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Salinity Variation of Ground Water and Hydro Chemical Characteristic of Brines Origin of Salts and Brine Evolution of Borazjan, Iran

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ABSTRACT

Borazjan plain, located in the south of Iran and located in Helleh basin, lies within a typical arid to semi-arid area. Within its drainage area of about 4540 km², the ground water of its shallow alluvial aquifer is relatively high in salinity. The present study integrates by hydrochemistry study has tried to mixing zone position and shape of mixture of saltwater and soft water of surface water effects on groundwater quality that have been studied for first time and by hydrochemical methods and composition diagrams with maximum accuracy, as well, that led to the aquifer salinity. Samples were analyzed for major ions, nitrates, BOD₅, COD, heavy metals, whilst in situ measurements of pH, electrical conductivity and water temperature were performed. The Na/Cl ratios of brines were approximately 0.621, respectively, which was close to the combined ratio of Na and Cl in pure crystals of halite, 0.65. The chemical compositions of K/Cl, Ca/(SO₄+HCO₃) and Mg/SO₄ of some groundwater were mostly greater than brines. The results of chemical analysis indicate that the ground-water salinity is highly variable and inconsistent along the course of the plain. This variability is probably due to the local hydrogeological conditions and to the intensive evaporation of effluent surface irrigation water that led to the precipitation of evaporites, e.g. calcite, dolomite and gypsum, especially affecting the ground-water at shallow depths. Extensive pumping has caused serious quantitative and qualitative problems in the aquifer and also plays a role in determining the risk of ground-water salinity in this aquifer.

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INTRODUCTION

Recent years, salinization and decreasing quality of groundwater have changed to serious environmental difficulties in the world. This subject increases the importance of proper management in groundwater consumption. Proper management in groundwater consumption without sufficient knowledge about distribution and expansion of fresh and saline groundwater and also determining effective procedures in its evolution is not possible [2]. Salinity of soil and water resources is one of the most important difficulties in Iran. This subject is dependent to numerous factors such as insufficient raining, high degree of evaporation and transpiration, topographic condition which results from closed or half closed basins, irrigation with low quality water and not proportionate drainage and irrigation systems [3]. The main groundwater salinity challenge and sea water intrusion in the semi-arid coastal aquifer is caused by recharge deficiency. This problem is further heightened by the fact that often in these areas groundwater utilization is the only available resource to fulfill demands and such a situation causes imbalances and water scarcity problems in these areas [4, 5]. Water quality of the Borazjan plain is influenced by the geological structure, agricultural activities, as well as by untreated waste effluent that is discharged from the villages and brine spread along the basin. Water quality deterioration has been recorded in the last decades in of Helleh and Dalki rivers and groundwaters, due to mineral dissolution of adjacent formation such as Halite and Gypsum in some parts of plain and human activities. River water seepage is known to considerably contribute to groundwater recharge in several basins and the Helleh river basin is considered amongst them. Thus, surface water quality affects groundwater quality of the aquifer system that is formed in the basin, which is the main source of potable water.

1.1.1. Study area:

Borazjan study area is located in Helleh basin. This area is restricted in longitudes 49° 29' 84" up to 53° 00' 40" East and latitudes 32° 22' 10" up to 32° 45' 93" and Genaveh study area in North, Ahram study

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area in South and Shahpoor and Dalaki watershed in West. Climatically, this region is located in area with mean annual rain fall of 259.8 mm and mean temperature of 29.9 °C and according to Emberger divisions is a desert district with middle warm climate. Borazjan area is located in one of the syncline of folded belt of Zagros mountain. The effect of tectonic forces on this region caused anticlines, tectonization formation and to from thrust faults and Qatar – Kazerun fault which with northern – southern direction passes through eastern part of plain. Qatar – Kazerun fault has divided study area into mountains and plain district which mountains district is located in eastern part of region. Surrounding heights of region in northern and southern areas include hills and high grounds of Bakhtiyari formation and in eastern area include of Gisakan anticline with north western – south eastern direction and maximum height of 1785 meters from sea level with river water from Cretaceous to Pliocene. Stratigraphy of this study area has been shown in figure 1.

Water samples were transported to the laboratory immediately after sampling, and their analyses were done in a short time after it. Samples analyses were done by the Ion chromatography method by means of a Metrohm-Compact IC 761. Parameters including temperature, pH, electrical conductivity and TDS were measured in situ and the chemical analyses of the samples were done at the laboratory of Zagros Abshenas Shiraz Company. Statistical parameters results of hydro chemistry data regarding to experimented water samples have been shown in tables 1and 2.

