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Hydrogeochemical Characteristics and Evaluation of the Drinking and Irrigation Water Quality in Marand Plain, East Azerbaijan, NW Iran

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Authors' contributions

This work was carried out in collaboration between all authors. Author FK designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript and managed literature searches. Authors FK, GHS managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

In order to study hydrogeochemistry of groundwater, samples of water were collected from Marand located in Eastern Azerbaijan province, NW of Iran at July, 2008. This region has 800 km^2 space and 87 locations. Samples which were collected from 74 water wells, 10 Qantas and 3 springs analyzed for major cations and anions processed by statistical methods. Parameters were compared with water quality standards and public health standards for domestic usage. Some of the locations are defined by high concentration of EC, TDS, Cl, Na and K. Half of the groundwater samples were contained Ca-Mg-Cl type of hydrochemical facies, followed by Ca-HCO3, Ca-Cl and Na-Cl types. Based on US salinity diagram, 42% of the samples fall in the field of C3-S1. Due to low sodium and medium-high salinity groundwater C3-S1 class can be used for irrigation on almost all soils with little danger of sodium problem. Majority of the samples are not suitable for domestic purposes meanwhile they were far from standards of drinking water. In the recent years, comparing average electrical conductivity and total dissolved solids of the studied area revealed that declines in water levels as a result of extensive agricultural activities and urbanization resulting in deterioration of groundwater quality in the major parts of the plain.

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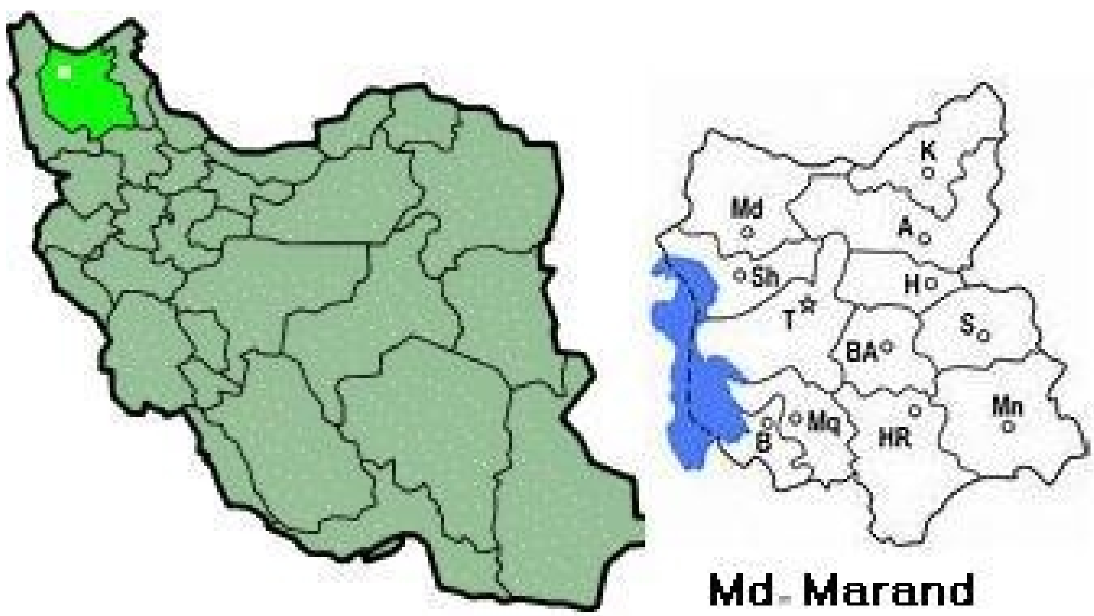
1. INTRODUCTION

It is estimated that about one third of world's population is using groundwater for drinking purpose [1]. Groundwater is the major source of water supplying for domestic purposes because it was generally believed that groundwater is healthy and safe [2]. Groundwater is the only water source for domestic, industrial and irrigation usages in Marand plain and so it is important to guarantee its quality for mentioned usages. Meanwhile it should be considered that problems of ground water quality are more acute in areas which are densely populated and partly industrialized. Quality of groundwater is result of various processes and reactions. Geochemical studies could provide a better understanding of possible changes in groundwater quality as development progress [3]. Assessment of groundwater quality is the main factor, which determines whether the water is suitable for domestic, irrigation and industrial purposes or not [4]. The studied region is located in 38° 18'- 38° 46' N and 45° 15'-46° 05' E in east Azerbaijan province, north west of Iran.

