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Research Article

The Relationship between Surface Water Quality and Watershed Characteristics

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Abstract

The healthy water resources are necessary and essential prerequisite for environmental protection and economic development, political, social and cultural rights of Iran. In this research, water quality parameters i.e. total dissolved solids (TDS), sodium absorption rate (SAR), electrical conductivity (EC), Na^+, Cl^-, CO_3^{2-}, K^+, Mg^{2+}, Ca^{2+}, pH, HCO_3- and SO_4^{2-} during 2010-2011 were obtained from Iranian Water Resources Research Institute in water quality measurement stations on Mazandaran province, Iran. Then, the most important catchment characteristics (area, mean slope, mean height, base flow index, annual rainfall, land cover, and geology) were determined on water quality parameters using stepwise regression via backwards method in the 63 selected rivers. The results showed that sodium absorption rate (SAR), total dissolved solids (TDS), electrical conductivity (EC), Na^+ and Cl^- parameters are strongly linked to geology characteristics, while K^+, Mg^{2+} and Ca^{2+} cations is linked to rainfall and geology characteristics. pH and HCO3- are related to area, rainfall, land cover and geology characteristics, CO_3^{2-} is related to area, rainfall, rangeland area and geology characteristics and SO_4^{2-} is related to area, rainfall, range and bar land area and geology characteristics. Adaptive Neuro-Fuzzy Inference System (ANFIS) was used for modeling the selected catchment characteristics and water quality parameters. The ANFIS models have a low Nash–Sutcliffe model efficiency coefficient (NSE) and high root mean squares error (RMSE) to estimate water quality parameters except EC, Cl^- and Ca^{2+} parameters.

Keywords: pH; TDS; EC; Water quality; Water cautions; Water anions; Modeling; Mazandaran province

Introduction

Clean water is an essential prerequisite for environmental protection and economic development, political, social and cultural development of a country [1]. World population growth in recent decades and the increasing demand for food and rising health problems, increased per capita water consumption and pressure on existing water resources, have made resource conservation and food production necessary. Resource conservation and food production in terms of quality and quantity especially soil and water resources are a public duty. Unfortunately in Iran, the entry of fertilizers and pesticides and plant diseases in agriculture, created an imbalance between what is needed and what is consumed. Inappropriate use of chemicals in agriculture, led to increasing pollution of water resources that are passing through the towns and villages which and were infected enough. According to the fact that changes in the environment, under the influence of chemicals need for a strategy and plan for protect water resources and its pollution control is important for its management [2]. Different factors affect the health of surface waters, so that the water quality at any point in a river, represents the major effects of land cover and existing land use, weather conditions, rainfall, population density, livestock density, petrology and geology in the watershed [3]. Several indirect methods to simulate natural systems, estimates more accurate, more comprehensive and more complex calculations using a computer has been invented. One of these methods is modelling or simulation. There are many models for predicting water quality parameters including white box and black box models. Among these use of the statistical methods to predict water quality parameters, in terms of taking into account the characteristics of the watershed and lack of complexity of white-box models has attracted the researchers [4]. In recent years, there has been an increasing interest in intelligence models e.g. Artificial Neural Network (ANN), Adaptive Neuro-fuzzy Inference System (ANFIS), Fuzzy Logic and Genetic Algorithm for systems control [5,6].

Zhao et al. [2] predicted water quality in Yuqiao reservoir, China using ANN. The results showed that this model has high performance for predicting water quality. Zhang et al. (2008) developed a numerical water quality model based on reactive chemical transportation in rivers and streams. The results indicated the importance of using numerical models to solve specific problems. Singh et al. [4] applied ANN for modelling the dissolved oxygen (DO) and biochemical oxygen demand (BOD) levels in the Gomti river (India). The results showed that ANN can be used as a tool for the computation of water quality parameters. Areerachakul [7] compared the predictive ability of the ANFIS and ANN models to estimate BOD through data obtained from

11 measurement sites of Saen Saep canal in Bangkok, Thailand during 2004-2011. The results showed that the performance of ANFIS model is better than ANN model. Rankovic et al. [8] modeled the DO variable using ANN based on a three-year date in Gruza reservoir, Serbia. The ANN input variables included: pH, Water temperature, chloride, phosphate, nitrates, nitrites, ammonia, iron, manganese and electrical conductivity. The results showed that effective inputs that had an effect on the DO variable were pH and temperature.