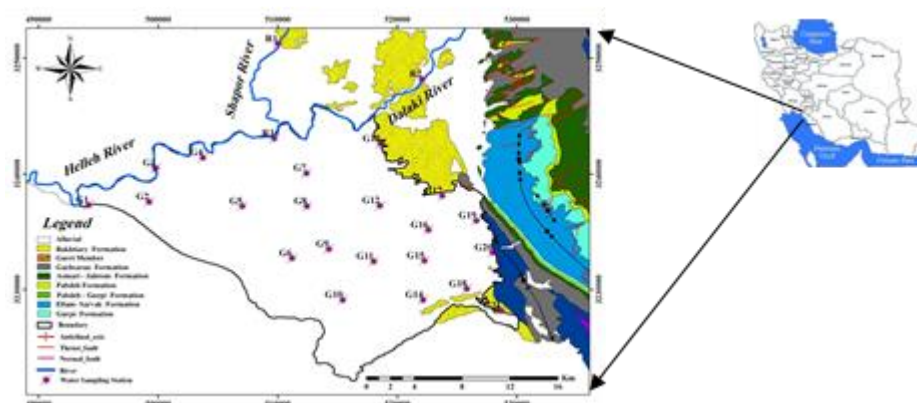


Fig. 1: Location map of the study area and sampling stations.

Table 1: Analytical data of the samples collected in May2012.

Sample	$\mu\text{m} / \text{cm}$	pH	mg/l							
	EC		TDS	SO ₄	HCO ₃	Cl	Ca	K	Na	Mg
G ₁	2890	8.6	1647.3	824.1	107.7	1687.4	653.9	8.8	1087.6	346.9
G ₂	2430	7.8	1312.2	239.1	70.4	656.7	242.2	4.07	422.1	127.7
G ₃	5430	7.2	2986.5	602.4	78.7	1233.6	478.1	6.46	795.1	253.6
G ₄	3037.5	7.6	1822.5	332.6	98.04	913.6	337	5.6	587.1	177.7
G ₅	2785	7.7	1531.7	748.4	71.7	393.9	763.6	7.8	239.3	117.5
G ₆	13450	7.6	7532	1341.2	169.8	3491.6	1198.2	47.3	1874.3	858.3
G ₇	12490	7.5	7244.2	1553.4	169.8	3382.7	1358.7	56.8	1895.1	878.2
G ₈	2697	7.6	1483.4	269.5	79.4	740.5	273.1	4.5	475.9	144.03
G ₉	3450	7.8	2208	401.2	118.2	1102.2	406.5	6.8	708.3	214.3
G ₁₀	8080	7.4	5009.6	631.2	137.5	2525	620	11.8	1475	451.2
G ₁₁	8050	7.2	4588.5	580.4	126.4368	2321.8	570.1	10.9	1356.3	414.9
G ₁₂	5320	7.3	3032.4	380.2	82.8	1521.1	373.4	7.1	888.5	271.8
G ₁₃	13240	7.5	8076.4	1242	174.8	1698.3	1159	10.7	1102.8	552
G ₁₄	7700	7.1	4312	1167.2	164.2	1596.1	1089.4	10.2	1036.4	518.7
G ₁₅	7820	8.1	4535.6	1454.5	172.7	1678.2	1145.4	12.1	1018.2	545.4
G ₁₆	5470	8.3	3336.7	1273.8	111.6	1363.9	986.7	10.6	827.02	436.7
G ₁₇	4270	7.4	2350	1323.4	136.1	949.4	1649.5	13.4	619.5	321.2
G ₁₈	8940	7.9	5274.6	1424.3	200.4	1947.6	1329.4	12.2	1264.6	633
G ₁₉	7870	7.6	4643.3	1262.2	177.6	1725.9	1178	10.8	1120.7	560.9
G ₂₀	8120	7.9	4628.4	7.8	1.1	1707	7.3	0.1	1108.4	3.5
G ₂₁	8834	8.9	5212.1	1386.2	195.1	1895.4	1293.7	11.9	1230.8	616
R ₁	4542.8	8.1	2595.9	524.8	68.6	1074.7	416.5	5.6	692.7	221
R ₂	7370	7.4	4200	1750	258	2012	1451	32	1120	544
R ₃	38900	7.2	24700	7905	89.9	12930.8	72.8	748.6	84668.7	2325

Table 2: Concentration of trace and heavy elements in groundwater and surface water.