The region has a semi-arid climate and the average annual rainfall is 236 mm. Geologically, the area is overlain by young alluvial sediments and quaternary deposits but at the same time different rock units like igneous rocks, Miocene evaporation sediment and Miocene conglomerate affect the quality of groundwater (Fig. 1), [5,6,9].



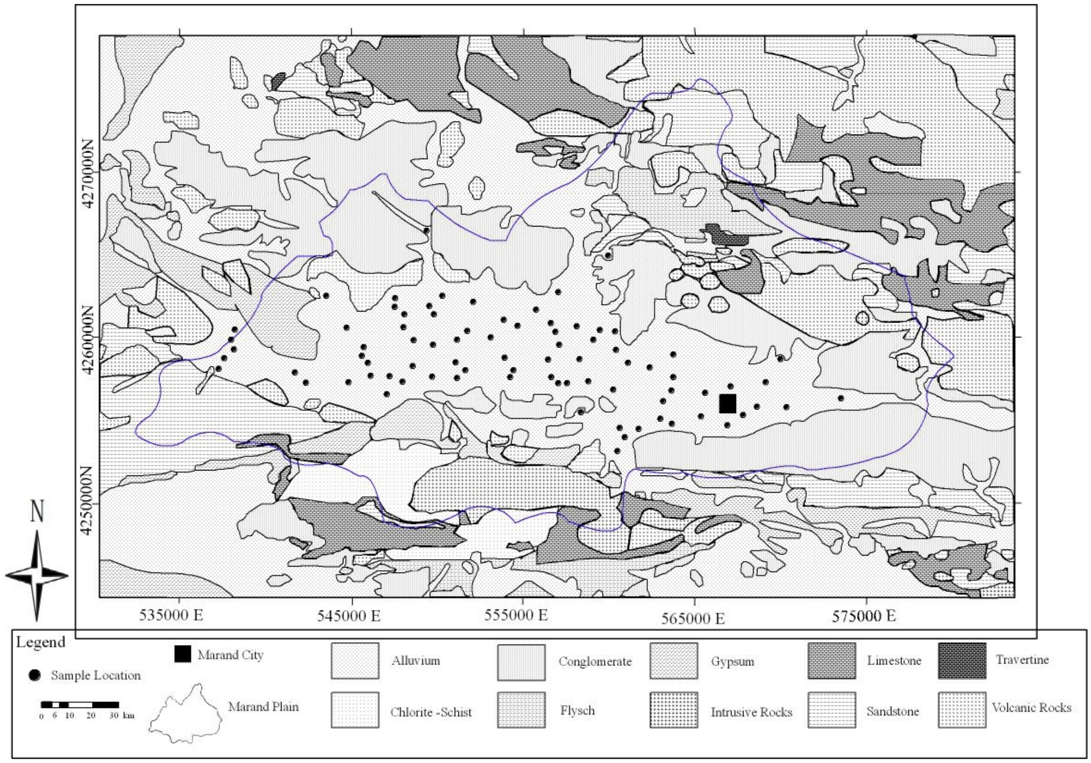


Fig. 1. Location and Geological map of the studied area [9] and Sampling locations

2. MATERIALS AND METHODS

87 water samples from 74 water wells, 10 Qantas and 3 springs were collected in July of 2008 and were analyzed by standard methods in order to determine chemical composition of groundwater besides the variety of parameters related to this factor. Locations of sampling selected to cover the entire Marand plain. Furthermore, local surveys were done to determine probable contaminants in water of the area. The results were evaluated by water quality standards given by the World Health Organization, 2003 [7].

