



Evaluation of water quality trends in the Maroon River Basin, Iran, from 1990 to 2010 by WQI and multivariate analyses

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Received: 8 June 2017 / Accepted: 13 November 2017 / Published online: 21 November 2017
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Abstract

This research aimed to investigate the long-term spatiotemporal changes of surface water quality of the Maroon River by implementing Water Quality Index (WQI) and multivariate statistical analyses such as non-metric multidimensional scaling and cluster analyses, as complementary tools to investigate spatial variations in water quality parameters and also delineate areas in terms of water quality conditions in the period under study. The other purposes of this study were to evaluate the physicochemical properties of the Maroon River water and assess the effects of each water quality parameter on the WQI values. Relationship between quality scale of hydrochemical parameters and the resulting WQI scores was determined employing linear regression analysis. Moreover, the suitability of water quality was evaluated for irrigation purposes using conventional indices, electrical conductivity (EC), sodium adsorption ratio (SAR), and percent sodium (Na%). The monitoring stations were placed in high and very high categories according to the assessment of irrigation water quality with EC. Considering WQI, the upper (S1, S2, and S4) and lower (S3, S5, and S6) monitoring stations of the Maroon River distributed in category C3 (high salinity) and C4–C5 (very high salinity), respectively. The findings of WQI presented an increasing trend from upstream toward downstream in the Maroon River. The findings of the linear regression analysis showed no significant correlation between WQI scores with pH and SO_4^{2-} concentrations even though the relationship is weak. These results suggest that pH and SO_4^{2-} concentrations could be the secondary driving parameters behind the variations in WQI scores. It can be inferred that the Maroon River water is appropriate for irrigation based on Na% and SAR. However, it also exhibits high EC. Therefore, for mitigating the adverse impacts of polluted water authors recommend multidimensional management practices such as transferable discharge permit programs in the study area.

Keywords Water Quality Index · Multivariate techniques · Surface water management

Introduction

Rivers have been of fundamental importance throughout the human history. Water from the rivers is a basic natural resource, essential for various human activities, and they are central to many of the environmental issues that concern

society. Anthropogenic activities degrade the quality of surface waters and impair their use for drinking, agriculture, industry and other purposes (Sánchez et al. 2007; Kazi et al. 2009; Sharifinia et al. 2016a, b). Therefore, there is a great need to evaluate surface water quality for the protection of fresh water resources (Pesce and Wunderlin 2000; Hou et al. 2016). Based on different scientific and policy objectives, various ecological functions of rivers have been studied and evaluated, including hydrology (Edet et al. 2013; Chen et al. 2014; Sharifinia 2016), water quality (Mostafaei 2014), and animal assemblage composition (Sharifinia et al. 2016b). Among these factors, water quality has generated substantial concern because it is not only essential for all biological process, but also directly interacts with other factors across multiple spatial and temporal scales (Varanka and Hjort 2017).

One of the main features of different types of water bodies is spatiotemporal variation in water quality and is mainly

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determined by the hydrodynamic characteristics of the water body (Chapman and Organization 1996; Varanka and Hjort 2017). Water quality varies in all three dimensions (monitoring, survey, and surveillance) which are further modified by flow direction, discharge, and time. Consequently, water quality cannot usually be measured in only one location within a water body but may require a grid or network of monitoring stations (Chapman and Organization 1996; Sharifinia et al. 2016a; Varanka and Hjort 2017).

Spatiotemporal variations in water quality can be considered as an important characteristic of several kinds of water bodies and is mostly defined implementing the physicochemical- and biological-based indices (Sharifinia et al. 2016a). Routinely assemblage and analyzing of information encompasses organized and deliberate observation, in other words an appropriate plan of action that considers space and time information very important. Long-term data demonstrate outstanding patterns can be implemented to define trends, cycles, and rare events (Burt et al. 2014). Furthermore, long-term evaluation of water quality variation could show possible problems in water quality and detect possible reasons including natural changes anthropogenic activities that will give useful information for a better management plan for water quality.

Water quality guidelines usually are comprised of pollution factors, and statistical indices of water bodies are meaningful to researchers; however, this kind of information must be sensible for managers in the water section for better understanding of water quality state (Nasirian 2007). The water quality-based indices (WQIs) have been considered as one criterion for surface water classifications based on the use of standard parameters for water characterization. These indices provide a concise and simple way for stating the quality of water bodies for varied uses (Lumb et al. 2011; Sharifinia et al. 2013, 2016a; Şener et al. 2017). WQI is a mathematical tool implemented to convert large quantities of water physicochemical data into a single number, which depicts the water quality level (Sharifinia et al. 2016a; Şener et al. 2017). For these reasons, WQIs are extensively employed as a useful technique for understanding and demonstrating the pollution issues in aquatic ecosystems.

Several methods have been applied to evaluate the water chemistry and status of the river water quality (Zhai et al. 2014; Sharifinia et al. 2016a; Şener et al. 2017; Varanka and Hjort 2017). Sharifinia et al. (2016a) used Water Quality Index (WQI) method to assess impact of anthropogenic activities on water quality of Shahrood River in the north of Iran. Şener et al. (2017) used Water Quality Index (WQI) and GIS method to determine geological and hydrogeological properties of the river basin and assess the physicochemical properties of the river water in the Aksu River. Varanka and Hjort (2017) used generalized additive models in order

to characterize spatiotemporal aspects of the environmental factors affecting water quality in boreal rivers.

Previous studies have applied WQIs in Iran. The well-documented examples are water quality monitoring in the Ghara-sou River (Atazadeh et al. 2007), Jajrood River (Razmkhah et al. 2010), Zarivar Lake (Sharifinia et al. 2013) and Shahrood River (Sharifinia et al. 2016a). Statistical analysis of surface water quality based on correlations and variations in the data set are expected to provide insights into the quality of the water, scientific references for the implementation of water pollution prevention in the future, and consequently enable managers to form appropriate action plans. Our purpose in using regression and correlation approaches is to determine relationship between WQI scores and water quality parameters during the relatively long span of time. Additionally, we employ multivariate statistical techniques such as non-metric multidimensional scaling (nMDS) and cluster analyses (CA), as complementary tools to investigate spatial variations in water quality parameters and also delineate areas in terms of water quality conditions in the period under study. The other purposes of this study are (1) to evaluate the physicochemical properties of the Maroon River water and (2) to assess the effects of each water quality parameter on the WQI values. The outcomes of this research give wisdom to the water quality, scientific information to be implemented for preventing water pollution, and subsequently make managers able to apply suitable activities at different parts of the study area. The findings represented in this research are according to physicochemical water quality factors defined in the area for a 20-year period from 1990 to 2010.