Sample	(mg/l)					(MPN)		(µg/l)		
	COD	BOD	NO ₃	NO ₂	NH ₄	F.C	T.C	Zn	Mn	Fe
G ₁	4	0	13.8	0.02	1.6	ND	120	ND	11	5
G ₂	6	3	11.3	0.23	1.4	ND	60	ND	10	6
G ₃	5	3	18	0.1	1.3	20	130	7	12	5
G ₄	3	0	10.3	0.21	1.7	10	105	7	9	6
G ₅	9	6	23	0.3	2.8	45	490	11	8	10
G ₆	7	4	21	0.05	1.2	48	490	14	9	11
G ₇	6	2	22.14	0.21	2.7	25	230	13	8	13
G ₈	3	1	3.2	ND	Nd	ND	60	7	7	ND
G ₉	3	0	4.8	ND	ND	Nd	45	ND	ND	ND
G ₁₀	6	3	12.3	0.2	2.1	25	280	13	14	9
G ₁₁	6	2	32.5	0.3	2.2	42	160	15	15	8
G ₁₂	8	4	24.3	0.1	0.68	30	205	13	7	8
G ₁₃	3	1	13.5	ND	2.2	25	150	10	8	6
G ₁₄	4	2	12.3	0.2	4.4	ND	105	12	7	ND
G ₁₅	6	3	11	0.12	0.32	35	230	9	6	8
G ₁₆	7	4	32	0.1	2.1	15	110	ND	21	6
G ₁₇	3	1	11	ND	2.7	ND	ND	ND	ND	ND
G ₁₈	8	4	43	0.13	2.1	20	130	13	16	9
G ₁₉	7	4	34	0.2	1.68	45	230	15	19	11
G ₂₀	0	0	6.4	ND	Nd	ND	115	ND	ND	ND
G ₂₁	4	0	5.7	Nd	Nd	Nd	120	5	11	4
R ₁	7	2	3.1	ND	1.1	90	390	18	23	28
R ₂	27	17	30	0.5	15	2100	13500	115	48	120
R ₃	13	2	2.5	ND	1.86	10	110	19	28	38

RESULTS AND DISCUSSION

1.2. Groundwater chemistry:

Percolating water flows through pore spaces very slowly in fine-grained sediments. Silt, clay, fine sand allows long exposure periods which favor the dissolution of minerals. However, the depth to water table from ground surface is typically shallow in the study area, resulting in relatively short travel times (weeks to months). On alluvial plains of study area, the soil conditions range from continuous reduction controlled by high groundwater to alternating reduction and oxidation because of artificial submergence and groundwater fluctuations. As soil is water-saturated or submerged most of the year due to seasonal flood and paddy cultivation, the diffusion of gases into the soil mass is drastically cut and aerobic organisms rapidly deplete the oxygen in the surface soil. To oxidize organic matter, these organisms use either reducible inorganic components such as nitrate, manganese, iron oxide and sulfate or certain reducible organic compounds. As a result, the soil is reduced.

Over the past few decades there has been a continuous increase in agricultural activity with increasing use of fertilizer. This may play a vital role on water chemistry. Nitrate values are from 2.5-43 mg/l (R3-G18) and nitrate sources are agricultural activities and sewage effluent through seepage from septic tanks [6]. It is pointed out that, both manure and fertilisers are applied at the cultivated crops of the study area.

Fertilizers, for e.g., Urea (N as NO₃⁻ or NH₄⁺) and Marinate of Potash (K₂O) are used by farmers in the area at the rate of about 2.5–43. Iron (Fe) and manganese (Mn) concentrations are high detection limit, which is high than 0.1 and 0.03 mg/l, respectively, in most of the examined samples. High Fe concentrations (0.12 mg/l) and Mn concentrations (0.48 mg/l) are recorded at samples collected from area. Likewise, zinc (Zn) concentration in the majority of water samples is under 3.76 mg/l, whilst a maximum value of 0.115 mg/l is recorded in a sample located Dalaki river. Significant spatial variations of the COD (from 0 to 27 mg/l) were noted, the highest values being recorded at the R3(Helleh river). The majority of the samples have BOD₅ values under WHO[7], which is 2.4-3 mg/l, depending on the sample quantity. Higher values (17 mg/l) are recorded at sampling point R2(Dalaki river) for the period of May 2012. In general, rivers BOD₅ and COD values increase.

It is therefore suggested and supported by the analyzed data, that apart from other existing mechanisms, the uncontrollable discharge of untreated domestic and industrial effluent in the river leads to groundwater quality deterioration.

2.2. Geochemistry of major ions:

Physicochemical data and major ionic concentrations of 24 analyzed groundwater and rivers samples are summarized in Table 1. Groundwater pH is predominantly near neutral to slightly alkaline (7.13–8.9).