The water samples were analyzed for electrical conductivity (EC), pH, total dissolved solids (TDS), major cations (K^+,Na^+,Mg^{2+},Ca^{2+}), and anions (SO_4^{3-},Cl^-,CO_3^{2-},HCO_3^-) by using the standard methods given by the American Public Health Association [8]. The methods used to analysis of the hydrochemical parameters are presented in (Table 1). The area is a part of the Caspian Sea basin [9]. For quality control measures the ionic error balance was calculated. The calculated error does not exceed 4%.

In the current study, univariate methods were applied to statistical analysis. The software SPSS12.0 was used for statistical assessments according to suggested techniques [10].

Hydrochemical facies of groundwater which were chosen to sample were determined by using the Piper diagram [11] and subsequently these data points with the UTM locations of sampled wells were inputted into Rock Work99 software for spatial and susceptibility interpretations. The maps that were plotted by this software were used to predict and detect vulnerable regions in the study area similar to method of [16]. Results of chemical analysis of samples from 2005 to 2008 (4 years time interval) were used to monitor Marand plain freshwater quality.

Table 1. Summarized the methods used to analyzed the physico-chemical parameters in groundwater samples of the region

Parameters	Test method
Electrical Conductivity	EC meter
pH	pH meter WTW
TDS	Calculation
CO_3^-	Titration
HCO_3^-	Titration
Total Hardness ($CaCO_3$)	Calculation
Ca^{+2}	Titration
Mg^{+2}	Titration
Na^+	Flame Photometer (EEL, UK)
K^+	Flame Photometer (EEL, UK)
Cl^-	Arganto meter
SO_4^{-2}	Turbidity metery, HACH 2100P

3. RESULTS AND DISCUSSION

3.1 Groundwater Chemistry

Results of statistical analysis of physical and chemical parameters of groundwater such as minimum, maximum, median, mean and mode are given in (Table 2). The EC value differs from 404 to 5580 mho cm^{-1} and the mean value is 1827.7 mho cm^{-1}. Values of pH are from 6.3 to 8.8 with an average of 7.70. The data shows changing from neutral to alkaline nature of groundwater in the region. TDS values also vary from 242 to 3348 mg/l with an average value of 1096.6 mg/l.

Table 2. Statistical characteristics of different chemical parameters in groundwater of the region

Water quality parameters	EC	TDS	pH	Ca	Mg	Na	K	HCO_3	CO_3	Cl	SO_4
Numbers of samples	87	87	87	87	87	87	87	87	87	87	87
Mean	1827.7	1096.6	7.69	91.56	58.4	199.06	6.36	340.7	1.67	360.3	118.02
Standard deviation	1220.2	732.1	0.5	66.86	41.36	153.31	5.59	172.2	5.67	379.8	88.93
Maximum	5580	3348	8.8	336	218.4	798.1	29.64	945.5	42	1712.9	496.8
Minimum	404	242.4	6.3	17.6	4.32	6.67	0.04	100.65	0	8.8	4.8
Mode	984	590.4	7.5	66.4	39.36	184	3.9	183	0	443.7	48
Median	1514	908.4	7.7	67.6	45.6	172.5	5.07	305	0	221.8	96

** All values are in mg/l except pH, EC (mho cm^{-1})*

3.2 Hydrogeochemical Facies

Geochemical evolution of groundwater was specified through plotting the concentrations of major cations and anions in the Piper diagram [11]. This aim has been performance by using of GROUNDWATER software Package (in Persian). On the basis of Piper diagram, groundwater is divided into five facies including mixed CaMgCl types, $CaHCO_3$, CaCl, NaCl, and $CaNaHCO_3$ respectively (Fig. 2). Therefore, it is observed that alkaline earth (Mg^{2+} and Ca^{2+}) exceeds the other cations and Cl^- exceeds the other anions.