Materials and methods

Study area and data

The Maroon River is a chief stream in the Iranian province of Khuzestan. The Maroon River Basin includes an area of about 6824 km² that is called the Tab River and has about 310 km long. It is also a very important water resource for irrigation, drinking, industrial, recreation, and other purposes in the basin. The Maroon River rises in the southern part of Zagros Mountains in the west of Iran, and reaching the Shadegan wetland. The Maroon River Basin has been significantly developed, and its urban areas have been increased; therefore, this basin is exposed to pollution with different sources including point and non-point. Moreover, considering the geology of this basin, one can note evaporate Gachsaran (Lower Fars) formation, red marly and sandy Aghajari (Upper Fars) formation, silty and marly Lahbari Member as the main natural, geogenic, non-point sources of the MR water pollution (i.e., salinity). Other origins of

pollution in this basin are domestic and industrial waste discharges and agricultural return flows.

The land surrounding the MR predominantly consists of cultivated lands, and forest and pasture areas. The basin is categorized in climate state of continental semi-arid having cold winters and hot summers. It is interrupted by the Maroon Dam. Six water quality monitoring stations exist in the basin. Cultivated areas, consisting of six irrigation and drainage networks, traditional irrigated and non-irrigated lands, cover 20.5% of the total drainage area (Fig. 1). The main agricultural products are beans, wheat and barley planted along the river during the annual growing season. Industries mainly include cement factory, gas refinery, and equipment manufacturing. High economic output is distributed in the urban belt, oil fields, and crop production. The wastewater flows majorly from urban and industrial parts of the catchment and is focused in the middle and lower reaches of the stream having highly populated tributaries (Fig. 1). Aside from the cultivated lands, there are rural areas and towns that are situated alongside the MR.

Twenty years (1990–2010) of data of six different stations were gathered on a periodic basis. Water quality factors were

measured monthly at the Eydanak (S1), Behbahan (S2), Cham Nezam (S3), Jow Kanak (S4), Moshrageh (S5), and Gorgor (S6) stations of the study area by Khuzestan Water and Power Authority. The average of the mentioned was calculated to gain seasonal and annual amounts. Water samples were routinely analyzed to measure the chemical composition of the major ions and are described in Table 1 (APHA 1989).

The pH Metrohm meter was implemented to measure pH and EC factors (©Metrohm, Herisau, Switzerland). Total dissolved solid (TDS) was calculated as below (Causapé et al. 2004):

$$TDS = EC \times 640$$

Table 1 Chemical composition of the major ions

Factor	Abbreviation	Factor	Abbreviation
Electrical conductivity	EC	Magnesium	Mg ²⁺
Bicarbonate	HCO ₃ ⁻	Sodium	Na ⁺
Chloride	Cl ⁻	Potassium	K ⁺
Sulfate	SO ₄ ²⁻	pH	pH
Calcium	Ca ²⁺		