Rothwell et al. [9] predicted water quality of rivers in North West England using the linear relationship between water quality parameters and watershed characteristics (terrain accidents, land cover, geology and base flow index and rainfall). The results showed that the approach works well for the prediction of nitrate concentrations and other constituents which have predominantly diffuse sources. In contrast, the linear approach to predicting orthophosphate concentrations using catchment characteristics is problematic. The major influence of point sources may mask the effect of wider basin attributes on orthophosphate concentrations. During recent years, the evolution of industry, commercial tourism and agriculture in the province is growing. Water quality undoubtedly has a direct impact on the sustainable development of human activities in the province. Therefore factors affecting water quality in rivers and the extent to which these factors affect water quality should be considered. This study aims to identify the most important factors affecting water quality parameters and also to determine the relationship between water quality parameters and characteristics of the watersheds of rivers using ANFIS in Mazandaran province.

Materials and Methods

Study area and data

Mazandaran province with a population density of 127 people per square kilometer in northern Iran is situated on the southern shores of the Caspian Sea. The study area equals 26132.13km^2 and is located within the latitudes 35º45′ N to 36º 59′ N and longitudes 50º10′ E to 54º 42′ E. Mazandaran province has 13 major rivers: Babolroud, Tajan, Siyahroud, Haraz, Nekaroud, Sardabroud, Cheshme-e- Gileh, Galandroud, Garmabroud, Chalosroud, Nesaroud, Chalakroud and Safaroud. These rivers flow from the Alborz mountains into the Caspian Sea. The water of the rivers is used in agriculture, industry and for drinking. The study area based on precipitation, temperature characteristics and topography is divided into Hyrcanian temperate and mountain climates. Position of the sampling sites is shown in Figure 1. In this research, water quality data, including: total dissolved solids (TDS), sodium absorption rate (SAR), electrical conductivity (EC), Na^+, Cl^-, CO_3^{2-}, K^+, Mg^{2+}, Ca^{2+}, pH, HCO_3^- and SO_4^{2-} from 63 sampling sites for the period October 2010 to September 2011 collected by Iran Water Resources Research Center (IWRRC) have been used for this study (Table 1). The sampling sites were selected based on two characteristics:

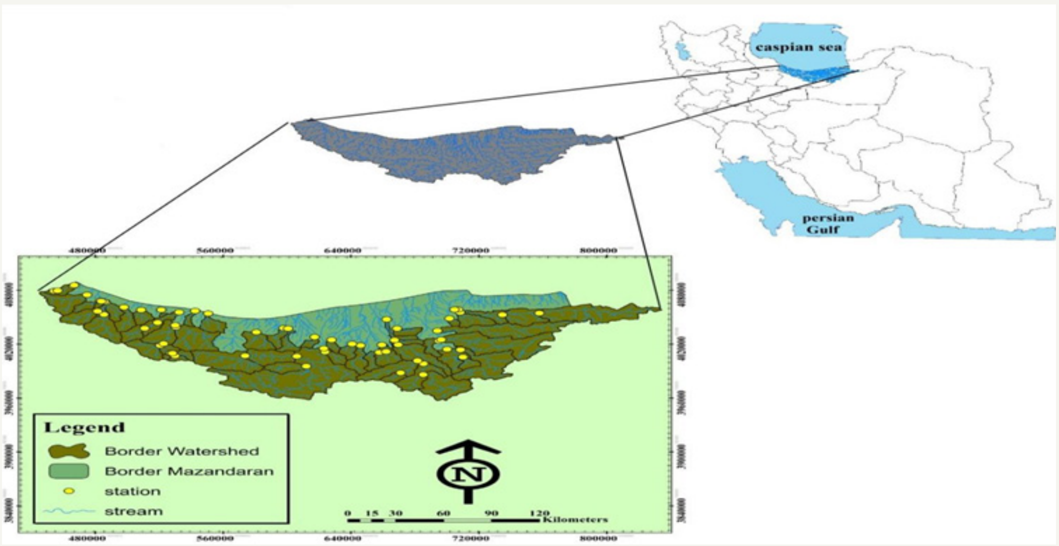

Figure 1: The sampling sites across Mazandaran province used in the study.