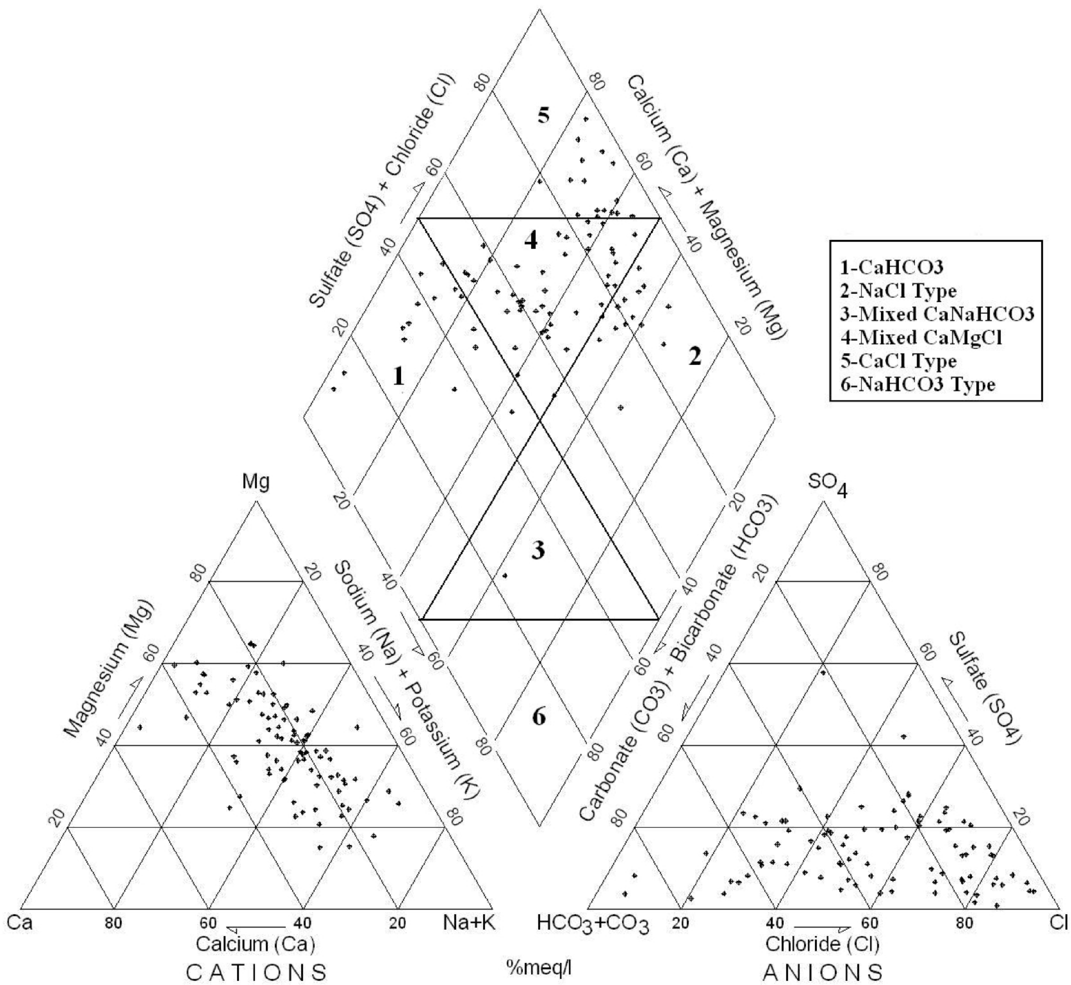


Fig. 2. Piper diagram showing hydrichemical facies of groundwater

3.3 Groundwater quality

The chemical parameters of water samples compared with water quality standards [7] and public health standards for domestic uses (Table 3). The cations concentration indicate that 12.64% of K^+, 40.2% of Na^+ and 6.9% of Ca^{2+} concentration exceed the standard limit of WHO. For chloride (Cl^-) 16% of samples, shows more concentrations than maximum allowable limit for drinking water. High amounts of alkaline concentrations in western and northwestern parts of Marand plain were associated to Miocene evaporation sediments (Fig. 1). These sediments are yellowish green gray gypsiferous marl, calcareous sandstone and red marl, conglomerate and sandstone containing salt and gypsum. To object of spatial interpretation, investigations were performed for studying groundwater chemistry variations and predicting more vulnerable places in the study area. Measured parameters were compiled as Pie chart diagram map (Fig. 3). According to this map, illustrate an increase in K, Na, Cl, Ca and Mg parameters toward the northwest and west of the study area. This gradual increase could happen due to natural agents such as geology and hydrography or may be a result of unnatural factors including irrigation with saline water and dissolution of the chemical fertilizers by irrigation water.