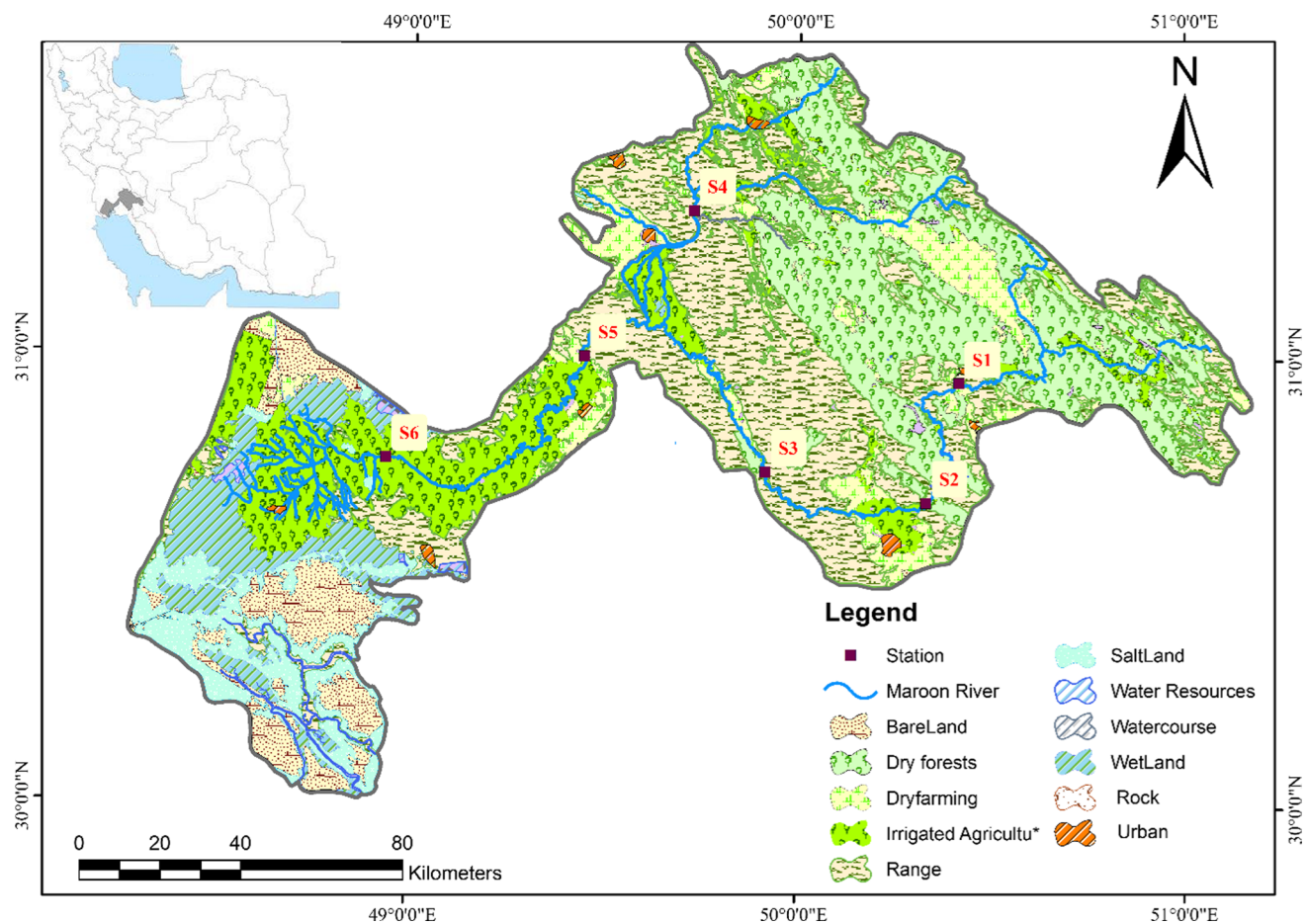


Fig. 1 Maroon River (blue line) Basin showing the water monitoring stations and land use patterns

Applied techniques

Sodium adsorption ratio (SAR) and percent sodium (Na%)

Two factors of SAR (Richards 1954) and Na% (Todd and Mays 2005) were employed for determining the suitability of the water for irrigation purpose. The SAR was estimated using as below:

$$\text{SAR} = \frac{\text{Na}}{[(\text{Ca} + \text{Mg})/2]^{0.5}} \quad (1)$$

The Na% was computed as follows:

$$\text{Na}\% = \frac{(\text{Na}^+ + \text{K}^+) \times 100}{(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+)} \quad (2)$$

Water Quality Index [WQI; (Yidana and Yidana 2010)]

Water Quality Index (WQI) aims at giving a single value to the water quality of a source by translating the list of parameters and their concentrations present in a sample into a single value, which in turn provides an extensive interpretation of the quality of water and its suitability for various purposes like drinking, irrigation, fishing. However, WQI illustrates the composite influence of different water quality parameters and communicates water quality information to the public and legislative decision makers. To investigate the water quality of the river samples, a WQI method was carried out using some variables (TDS, pH, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, and HCO₃⁻) and computed (Yidana and Yidana 2010). The WQI is regarded as an evaluation which represents the mixed effect of several water quality factors (Sahu and Sikdar 2008). The influence of the factors on water quality was considered in determining their weights (Table 2).

Water quality of the Maroon River was determined according to a comparison with the highest admissible amount of WHO (1984, 1993) for domestic purposes in addition to the world mean amounts. Quality scale (*Q*), relative weight (*W_r*) and WQI were calculated for each factor as below (see Eqs. 3, 4 and 5; Table 3):

Multivariate statistical techniques

Hierarchical cluster analysis (CA) was performed for the normalized data set implementing the Ward's linkage model, employing Bray–Curtis distances regarded as a similarity measurement. Ward's model employs analysis of variance for calculating distances among

Table 2 Hydrochemical parameters, standard values, relative and assigned weighting factors used in the study

Parameter	WHO (1984, 1993)	World average (Turekian 1977)	Assigned weight	Relative weight
TDS	1000	–	3	0.136
pH	7.5	–	4	0.182
Na ⁺	200	5.2	1	0.045
K ⁺	12	1.3	1	0.045
Ca ²⁺	100	13.4	2	0.091
Mg ²⁺	30	3.4	1	0.045
Cl ⁻	250	5.8	5	0.227
SO ₄ ²⁻	250	8.3	3	0.136
HCO ₃ ⁻	–	52	2	0.091
Total			22	1

clusters for reducing the sum of squares of any two possible clusters at each step. Dendrogram indicates the arrangement of clusters produced by hierarchical clustering. Stations with a high similarity value demonstrate similar expression profiles, while those with a high dissimilarity value demonstrate opposing expression profiles. Highly correlated clusters are nearer the bottom of the dendrogram. To validate our interpretation, we performed ANOSIM tests, which are created based on a simple nonparametric permutation process, and carried out it to the similarity matrix underlying the ordination of the samples (Clarke and Warwick 2001). Finally, nMDS was executed.

Statistical analysis

The relation of quality scale of hydrochemical parameters and the resulting WQI index scores was checked using the linear regression. WQI scores of the monitoring stations were compared using repeated measures ANOVA. Multiple comparisons between stations were performed by Tukey's test. PRIMER (Plymouth Routines in Multivariate Ecological Research) V5 software and SPSS Statistics 19.0 software (SPSS Inc., Chicago, USA) were used for data processing and analyses.

Results

Hydrochemical parameters

Water quality monitoring of the Maroon basin has been done for a 20-year period (1990–2010) at six stations. The gathered samples were analyzed for some hydrochemical factors, and their station wise average amounts, standard deviations,

Table 3 Quality scale (Q), relative weight (W_r) and WQI formulas for each factor

$W_r = \sum W$ (3)	W weight allocated to each factor $\sum W_c$ the sum of the weights of all the variables
$Q = (C_i/S_i)$ (4)	C_i and S_i represent the concentration for each factor and the WHO standard/World average for that parameter
$WQI = \sum (C_i/S_i) \times W_r$ (5)	WQI was classified into five categories and ranked as: excellent (< 25), good (25–50), moderate (51–75), poor (76–100), and very poor (> 100)

Table 4 Changes of the hydrochemical parameters with mean value, maximum (Max), minimum (Min) and standard deviation (SD) at different stations of the Maroon River