Table 1: List of sampling sites used in the analysis.

Code	Sampling Site	River	Code	Sampling Site	River
13-005	Sefidchah	Nekaroud	16-001	Aghuz Keti	Lavij
13-009	Golurd	Nekaroud	16-009	Kheyroud Kenar	Kheyroud
13-011	Paeen Zarandin	Leshka	16-011	Kurkorsar	Noshahr
13-013	Abolu	Nekaroud	16-016	Vaz-e Tangeh	Vazroud
13-017	Darabkola	Darabkola	16-017	Dareh Harijan	Harijan
13-018	Aliabad	Shirinroud	16-019	Doab-e Chalous	Henisk

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13-019	SoleimanTangeh	Tajan	16-021	Polzoghal	Chalous
13-021	Vastan	Lajimdare	16-023	Kelardasht	Sardabroud
13-023	Varand	Chahardangeh	16-029	Charz	Palangaroud
13-027	Garmroud	Zalemroud	16-033	Mashalahabad	Kazemroud
13-031	Karkhanesiman	Nahrabelu	16-036	Tuban	Do heraz
12-206	Pavichabad	Sefidroud	16-037	Sarvash Poshteh	Se heraz
14-001	Shirgah	Talar	16-041	Haratbar	Cheshm-e Kileh
14-002	Pole Shapur	Tajun	16-043	Ghalehgardan	Velamroud
14-005	Shirgah	Kasilian	16-049	Ganeksar	Chalakroud
14-007	Kiakola	Talar	16-079	Pol-e Mergen	Zanguleh
14-008	Pole Sefid	Talar	16-081	Valiabad	Chalous
14-011	Ghorantalar	Babolroud	16-083	Abshar	Chalous
14-013	Galugah Bandpey	Sajadroud	16-085	Valt	Sardabroud
13-015	Diva	Kelaroud	16-157	Gavormak	Simroud
14-020	Khatirkuh	Duabesavadkuh	16-159	Hardroud	Zarduk
14-021	Kerikola	Alasht	16-161	Mazubon	Zarduk
14-024	Sarokola	Siahroud	16-163	Madkuh	Zarduk
14-028	Palande Rudbar	Shesh Rudbar	16-200	Oskumahaleh	Alishroud
14-055	Tamar	Babolak	16-209	Vaspul	Anguran
14-071	Pashkola	Babolroud	16-211	Vazak	Galandroud
15-011	Panjab	Namarestagh	16-509	Paltan	Sorckroud
15-013	Balade	Noor	16-089	Dinarsara	Azadroud
15-015	Razen	Noor	16-051	Ramsar	Safaroud
15-017	Karehsang	Haraz	16-203	Rezapat	Tirem
15-027	Chelav	Haraz	16-025	Zavat	Sardabroud
15-041	Baleyran	Garmroud			

a) The dam, diversion and direct water utilization did not exist in their upstream

b) Data are complete and continuous. Ultimately these 63 sampling sites with continuous and complete data were selected. Water quality parameters have been collected monthly by IWRRC. Samples have been picked in areas with low slope river, a calm and non-muddy river and from the middle of the river. After collecting samples, water quality parameters are measured according to standard methods. After organizing data, their annual mean in order to analyze has been utilized.