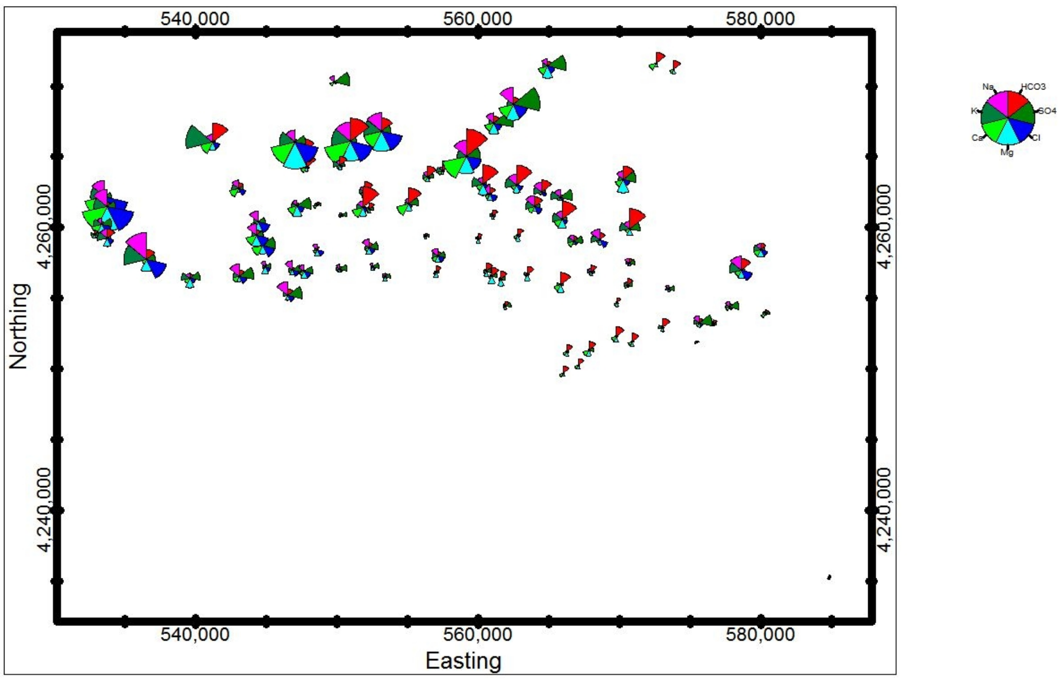


Fig. 3. Hydrogeochemistry map (pie chart diagram) of groundwater samples that illustrate an increase in Parameters of Cl, K, Na toward the northwest and west of the study area

The comparison of the average electrical conductivity and total dissolved solids from July 2005 to July 2008 demonstrated that the EC and TDS values had increased in the study area (Fig. 4). In addition, the unit hydrograph confirms that water levels have declined [6]. Declining in groundwater level due to over-exploitation of the aquifer in the Marand plain has caused the deterioration of groundwater quality in the major parts of the region.