Parameter	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	SO ₄ ²⁻	Cl ⁻	HCO ₃ ⁻	pH	EC	TDS
S1										
Mean	0.04	3.25	1.63	4.38	3.15	3.43	2.63	7.94	950.86	594.85
Min	0.02	0.30	0.10	1.84	0.07	0.58	0.49	6.70	452	6.60
Max	0.16	24.5	4.29	19.80	14.31	24.71	6.15	8.70	6058	1995
SD	0.01	0.92	0.17	0.59	0.38	0.93	0.30	0.24	173.06	80.37
Count	186	186	186	186	186	186	186	186	186	186
S2										
Mean	0.06	10.00	2.15	8.59	8.43	10.04	2.21	7.95	2018.84	1325.25
Min	0.03	2.00	0.22	3.80	2.08	2.00	0.63	7.40	830	12.11
Max	0.16	23.65	9.80	17.52	26.25	23.34	4.03	8.80	3704	2296
SD	0.01	2.24	0.46	1.08	0.87	2.15	0.19	0.13	245.37	132.90
Count	232	232	232	232	232	232	232	232	232	232
S3										
Mean	0.10	11.20	3.36	9.64	11.21	11.18	2.31	7.95	2342.45	1536.70
Min	0.01	1.30	0.60	2.50	1.19	1.65	0.79	7.00	970	13.80
Max	1.20	26.20	8.58	23.65	137.10	26.50	5.29	8.60	3860	2570
SD	0.02	1.91	0.64	0.83	2.72	2.00	0.25	0.15	273.94	166.93
Count	228	228	228	228	228	228	228	228	228	228
S4										
Mean	0.08	7.30	3.59	11.75	13.10	7.39	2.10	7.89	2088.65	1461.67
Min	0.02	0.47	0.76	2.70	2.39	0.55	0.38	7.00	871	13.16
Max	0.52	25	13.50	29.50	43.46	23.30	3.78	8.60	5907	4651
SD	0.02	2.04	0.61	1.52	1.65	2.05	0.25	0.12	296.30	189.37
Count	201	201	201	201	201	201	201	201	201	201
S5										
Mean	0.10	11.61	3.99	10.94	12.72	11.55	2.27	7.91	2515.69	1693.00
Min	0.01	1.27	0.30	1.50	2.02	1.37	0.50	6.50	480	19.72
Max	0.20	35.80	14.00	19.40	29.11	30.96	4.21	8.40	5984	3830
SD	0.01	2.69	0.79	1.05	1.43	2.47	0.27	0.20	345.94	203.28
Count	239	239	239	239	239	239	239	239	239	239
S6										
Mean	0.12	19.62	6.10	12.52	16.30	19.62	2.31	7.90	3614.81	2351.60
Min	0.01	2.20	1.10	4.00	3.20	2.10	0.35	7.00	809	19.60
Max	0.90	96.25	33.55	27.60	58.22	96.36	4.62	8.50	3837	8731
SD	0.04	7.36	2.06	1.33	3.24	7.25	0.23	0.21	976.23	584.75
Count	227	227	227	227	227	227	227	227	227	227

All the hydrochemical parameters are expressed in mg/l, except pH, EC (µS/cm)

highest, and lowest amounts are summarized in Table 4. The parameters pH, HCO₃⁻, and K⁺ were comparable in all monitoring stations. TDS, EC, Cl⁻, Mg²⁺, Ca²⁺, and SO₄²⁻ showed an increasing trend toward downstream in the MR. The mean

TDS changed between 594.8 and 2351.6 mg L⁻¹. The mean EC changed between 950.8 and 3614.8 µS cm⁻¹. It needs to be explained that highest and lowest values of EC were recorded at S6 and S1 stations, respectively. The mean values of pH

Table 5 Changes of measured mean amounts of water quality factors in the Maroon River

Cations	Anions
Potassium from 0.04 to 0.12 mg/l	Sulfate from 3.15 to 16.30 mg/l
Sodium from 3.25 to 19.62 mg/l	Chloride from 3.43 to 19.62 mg/l
Magnesium from 1.63 to 6.10 mg/l	Bicarbonate from 2.10 to 2.63 mg/l
Calcium from 4.38 to 12.52 mg/l	

varied between 7.8 and 7.9 for the different monitoring stations (Table 4). The list below illustrates changes of measured mean amounts of water quality factors in the Maroon River (Table 5).

Classification of the Maroon River water quality regarding irrigation purpose

The mean values of EC, SAR, and Na% are shown in Table 6. These parameters were measured to investigate the appropriateness of water for irrigation purpose. Based on the EC categorization, the quality of water at stations S1, S2, and S4 is in the class C3 having high salinity. Station S3 and downstream stations (S5 and S6) are in the classes C4–C5, having very high salinity (Table 7). The monitoring stations were classified into three groups regarding the irrigation water assessment with Na% (Table 8). Based on the Na%, the river water at all considered monitoring stations is placed in the good and permissible, for irrigation use, categories. The headstream stations (S1 and S4) were grouped as good category. The middle (S2 and S3) and downstream (S5 and S6) stations were classified as permissible category for irrigation. Based on sodium adsorption ratio, all of monitoring stations were grouped into excellent category (Table 8).

Spatiotemporal variation of water quality from 1990 to 2010

Temporal values of WQI scores are depicted in Fig. 2 for all monitoring stations. Ends of the whiskers show the lowest and highest amounts of all factors. As shown in Fig. 2, WQI scores increased from 1990 to 2000 and then decreased between 2001 and 2007. The largest reduction rate of WQI reached 100 at station S6 from 2000 to 2005. The lowest and highest average amounts of WQI existed in the stations S1

Table 7 Classification of waters based on of EC (Handa 1969)

EC ($\mu\text{S}/\text{cm}$)	Salinity hazard class	Water salinity	Station
0–250	C1	Low (excellent quality)	–
251–750	C2	Medium (good quality)	–
751–2250	C3	High (permissible quality)	S1, S2, S4
2251–6000	C4 and C5	Very high	S3, S5, S6
6001–10,000	C4 and C5	Extremely high	–

Table 8 Suitability of the different river waters for irrigation

Quality parameter	Range	Classification	Station
SAR (Richards 1954)	< 10	Excellent	S1–S6
	10–18	Good	–
	18–26	Doubtful	–
	> 26	Unsuitable	–
Na (%) (Raghunath 1987)	< 20	Excellent	–
	20–40	Good	S1, S4
	40–60	Permissible	S2, S3, S5,
	60–80	Doubtful	S6
	> 80	Unsuitable	–

and S6, respectively. WQI showed its lowest changes in 2005 (altering between 41.69 ± 7.86 at station S1 and 83.48 ± 8.61 at station S6) and the highest variation in 2008 (ranging from 45.64 ± 9.25 at station S1 to 178.75 ± 72.20 at station S6). Station S1 in 2006 had the lowest WQI score (41.69 ± 7.86), and station S6 in 2008 had the highest one (178.75 ± 72.20) (Fig. 2).