Methodology

Physical characteristics of watershed

At this stage, statistics, information and maps needed were collected. Independent variables, including physiographic variables, mean annual rainfall, base flow index (BFI), land use and geological characteristics were considered. To extract physiographic variables, digital elevation model (DEM) with a scale of 1:50,000 were prepared within Arc/GIS 9.3. Then sampling sites location was determined on DEM. Watershed containing each sampling site was determined and drawn using ArcHydro extension within Arc/GIS 9.3 (Figure 1). Finally physiographic characteristics, including area, weighted mean slope and weighted mean height were derived. To calculate mean annual rainfall, monthly rainfall data for water-year 2010 (October 1, 2010 to September 30, 2011) were received from Iran Water Resources Research Company (IWRRC). Then the closest weather station to the selected watershed areas was chosen. According to ratio of weighted mean height of watershed area to mean height of weather station, mean annual rainfall was determined. To calculate BFI, monthly discharges were obtained from IWRRC for 63 sampling sites in water-year 2010. Monthly hydrographs were drawn and amount of the base flow rate was determined by a straight line on the hydrograph. Finally, BFI was determined as ratio volume of water beneath separation line to volume of water beneath recorded hydrograph [10]. To determine land use, land use map was derived using a 2002 land use map with scale of 1:250,000 obtained from the Iran Forest, Ranges and Watershed Management Organization. The land use map was categorized into seven types, including forest, rangeland, bare land, dry farming land, irrigated land, urban and water body (Figure 2). To determine lithology, geological maps with scale of 1:100,000 were obtained from Iran Geological Survey and Mineral Exploration. All geological formations in upstream areas of watersheds were identified and classified in 14 groups, including: Lavas and Granite, Chalk, Shales, Sandstone, Lime, Conglomerates, Marl, Lime & Shales, Conglomerates & Sandstone, Lime & Sandstone, Shales & Sandstone, Lime & Marl, Tuff & Marl and Alluvial formations [11].

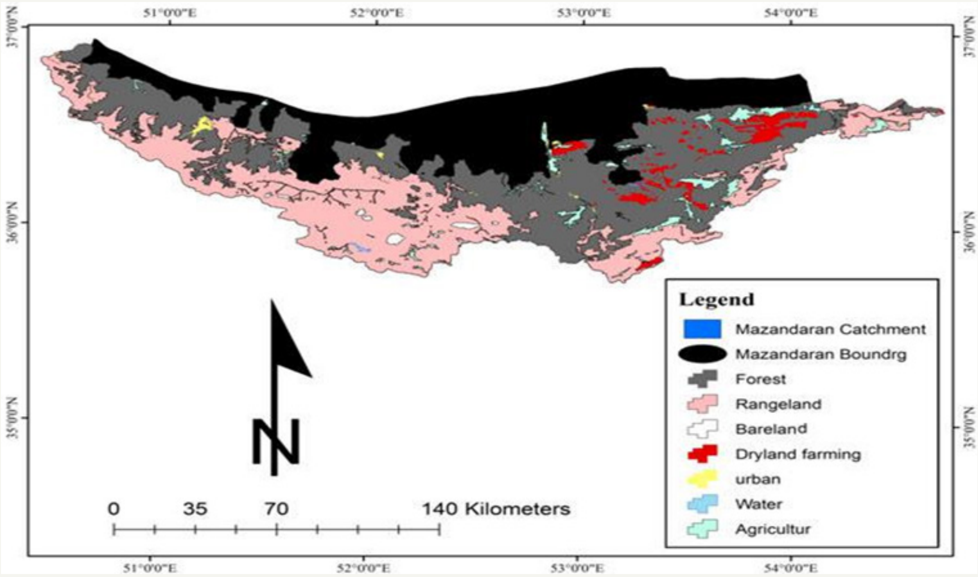

Figure 2: Land use type of sampling sites used in the study.

Stepwise regression

Linear relationship between variables was performed using stepwise regression. Stepwise regression can be performed in three methods, including forward, backward and step by step methods. In backward method, all independent variables were considered into the model, then the effect of each variable elimination is assessed [12].

Adaptive Neuro-Fuzzy Inference System (ANFIS)

The Sugeno type with five layers, namely, a fuzzy layer, a product layer, a normalized layer, a defuzzy layer and a total output layer was used in the study [13]. The Sugeno type used in the study was grid partitioning with four different types of membership functions (MFs) named gaussian1 (gauss1MF), gaussian2 (gauss2MF), generalized bell-shaped (gbellMF) and triangular (triMF) [13]. The inputs and outputs data were normalized before modelling based on the ANFIS between 0.1 and 0.9 as follows:

$$X_{max} - X_{min}$$

Where N_i is the normalized value, xi is the original data, x_{min} and x_{max} are, respectively, the minimum and maximum of data.

