mentioned in previous sections, streamflow discharge is the main controller of stream water quality around the world, but it is not responsible for the whole change in river water quality. The trend in precipitation of three rain gauges R_1, R_2, and R_3 (Figure 1) was analyzed. More details are available in Mahmoodi *et al.* (under review). They reported that the trends were not significant for any of the mentioned stations, but streamflow reductions were possibly caused by overall reductions in precipitation. Due to a general strong relation between both precipitation and discharge with water quality, any small changes in precipitation, and consequently streamflow rates, can lead to significant changes in water quality parameters. Therefore, it can be concluded that precipitation may justify parts of the observed trends in the Dez River water quality thorough changes in the Dez River water quantity.

Temperature and evaporation variations

The effects of temperature on evaporation rate, discharge, and, in addition, on dissolution can influence river water quality. Hence, the temporal changes in temperature at three stations T_1, T_2, and T_3 were analyzed by modified Mann–Kendall test. The overall results show positive significant trends in T_2 (at confidence level of 90%), T_1 and T_3 (at confidence level of 99%). Hence, variations in temperature are in accordance with trends of residuals' time series of water quality extracted from LOWESS test. Therefore, beside discharge effects, temperature variations may have a considerable influence on water quality by changing the river water quantity in the Dez River Basin.

Evaporation, as one of the related factors under the influence of temperature, can change water quality by change in salt quantity. The variations of potential evaporation in the five stations of E_1, E_2, E_3, E_4, and E_5 (Figure 1), is also provided in more detail by Mahmoodi *et al.* (under review). The results highlight positive significant trends at confidence level of 95% in all monitoring stations, which is in agreement with trend in river water quality (the residuals from LOWESS test). Figures 5 and 6

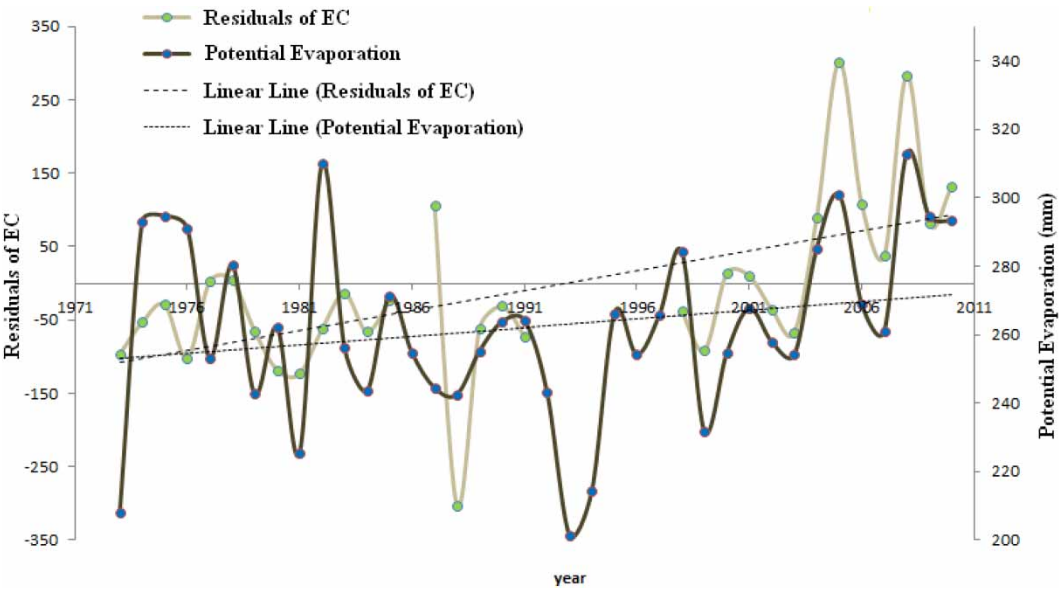


Figure 5 | Residuals of EC at S_8 versus evaporation records of E_5 in October. Note: there are some missing values in EC time series.