Figure 3 shows that there are significant spatial changes of water quality between all the stations of the river. Water quality based on WQI ranked as excellent (< 25), good (25–50), moderate (51–75), poor (76–100), and very poor (> 100), according to the WQI scale. The water quality of each station has changed from good to very poor qualities. WQI analyses depict that an increasing trend of WQI scores was observed from station S1 to S6 in the Maroon River (Tukey's test, $P < 0.05$), which shows a statistically significant differences among head-, middle-, and downstream stations.

Table 6 Chemical indices derived from hydrochemical parameters

	S1	S2	S3	S4	S5	S6
EC	950.85	2018.84	2342.45	2088.65	2515.69	3614.81
SAR	1.84	4.36	4.38	2.61	4.23	6.14
Na (%)	32.99	46.66	45.22	30.84	43.06	48.07

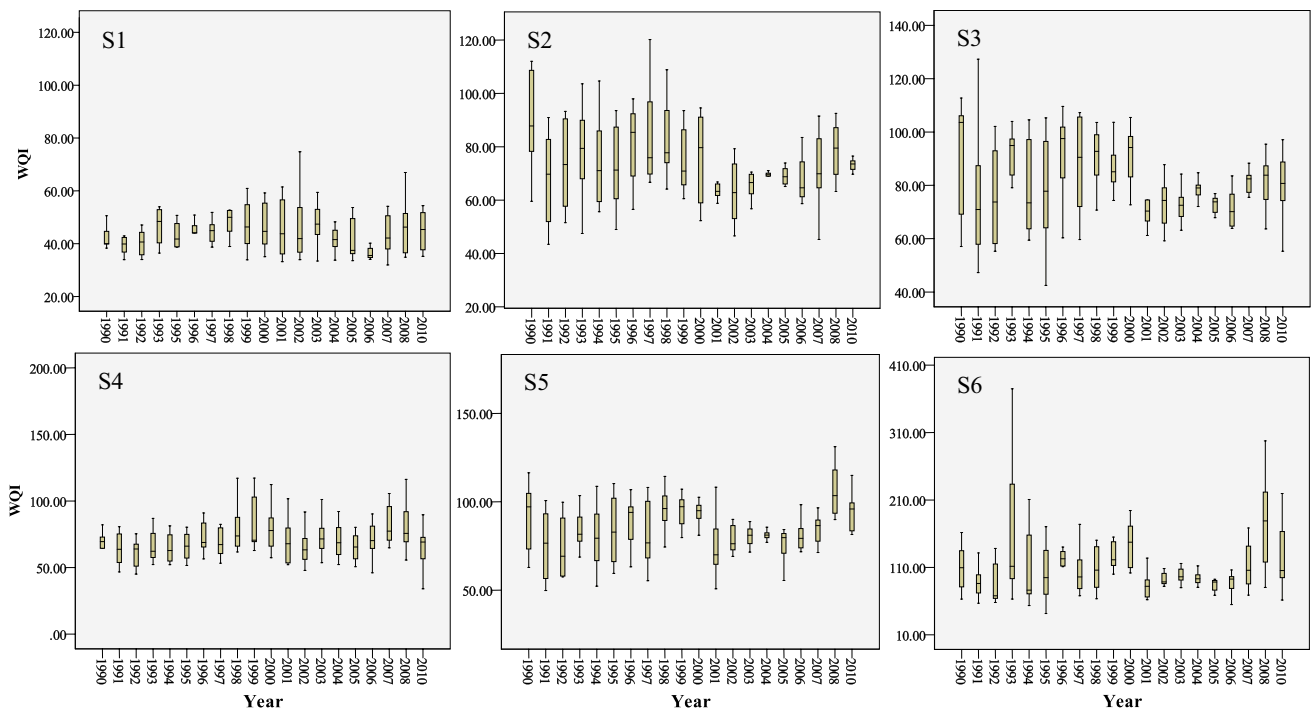


Fig. 2 WQI scores at different stations in 1990–2010

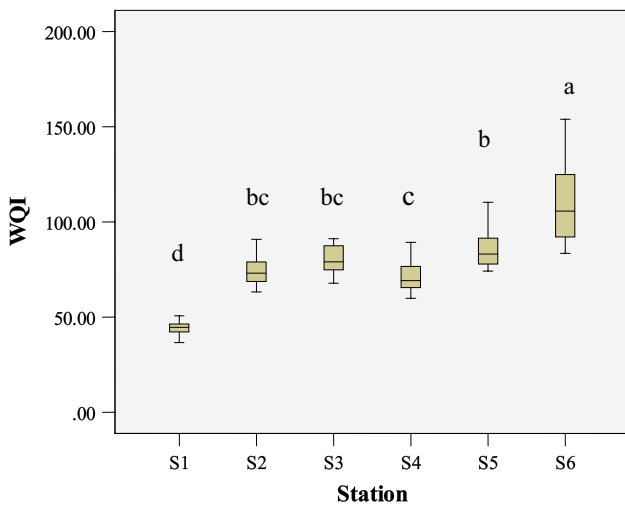


Fig. 3 Box plots of WQI scores in different monitoring stations [values not sharing a common letter were significantly different ($P < 0.05$)]

Relation between WQI and assigned quality scale for each parameter

Linear regression analysis between WQI scores and assigned quality scale for each parameter at the six monitoring stations for the 20-year period indicates distinct influence of quality scale on Water Quality Index. As shown in Fig. 4,

there were strong and significant correlations ($P < 0.05$) between TDS, HCO_3^- , Cl^- , Ca^{2+} , Mg^{2+} , Na^+ , and K^+ concentrations and the index scores, indicating that they make a remarkable contribution to WQI. Surprisingly, no significant correlation ($P > 0.05$) was found between WQI score with pH and SO_4^{2-} concentration.