Performance assessment

Two statistical indices, including Nash-Sutcliffe efficiency coefficient (CE) and normalized root mean squares error (NRMSE) used to evaluate modeling performance can be computed using following equations:

$$CE = 1 - \frac{\sum_i^n = 1(Y_0 - Y_e)^2}{\sum_i^n = 1(Y_0 - \overline{Y}_e)^2}$$

$$NRMSE = \sqrt{\frac{1 - \sum_i^n = 1(Y_0 - Y_e)^2}{n}}$$

Where,

Y_0 = The observed value of the dependent variable

Y_e = The estimated value of the dependent variable

$\overline{Y}_e$ = The mean observed value of the dependent variable

n=the number of data points

RMSE values change between 0 and 1, values which are closer to zero indicate high accuracy predicted. The CE coefficient varies between negative infinitely and one and values which are closer to 1 indicate higher performance model.

Results and Discussion

Table 2: Statistical summary of water quality parameters rivers of the Mazandaran province.

Parameters	Mean±Standard Diviation	Parameters	Mean±Standard Diviation
TDS	367.47±338.62	Cl^-	1.45±3.79
EC	560.86±508.15	Ca^{2+}	2.83±1.72
pH	8.18±0.29	Mg^{2+}	1.46±0.77
CO_3^{2-}	0.054±0.061	K^+	0.045±0.025
HCO_{3-}	2.79±0.88	Na^+	1.23±3.45
SO_4^{2-}	1.13±1.85	SAR	0.68±1.64

TDS: Total Dissolved Solids; EC: Electrical Conductivity; SAR: Sodium Absorption Rate

Table 2 shows statistical summary of water quality parameters rivers of the Mazandaran province during water-year 2010. The highest value of TDS, EC, Cl^-, K^+, Na^+ and SAR were observed in Baleyran stations, pH in Dinarsara station, CO_3^{2-} in Mashalahabad station, HCO^{3-} in Sarokola station, SO_4^{2-} and Mg^{2+} in Khatirkuh station and Ca^{2+} in Pol-e Mergen station. While the lowest value of TDS, EC, K^+, HCO^{3-}, Ca^{2+} and Mg^{2+} were observed in Kelardasht station, pH in Sarokola station, SO_4^{2-} and Cl- Dinarsra station, Na^+ in Ghalehgardan station and SAR in Ganeksar station.

Table 3: Statistical characteristics of independent variables used in this study.

Row	Variables	Mean	Minimum	Maximum	Standard Deviation
1	Area (km^2)	561.75	3.19	3983.46	744.67
2	Weighted mean height(m)	1684.71	252.39	3074.25	774.65
3	Weighted mean slope(%)	39.96	8.6	64	11.09
4	Annual mean rainfall(mm)	757.24	287.5	1884	329.4
5	Base flow index	0.13	0	0.55	0.14
6	Forest(%)	60.54	0	100	31.17
7	Rangeland(%)	33.12	0	95.24	31.08
8	Bare land(%)	0.16	0	2.65	0.57
9	Urban(%)	0.81	0	12.88	2.28
10	Dry land farming(%)	2.65	0	47.83	7.04
11	Irrigated land(%)	3.22	0	12.88	3.84
12	Water body(%)	0.01	0	0.28	0.05
13	Lavas and Granite(%)	8.66	0	45.05	11.96
14	Chalk(%)	0.32	0	2.65	0.59
15	Shales(%)	1.56	0	26.04	4.46
16	Sandstone(%)	0.89	0	9.12	2.03
17	Lime(%)	18.77	0	74.32	16.27
18	Conglomerates(%)	8.91	0	73.18	16.84
19	Marl(%)	7.67	0	80.12	16.13
20	Lime & Shales(%)	2.07	0	21.73	3.86
21	Conglomerates & Sandstone(%)	3.83	0	70.4	11.55
22	Lime & Sandstone(%)	0.7	0	20.78	2.8
23	Shales & Sandstone(%)	30.05	0	83.26	19.84
24	Lime & Marl(%)	11.41	0	59.94	15.09
25	Tuff & Marl(%)	0.095	0	2.4	0.38
26	Alluvial formations(%)	5.06	0	27.86	5.97