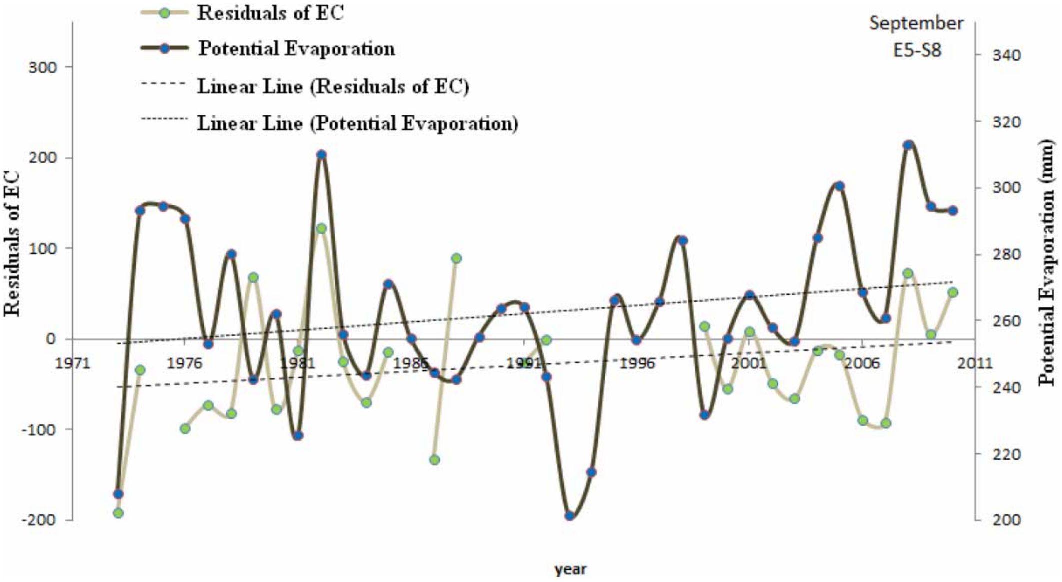


Figure 6 | Residuals of EC at S_8 versus evaporation records of E_5 in September. Note: there are some missing values in EC time series.

show the relationships between residuals of EC (as a principal water quality parameter) at S_8 and monthly evaporation at E_5 for October and September. These graphs draw attention to changes in evaporation, resulting from trends in temperature in the Dez River Basin, which might have a key role in water equality degradation.

DISCUSSION

After an integrated temporal trends' analysis of river water quality, the role of environmental and human factors (in agreement with Ballantine & Davies-Colley 2014) as well as seasonal changes and discharge affect are presented in a comprehensive analysis by a set of non-parametric tests (seasonal Kendall, Sen's slope, and LOWESS). Our results declared that non-parametric tests are powerful tools for trend analysis in water quality time series (previously proved by Helsel & Hirsch 2002; Yenilmez *et al.* 2011; Naddeo *et al.* 2013; Ballantine & Davies-Colley 2014; Entry & Gottlieb 2014; Hughes & Quinn 2014; Dabrowski *et al.* 2014). By removing the effects of seasonality and streamflow fluctuations, trends in water quality remained significant. It clarifies the roles of some other factors on river water quality in the Dez Basin. By trend analysis of modified water quality time series (the residuals from LOWESS test) besides analyzing environmental and human factors, it is revealed that changes in land use and groundwater table were not in accordance with the observed trends in water quality. Our analyses show that besides powerful seasonality pattern in river water quality and discharge-related fluctuations, positive trends in temperature and evaporation show a pattern, which may explain significant parts of observed trends in treated water quality time series (after removing the effects of seasonality and streamflow fluctuations). By our findings, it can be concluded that, besides changes in streamflow and seasonality, water quality degradation in the Dez River Basin is accelerated by increasing trend in temperature and, consequently, in evaporation (the same findings are reported by Crossman *et al.* (2013) and Abdel Wahed *et al.* (2014)). Stable isotope application in the upper Karkheh River Basin (Osati *et al.* 2014), located in the west of the Dez River Basin, has shown that the largest seasonal isotope variations are in correspondence with clear seasonal patterns and evaporation impacts on streamflow. Such analysis in the Dez River Basin can verify and trust our results about evaporation influences on river water quality and quantity. It should be noted that changes in groundwater–surface water relationships (as it is reported as a main cause of trends in river water quality of the Karkheh River Basin after removing the effects of seasonality and streamflow fluctuations by Osati *et al.* (2012)) may have some impacts on river water quality, especially in Azna-Aligudarz and Doroud-Borujerd plains, which are located in the upstream part of the Dez Basin. This is because of potential changes in groundwater contribution in streamflow.

Our findings can provide important information needed for proper management of streamflow resources in the Dez River Basin and guarantee sustainable water supplies for drinking, domestic uses, and agriculture purposes. There are diverse river water quality controllers which altogether might result in important changes in river water quality under improving/degrading conditions.

CONCLUSION

This study identified the effects of climate change, environmental, and anthropogenic factors on water quality of the Dez River Basin using statistical tests, i.e., modified Mann–Kendall test in conjunction with Theil–Sen method and LOWESS. Our findings show the following:

1. Combination of non-parametric statistical methods is a suitable approach to evaluate the temporal variability of hydrochemical components as well as to separate the impact of climate change, environmental, and anthropogenic factors on variability of these components.
2. In addition to alterations in streamflow as a main factor, climate variability present in temperature and, consequently, in evaporation plays a key role on temporal trends of hydrochemical components.
3. Impact of groundwater contribution on stream water quality is more pronounced in subbasins where the groundwater–surface interaction is higher.
4. Comparing subbasin 2, with a considerable land-use alteration, with other subbasins corroborates that although land-use change could have an impact on water quality of the Dez River Basin, it is not the main driver over the study period.

Changes in temperature and evaporation emphasize a new aspect of climate change effects on river water quality and warn of a new challenge for water resources management in semi-arid areas facing climate changes.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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