Multivariate statistical techniques

The Pearson’s correlation coefficients between all the hydrochemical variables represented in Table 9 indicate the significant amounts of correlation among a subset of variables. This statistical analysis revealed a positive correlation among EC and TDS ($r = 0.975$, $P < 0.01$). The most significant negative correlation was seen among HCO_3^- concentration and pH ($r = -0.589$, $P < 0.01$), which stated that with the increase in HCO_3^- concentration, pH decreased accordingly. This study also revealed that pH had no significant correlation with other hydrochemical parameters ($P > 0.05$). The correlation among other factors is shown in Table 9.

Cluster analysis gave a dendrogram (Fig. 5), in which all the six monitoring stations of the Maroon stream were classified into 3 statistically significant clusters based on WQI scores. The clustering process produced three classes of stations in convincingly, as the stations in these classes have similar features: cluster I included monitoring stations in less-impacted area (S1 and S4), which located in

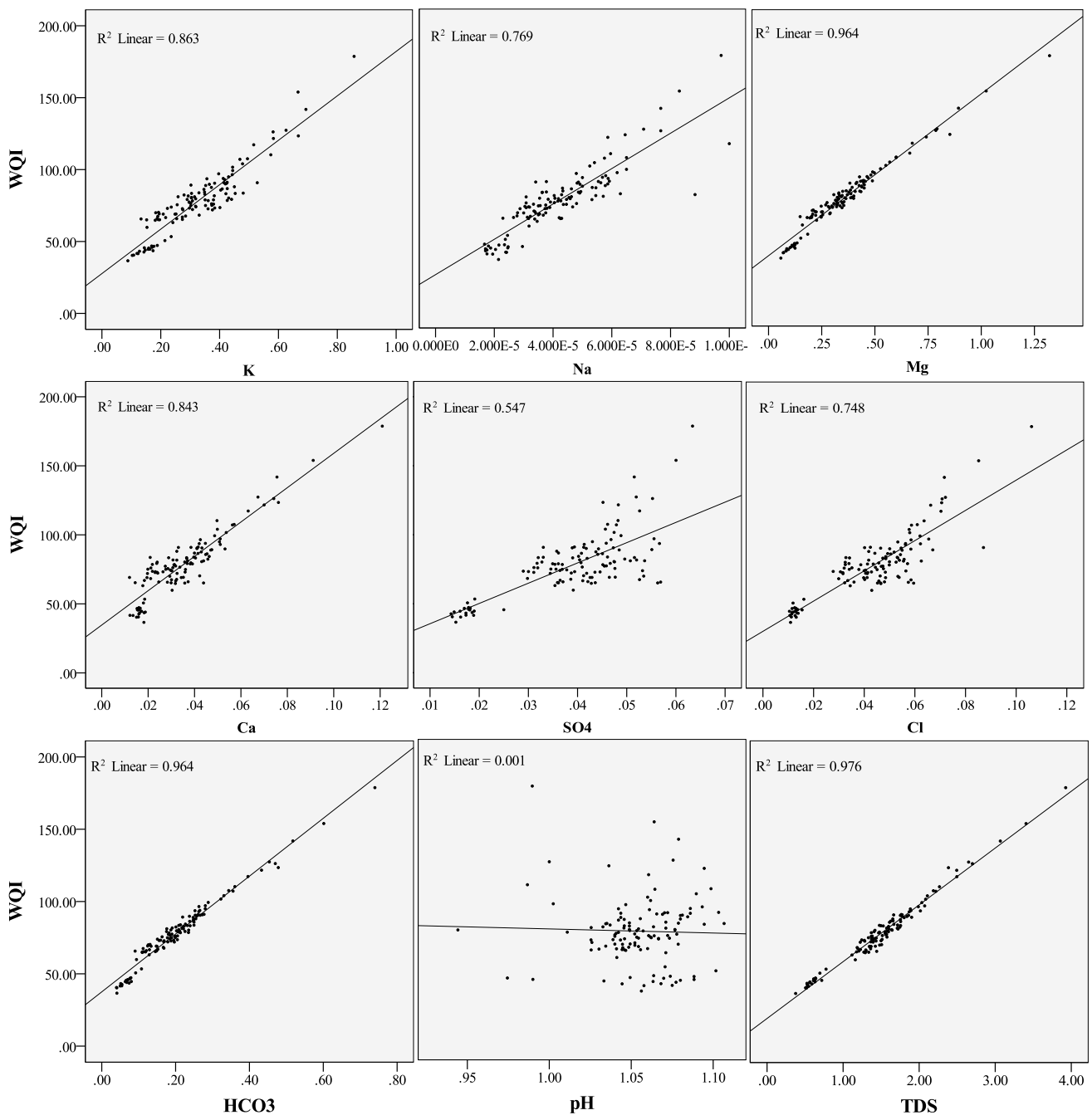


Fig. 4 Regression diagrams between WQI and the parameters used in calculation

upstream and have origins of water from comparatively unpolluted or less-impacted parts; and cluster II comprise of station S6 (had relatively very poor water quality) and cluster A. Cluster A includes stations S2, S3, and S5, that had comparatively poor water quality (Fig. 5). These changes are obviously detectable visually on the nMDS ordination plot, obtained from the fourth-root transformed data of 6 stations. The two-dimensional nMDS configuration, clearly differentiated (stress: 0.07) differences among

headstream (S1 and S4), middle (S2 and S3), and downstream stations (S5 and S6), particularly among headstream and downstream stations, with the points for the middle stations showing limited overlap with those for the downstream station (Fig. 5). The influence of anthropogenic forces was done in the Maroon River water quality status and ANOSIM identified considerable differences (Global $R = 0.246$, $P = 0.01$) between reference, influence, and impact stations (Fig. 5).