In general, sampling sites with the highest value for water quality parameters have been located in the western areas of the province. It was observed that sampling sites existing in the western areas of the province have often been located at a lesser distance from the coastline of Caspian Sea and are more greatly affected by human activities. This finding is in agreement with Mirzaee et al. (2014) findings which showed that most stations located in the western areas of Mazandaran province has water quality classes between moderate to bad. Descriptive statistics of physical characteristics are given in Table 3. As can be seen from Table 3, 26 variables included four physiographical, fourteen geological, one meteorological and seven land use variables have been considered to model water quality. A considerable amount of literature has been published on water quality using physiographical, meteorological and land use variables [7,8,14]. However, far too little attention has been paid to geological variables [9]. The highest value of area and weighted mean slope belong to Karehsang and Vaspul stations, respectively. The highest value of weighted average height and rainfall belong to Kelardasht station. The highest value of base flow index belongs to Doab-e Chalous station. In terms of land use, the greatest amount of forest area (100 percent) belongs to Baleyran, Diva, Gavormak and Palande Rudbar stations. The greatest amount of rangeland belongs to Razen, Pol-e Mergen and Dareh Harijan stations. The greatest amount of dry land farming belongs to Sarokola station.

In terms of geological formations, the greatest amount of Lavas and Granite group is observed in Razan station, Lime in Charz station, Conglomerates in Paltan station, Marl in Darabkola station, Conglomerates & Sandstone in Sarokola station, Shales & Sandstone in Vaspul station, and Lime & Marl in Kheyroud Kenar station. Table 4 shows correlation coefficients of water quality parameters and variables in this study. Table 5 shows the results of the backward stepwise regression method. As can be seen from Table 5, rainfall and land use showed high correlation with the

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most water quality parameters while among geology formations, only Tuff & Marl group formation which is not widespread in the study area showed high correlation with water quality parameters. The effect of land use on surface water has been investigated in a lot of studies such as that observed by Amiri & Nakane [15] who had reported a significant relation between land use and water quality. Also Na+ and SAR did not show significant correlation with effective parameters.

Table 4: Correlation coefficients of effective variables and water quality parameters in the study area.

Variables	Area	Height	Slope	Rainfall	Forest	Range	Irrigated	Dry	Shales	Tuff &Marl
TDS										0.41
EC										0.41
pH	-0.28		0.36	0.32		0.28				
CO_3^{2-}				0.29						
HCO^{3-}	0.25	-0.33	-0.55	-0.49		-0.39	0.38	0.48		
SO_4^{2-}		0.4			-0.41	0.43				0.56
Cl^-										0.26
Ca^{2+}				-0.31	-0.3	0.27				0.46
Mg^{2+}	0.25			-0.4					0.26	0.63
K^+	0.26				-0.34					0.38

Table 5: Results of stepwise regression procedure via backward method.

Regression Equation	RMSE	CE	R^2	Significant Level
SAR=0.293+0.042 Lime & Marl	1.875	0.072	00.093	0.04
TDS=286.65+364.12 Tuff & Marl+5.14 Lime & Marl	352.35	0.19	0.047	0.006
EC=448.11+548.19 Tuff & Marl+7.67 Lime & Marl	531.5	0.18	00.47	0.003
pH=7.959+0.0001A+0.0001P+0.004R+0.143BL+0.054	0.223	0.368	00.71	0.002
Sandstone+0.077 Lime & Shales-0.159 Lime & Sandstone-0.18 Tuff & Marl-0.015 Lime	3.91	0.75	0.31	0.05
Na+=0.411+0.091 Lime & Marl	0.024	0.24	0.52	0.001
K+=0.060-0.0000227P+0.025 Tuff & Marl	0.6	0.53	0.75	0.00
Mg^{2+}=1.996+0.0001P+1.266 Tuff & Marl	1.62	0.28	0.56	0.00
Ca^{2+}=3.78-0.001P+2.075 Tuff & Marl	4.32	0.07	0.31	0.043
Cl^-= 0.566+0.098 Lime & Marl	0.61	0.51	0.77	0.00
HCO_3-=3.966+0.0001A-0.001P-0.07AGR+0.046DF-0.009R-0.61 Shales+0.474 Tuff & Marl	0.044	0.37	0.68	0.00
CO32-=0.033-2.736*10-5A+0.001R+0.017 Lime & Shales-0.021 Lime & Sandstone-0.042 Tuff & Marl-0.002 Lime	0.044	0.37	0.68	0
SO_4^{2-}=1.403-0.001P+0.028R-0.764BL+2.335 Tuff & Marl	11.42	00.52	00.75	0.00