Table 3. Groundwater samples of the study area exceeding the permissible limits prescribed by WHO (2003) for domestic purposes

Water quality parameters	WHO [7]		Percentage of abnormal samples	No table effects
	Allowed limits	Maximum allowable limits		
pH	6.5-8.5	9.2	-	Taste
TDS(mg/l)	500	1500	18.4	Gastric Diseases
Ca^{2+} (mg/l)	75	200	6.9	Scale formation
Mg^{2+}(mg/l)	50	150	5.75	-
K^{+}(mg/l)	-	12	12.64	Bitter taste
Na^{+}(mg/l)	-	200	40.2	-
Cl^{-}(mg/l)	200	600	16	Salty taste
SO^{-4}(mg/l)	200	400	4.6	Laxative

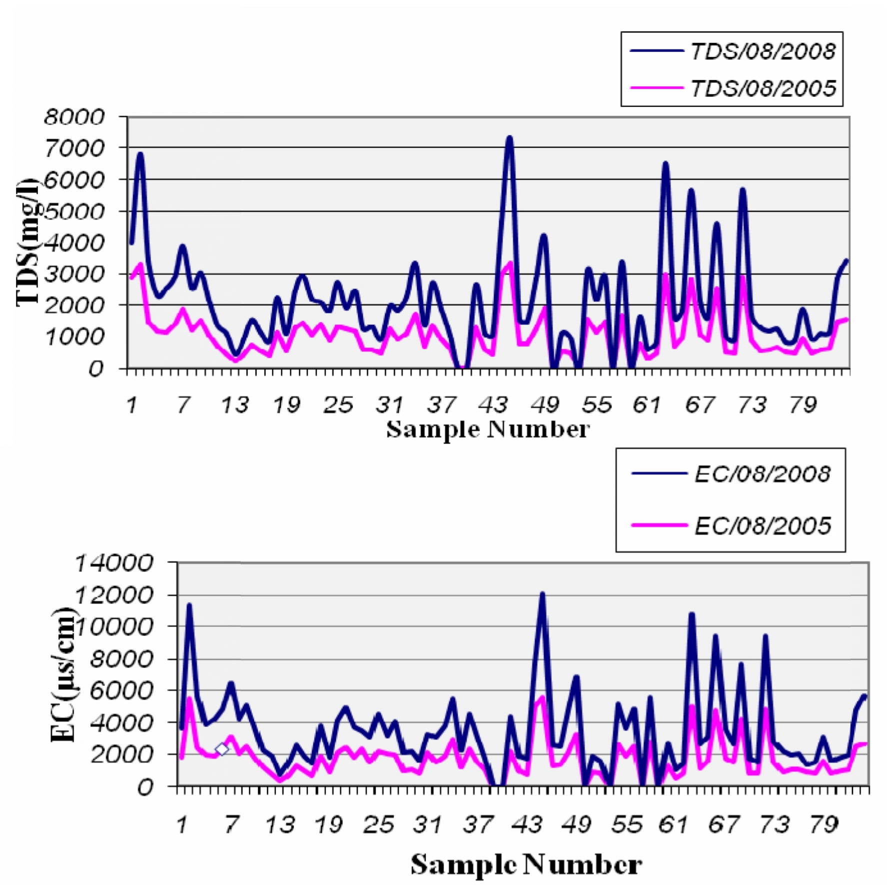


Fig. 4. Piper Comparison of the average electrical conductivity and total dissolved solids from July 2005 to July 2008 in Marand plain

3.3.1 Total dissolved solids and electrical conductivity

To ascertain the suitability of groundwater for different consumptions, it is essential to classify the groundwater based on their TDS values [12]. Approximately 55% of samples in the region are fresh water (TDS <1000) while the rest of the samples represent brackish water (TDS = 1000-10000) based on Freeze and Cherry (1979). Only 19.5% of the samples have TDS less than 500 mg/l and can be used for drinking without any problem based upon classification of Davis and DeWiest [13], whereas only 2% are not suitable for irrigation purposes (Table 4). Study of electrical conductivity of groundwater in Marand plain reveals that 48% of the samples are within the permissible limit (EC< 1500) and 40% of the samples fall in not permissible limit (EC =1500-3000 *mho* cm^{-1}).