Table 9 Pearson’s correlation coefficients of hydrochemical parameters in MRB from 1990 to 2010

	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	SO ₄ ²⁻	Cl ⁻	HCO ₃ ⁻	pH	EC	TDS
K ⁺	1									
Na ⁺	0.667**	1								
Mg ²⁺	0.628**	0.790**	1							
Ca ²⁺	0.530*	0.263	0.179	1						
SO ₄ ²⁻	0.808**	0.757**	0.737**	0.735**	1					
Cl ⁻	0.685**	0.993**	0.827**	0.279	0.764**	1				
HCO ₃ ⁻	-0.091	0.088	-0.102	0.535*	0.165	0.086	1			
pH	-0.060	-0.263	0.070	-0.415	-0.297	-0.205	-0.589**	1		
EC	0.743**	0.955**	0.808**	0.491*	0.873**	0.969**	0.198	-0.293	1	
TDS	0.786**	0.913**	0.796**	0.589**	0.937**	0.921**	0.219	-0.320	0.975**	1

**P* < 0.05; ** *P* < 0.01

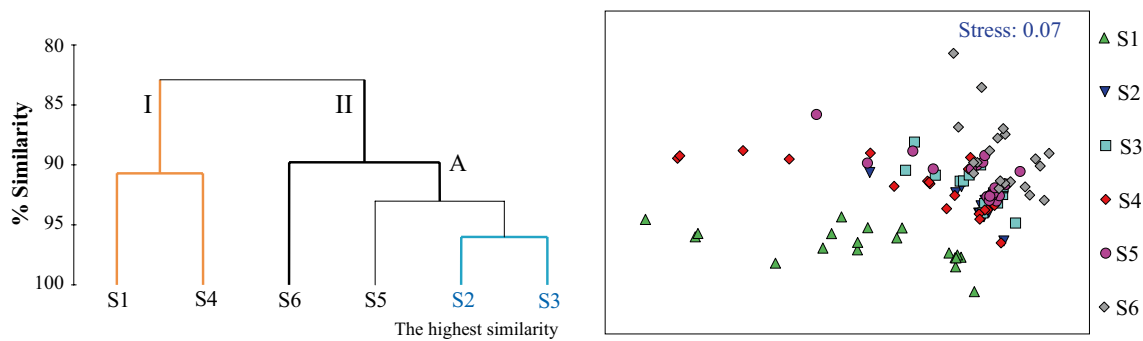


Fig. 5 Hierarchical clustering and non-metric multidimensional scaling (nMDS) plots using the Bray–Curtis similarity metric

Discussion

Irrigation water quality

Application of hydrochemical indices (e.g., EC, SAR, and Na%) can be constructive in investigating the appropriateness of surface water for irrigation purposes and management strategies. The status of water quality in surface waters can preserve suitable for different purposes just if assessing campaigns contemplate the different influences of human activities on waters by examining the trends of hydrochemical parameters. Holistic assessing according to various hydrochemical parameters is an important aspect for employing intensive control networks which amass several fields of study. Accordingly, management plans must be dependent to a comprehensive outlook which pursues multiple criteria to evaluate the condition of rivers and builds appropriate financial and legislative conditions.

Cultivation has been done as a main source of income in the Maroon River, Iran. The quantity and quality of grain products rely to the irrigation water quality. In general view, the evaluation of water quality using hydrochemical indices, EC, SAR, and Na% (Richards 1954; Handa

1969; Raghunath 1987), indicates that the MR water at all monitoring stations can be used for irrigation. The monitoring stations were grouped into two and three classes based on the irrigation water assessment with EC and Na%, respectively. The class of good to permissible for irrigation includes all river water at different monitoring stations. Headstream stations (S1 and S4) were classified as good class. The middle (S2 and S3) and downstream (S5 and S6) stations were classified as permissible category for irrigation. Based on EC classification, the water quality at stations S1, S2, and S4 appears to be in the class C3 having high salinity and station S3 and downstream stations (S5 and S6) are located in the classes C4–C5, having very high salinity. The detection of high EC in the river water at the headstream stations is mainly due to the existence of relatively high soluble evaporite deposits of the Gachsaran Formation. Other studies in the Persian Gulf Basin such as Rahi and Halihan (2010) also considered the dissolution of evaporite minerals as one of the sources of surface water salinity. The withdrawal of fresh water from the river and return of domestic and industrial wastewater and saline drainage water in addition to relatively high evaporation condition (semi-arid climate)

is resulted in the river water with very high EC at the downstream stations. The MR water at all considered stations could be applied for irrigation in a medium amount of leaching incident. In other words, the required water for irrigation purpose in arid and semi-arid climatic conditions is practically double to provide the high crop water needs and to supply the excess water for removing or at least diluting the excess salts (Smedema and Shiati 2002). This is obvious that the utilization of relatively saline, or saline, water for irrigation is not a sustainable practice and would increase the risk of land degradation, but concerning socio-economic issues, solutions such as putting an end to all farming activities, even in drought conditions which usually result in an increase in the salinity levels of freshwater resources, would not be feasible in regions like the MR basin. As the prevailing soil texture in arable lands of the study area is silty clay loam, an appropriate strategy should be developed based on the results of conducted studies on the impact of using water with different levels of salinity on the yields of various crops and the accumulation of salts, and also the performance of different leaching practices in the silty clay loam soils of Khuzestan province (e.g., Akbari Fazli et al. 2013; Mohsenifar et al. 2006; Asadi Kapourchal et al. 2013; Egdernezhad and Jamshidi 2015). It is worth noting that as Smedema and Shiati (2002) mentioned soil salinization could be controlled using leaching, but it will almost always bring about an intensification in the river salinization rate and in most cases there are no easy win-win strategies for resolving this dilemma: either the soil or the river gets salinized. In the other word, no straightforward solution exists for the complicated issues of salt-induced soil and water resources diminishment (Qureshi et al. 2007) such as most parts of Iran (e.g., the MR basin).