A: Area(km2); P: Annual rainfall(mm); Lime & Marl: Lime & Marl formations (%); Tuff & Marl: Tuff & Marl formations (%); Lime: Lime formations(%); Lime & Sandstone: Lime & Sandstone formations(%); Lime & Shales: Lime & Shales formations(%); Sandstone: Sandstone formations(%); DF: Dry land Farming(%); AGR: Irrigated land farming(%); BL: Barren Land(%); R: Rangeland(%)

Table 6: Results of stepwise regression procedure via backward method.

Variables	Modeling		Testing	
	NRMSE	CE	NRMSE	CE
TDS	0.059	0.89	0.089	-0.37
EC	0.083	0.99	0.262	0.99
pH	0.024	0.98	8.37	-1187
CO_3^{2-}	0.036	0.98	3.25	-0.57
HCO_3-	0.068	0.89	1.15	-0.13
SO_4^{2-}	0.114	0.74	0.31	-3.38
Cl^-	0.076	0.99	0.13	0.99
Ca^{2+}	0.124	0.99	0.25	0.95
Mg^{2+}	0.097	0.72	0.088	0.09
K+	0.177	-0.26	0.16	-1.73
Na+	0.014	0.99	0.021	-27.57
SAR	0.042	0.92	0.069	-1.39

Considering to the results of the backward stepwise regression method in SAR, Na^+ and Cl^- parameters, Tuff & Marl geology group, in EC & TDS parameters, Tuff & Marl, Lime & Marl geology group, in pH parameter, area & rainfall factors and Barren land & rangeland, Sandstone, Lime & Shales, Lime & Sandstone, Tuff & Marl, Lime, in K^+, Mg^{2+} and Ca^{2+} parameters rainfall and Tuff & Marl factors, in HCO^{3-}, area, agriculture, dry land and rangeland and Shales, Tuff & Marl geology group, in CO_3^{2-} parameter area, rangeland and Lime & Shales, Lime & Sandstone, Tuff & Marl and Lime geology groups, in SO_4^{2-} parameter, rainfall factor, rangeland and Barren Land and Tuff & Marl geology group, were chosen as effective variables. Since there were no differences between results modelling using the four different types of MFs, the results

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of ANFIS procedure using g bell MF are shown in Table 6. Use of ANFIS for modeling water quality parameters have been used in a lot of previous studies [7,16]. In general, the ANFIS model has a low efficiency and high error for estimating water quality parameters except EC, Cl^- and Ca^{2+}. The major influence of point sources may mask the effect of wider basin attributes on water quality parameters [9]. This result is in agreement with Rothwell et al. [9] findings for predicting orthophosphate concentrations in North West rivers. Also, the effect of point pollutant sources on water quality in the rivers of Mazandaran province has been indicated by Nasirahmadi et al. [3].

Conclusion

The purpose of the current study was to model the relationship between water quality parameters and characteristics of the watersheds of rivers using ANFIS in Mazandaran province. This study has found that generally sampling sites with the highest values of water quality are located in the western areas of the province. On the other hand, rainfall and land use showed high correlation with most of the other water quality parameters. Therefore, it is recommended to use the results of this study in order to improve water quality management in the rivers of Mazandran province. The suitable management practices can be used for water pollution control in the rivers of the Mazandran province. In addition, according to low efficiency of ANFIS models, other modeling methods viz. support vector machines were used for modeling water quality parameters. Also, ANFIS models could be successfully used in estimating EC, Cl- and Ca2+ using watershed characteristics. The current study was unable to model some biological water quality parameters (e.g. DO, BOD) due to the data unavailability.

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