Temperature is found to be almost uniform in all the samples, ranging from 14.3 to 23 °C. Electrical conductivity (EC) of groundwater widely varies from 2430 to 38900 $\mu\text{m}/\text{cm}$ at different depths. Highest EC value observed at deep aquifer. High EC values of some samples indicate the presence of saline groundwater. The concentration of major cations, e.g. Ca^{2+} (7.3–1649.5 mg/l), Mg^{2+} (3.5–2325 mg/l), Na^+ (239.3–84668.7 mg/l) and K^+ (0.1–748.6 mg/l) levels do not change systematically with wells depth. The Schoeller diagram shows the concentration differences of chemical constituents of groundwater (Fig. 2). From this figure one can see that major ions in groundwater are quite variable in concentration.

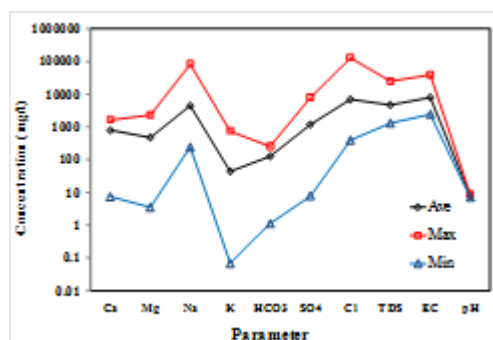


Fig. 2: Schöeller diagram showing the level difference between major ions of the groundwater

3.2. Piper diagram:

To classify the major in ions for groundwater and to summarize themajor contrasts in hydrogeochemical composition between different water sources, Piper diagrams are widely used. Plots of major ions on a Piper diagram[8] (Fig. 3) show that most of the samples are clustered at group-I of the central diamond and only two samples (G1 and R3) are clustered in group-IV. Detailed compositions of the studied samples are shown in Table 1. Most of the samples are Na – Cl type. Groundwater samples from districts are representing saline water type. EC (2430–38900 $\mu\text{m}/\text{cm}$) and concentrations of Na^+ (239.4–84668.7mg/l) and Cl^- (393.9–129308.8 mg/l) of these samples are high. Total dissolved solid (TDS) is an important parameter that can be used to observe the influence of major components in groundwater quality. The groundwater concentrations of Na^+ and Cl^- are plotted against TDS (Fig. 4a and b). The plot shows that most ions are positively correlated with TDS. In particular, the concentrations of Na^+ and Cl^- of samples as mentioned above show a strong correlation ($R^2 = 0.71$ and 0.67 , respectively) with TDS. Samples G1 and R3 fall on the marine origin site of Piper diagram.

These are brackish water due to sea spray. The brackish chemistry probably results fromrelict seawater entrapped in these sediments during the Holocene transgression [9]. If fresh groundwater is simply mixed with saline water, the groundwater will be plotted with seawater portion of the piper plot, all samples represent brines origin site of the piper plot having Na-Cl type indicating mainly a result of mixing with brines. To observe the major components that influence groundwater quality, the relationship between TDS and major ions in the groundwater were plotted (Fig.4). The plot shows that most ions are positively correlated with TDS. In particular Na^+ and Cl^- show a strong correlation ($R^2 = 0.7092$ and $R^2 = 0.6739$, respectively) with TDS indicating that such ions are derived from the same source of saline waters. The Cl^- concentrations of groundwater samples ranges from 393.9 to 129,308.8 mg/l which can be considered as mixtures of fresh water and saline water ($\text{Cl}^- = 50$ –5,000 mg/l, mixture of fresh water and saline water) according to Yongje Kim et al. (2003). The most saline waters are observed in the wells (R3 and G6) of east and south of the area.

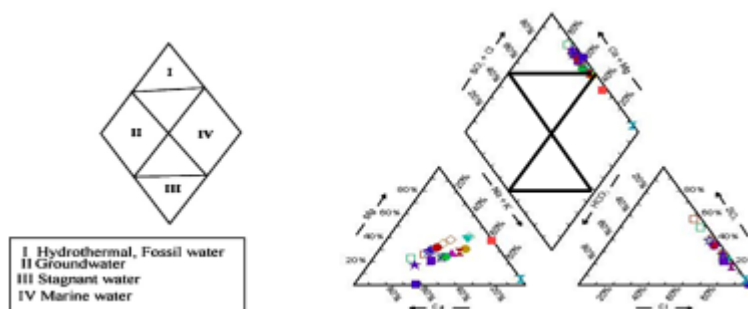


Fig. 3: Piper diagram showing the chemical composition of groundwater samples in the study area.