3.3.2 Sar

S.A.R (sodium adsorption ratio) is an important parameter for irrigation because it is a measure of alkali/sodium hazard to crops. The analytical data plotted on the US salinity diagram [14, 15] (Fig. 5) to determine groundwater suitability for irrigation purposes similar to the approach [16]. Results show that approximately 42% of the groundwaters fall in the field of C3-S1, indicating water of medium-high salinity and low sodium and can be used for to irrigate. However, 26.5% of the samples fall in the field of C4-S2, indicating high salinity and medium alkalinity hazard. One sample comes under C4-S4 classification and may not be suitable for irrigation.

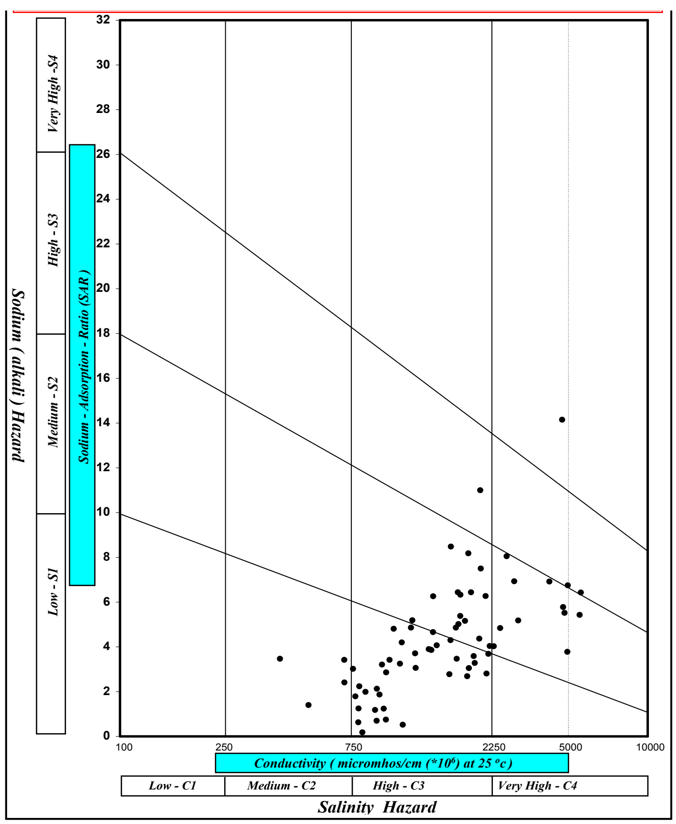


Fig. 5. Salinity and alkalinity hazard of irrigation water in US salinity diagram

Table 4. Groundwater classification of the study area based on Total dissolved solids and electrical conductivity

TDS (mg/l)	Classification [12]	Percentage of samples	EC (µs/cm)	Classification [7]	Percentage of samples
<500	Desirable for drinking	19.5	-	-	-
500-1000	Permissible for drinking	36	<1500	Permissible	48.2
1000-3000	Useful for irrigation	42.2	1500-3000	Not permissible	40.23
>3000	Unsuitable	2.3	>3000	Hazardous	11.5
Sum		100	Sum		100

4. CONCLUSION

The hydrochemical analysis demonstrates that the groundwater in Marand plain is fresh to brackish water and neutral to alkaline in nature. The alkaline earth ions (Ca^{2+} + Mg^{2+}) are more than alkaline ions (Na^+ and K^+) and value of Cl^- is more than the other anions. This leads to formation of CaMgCl type of groundwater. However, few groundwater samples represent $CaHCO_3$ and NaCl types. Sodium value of groundwater in one third of the study area exceed the permissible limit for drinking and the TDS values in 29% of samples are higher than World Health Organization (WHO) standard and 40% of the samples are classified as not permissible based on Electrical conductivity. 42% of the groundwater samples are in the field of C3-S1 on the Wilcox diagram and can be used for irrigation in almost all types of soil with little danger of exchangeable sodium. SAR values and the sodium percentage (Na %) in locations indicate that majority of the groundwater samples are suitable for irrigation. Due to grow in population and agricultural activities, the aquifer of the Marand plain is already, being over-exploited which caused the salinity of groundwater and would be making it unsuitable for the domestic purposes and the irrigation of some lands in the studied area.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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