Spatiotemporal variation of water quality

Investigation of the river water quality in this research was carried out by WQI using the WHO (1984, 1993) highest admissible amounts and the world's average. WQI scores in the upstream monitoring stations (S1 and S4) demonstrated higher quality than the stations situated downstream. This observation can be related to erosion by tributary inflow, land use, and population density (Keshtkar et al. 2011; Mostafaei 2014). Significant water quality deterioration was detected for WQI scores during 1990 and 2010 at the spatial scales and was majorly among the head- and downstream monitoring stations of the Maroon Basin. The gradual degradation of water quality was firmly dependent on lack of governmental help, and the deteriorated water quality majorly comprised of increasing pollution emission, sewage disposal projects and deficiency of pollution hindrance plans. In terms of temporal scale, one can barely recognize

a trend in the mean annual WQI series at six monitoring stations. This could be due to the existence of contrasting seasonal hydrochemical variations in the MR. As witnessed by Tabari et al. (2011), significant increasing and decreasing trends were seen in the concentrations of water quality factors of the MR in spring and winter seasons and summer and autumn seasons, respectively. It needs to be mentioned that reduction of water quality in the study areas is a consequence of the continuous charging of the river by pollutants associated to anthropogenic activities, and nonexistence of a suitable management plan (Tabari et al. 2011). This is also consistent with the trends seen in waters in the Karun River (Noori et al. 2010), Kashkan River (Mostafaei 2014), and the Sebou River (Perrin et al. 2014). As an influence measure for water quality management, source restrain could be considered as the most to pollutants diminishment and environmental remediation, including sewage treatment plants construction. In addition, the scientific regulation of sluices and water rationing by managers should have a constructive function in preventing and reducing pollution hazards (Zhai et al. 2014).

Our results also show that there was an increasing trend of WQI scores from station S1 to S6 in the Maroon River (Tukey's test, $P < 0.05$), showing that a significant difference exists among the head-, middle-, and downstream stations. Previous studies have represented a direct relationship among urban areas and water quality status in rivers (Sadeghi et al. 2009; Keshtkar et al. 2011; Bu et al. 2014; Yu et al. 2016). In the higher developed parts, S2, S3, S5 and S6 were near highly anthropogenic activities that could be a main drainage pathway from parts having extensive urban growth and agricultural effluents, whereas S1 and S4 had higher distances from these elements. The mentioned findings demonstrate that water quality of the MR has a high sensitivity to the land use of near parts and the land use can possess a high influence on water quality. The changes of water quality can be related to point source pollution and routine sluice regulation. Furthermore, water quality can be influenced by different variables including topography, geology, and climatic conditions (Sliva and Williams 2001; Nasirian 2007; Whitehead et al. 2009).

Regression between WQI scores and hydrochemical parameters

The current research tied to determine factors which would give insights into the quality of the water, scientific references for the employment of water pollution preventing in future decades, and subsequently make managers able to create suitable plans at the different parts of the MRB. Results of linear regression analysis indicate that there were strong and significant correlations between TDS, HCO_3^- , Cl^- , Ca^{2+} , Mg^{2+} , Na^+ , and K^+ concentrations and the index

scores, indicating that they make a remarkable contribution to WQI. Surprisingly, there were no significant correlation between WQI score with pH and SO_4^{2-} concentration even though the relationship is weak. These results suggest that pH and SO_4^{2-} concentration could be the secondary driving parameters behind the variations in WQI scores.

Multivariate statistical techniques

The clustering process produced 3 classes of stations convincingly, since the stations in the mentioned classes owe alike features and natural background sources. The aforementioned changes are obviously detectable visually on the nMDS ordination plot, obtained from the fourth-root transformed data of the stations. The two-dimensional nMDS configuration clearly differentiated (stress: 0.07) differences among the headstream (S1 and S4), middle (S2 and S3), and downstream stations (S5 and S6), particularly among headstream and downstream stations, with the points for the middle stations representing limited overlap with the ones of the downstream station. The influence of anthropogenic actions was reflected in the Maroon River water quality status, and ANOSIM identified considerable differences between reference, influence, and impact stations. The downstream stations (S5 and S6) took in pollution mainly from domestic wastewater, wastewater treatment plants, industrial effluents and farming return flows. The monitoring stations, S2 and S3, however, located in the middle section of the Maroon River, took in pollution majorly from domestic wastewater. Cluster I (S1 and S4) are moderately polluted stations and took pollution in from non-point sources which means that they take in major part of their pollution from farming and orchard land uses. This demonstrates that the cluster (CA) and nMDS techniques are effective in giving trustable categorization of waters and will give a chance to sketch a new spatial sampling tactic that could diminish the number of sampling places and related costs. Other researches exist (Keshtkar et al. 2011; Mostafaei 2014; Taherizadeh and Sharifinia 2015) where the implemented methodology in the current study has been successfully applied.

Conclusions

The detection of water quality trend and distinguishing of contribution factors for water quality deterioration would make available a reference and basis for further water pollution prevention and control in Iran. The outcomes indicated that:

1. Drought had the most effects on turbidity and Cl, whereas the least variations were observed in pH and water temperature during drought period. Due to the close relationship between river flow and water quality, it could be concluded that water quality is vulnerable to reductions in flow.
2. The cluster (CA) and nMDS techniques are effective and useful in offering reliable classification of surface waters to group water samples in the whole region and will make it possible to design a future spatial sampling strategy in an optimal manner, which can reduce the number of sampling stations and associated costs.
3. Water Quality Index (WQI) is a useful assessment method for investigate impacts of anthropogenic activities on water quality status. The present approach can find a widespread use in the assessment of the specific impacts of land use on the receiving water quality.
4. Results of linear regression between WQI scores and hydrochemical parameters suggest that pH and SO_4^{2-} concentration could be the secondary driving parameters behind the variations in WQI scores. In the future, it may be expected that additional effort for integration will be fostered in the context of WQIs.
5. In order to mitigate the adverse impacts of land and water pollution, salinization, in the MR basin, authors recommend that future studies focus on developing a multidimensional model to derive optimal land and water resources allocation policies in various water availability scenarios by considering objectives and constraints like maximizing the benefit and efficiency of agricultural activities and aside from domestic, industrial and agricultural water requirements, meeting quantity and quality of water needed for the Shadegan wetland and by respecting aspects such as socio-economic circumstances of local communities, the yield and comparative advantages of different crops in several areas of the river (i.e., the upper, middle and lower reaches) and also taking into account a suitable and workable trading system for industrial wastewater discharge and saline irrigation-return flow credits.

Acknowledgements The authors would like to appreciate Khuzestan Water and Power Authority for providing the water quality data for the Maroon River. Many thanks to Mostafa Adibnezhad and Vali Sheikhy for his help and technical advices. We also would like to appreciate the Editor and anonymous reviewers who provided valuable feedback on previous versions of this manuscript.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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