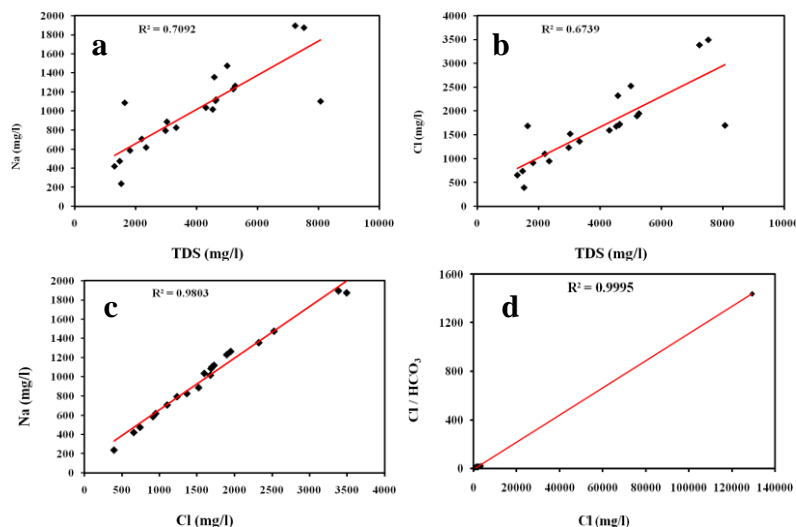


Fig. 4: Bivariate plots showing relationship between (a) TDS and Na, (b) TDS and Cl⁻, (c) Cl⁻ and Na⁺, (d) Cl⁻/HCO₃⁻ and Cl⁻

4.2. Salinity map:

As shown in figure.5. higher salinity is observed in North part of the study area and the lowest and medium salinity is bounded in the southeast and wards west respectively. In addition to the EC map, the chloride, magnesium and boor ion concentrations have confirmed the saline water intrusion towards the coastal aquifer. Figure 4 indicates this case with an increasing of the electrical conductivity (EC) concentration of the chloride ion which is considered as a sea water intrusion index. Irrespective to the three of mentioned zones, it is evident that a maximum salinity anomaly is developed in the northern part due to a heavy withdrawal (Figure 5).

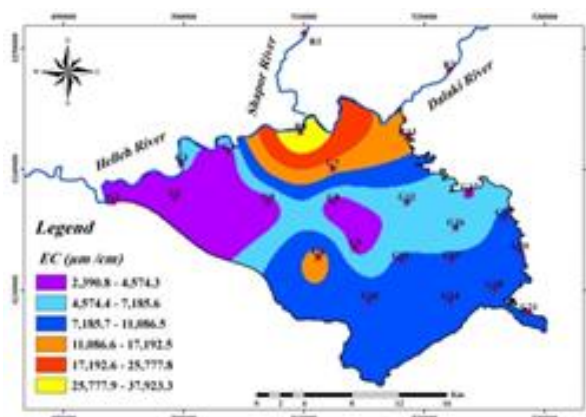


Fig. 5: Salinity distributions in the study area.

Potential salinization sources are diverse, including natural saline groundwater, halite dissolution, presence of paleo-brackish water, seawater intrusion, oil and gas-field brine, domestic, agricultural and industrial

effluents, and road salts. Among these sources, seawater intrusion is the most common and widespread in coastal areas, and forces the abandonment of water wells in many instances. In addition, inland salinization may occur due to the presence of paleo-brackish water entrapped in a small area during rapid regressive events or by halite dissolution. Agricultural application of K^+ as a plant nutrient commonly results in Cl^- contamination of recharging shallow groundwater. The fate of K^+ is complicated in part by ion exchange with clay minerals and by assimilation into growing plants. Therefore, K^+/Cl^- ratios in agricultural recharge are generally less than 1 (Fig. 6), and evidence for agricultural K^+ enrichment over background concentrations [10].

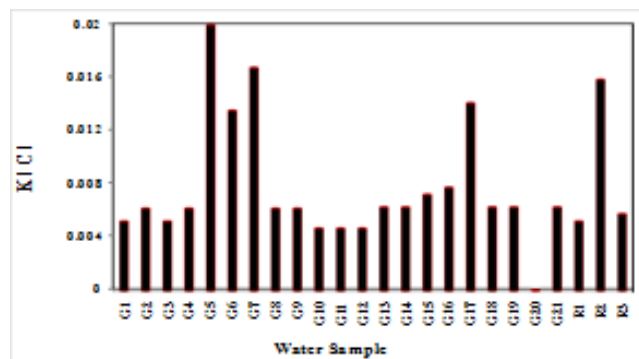


Fig. 6: Distribution of K/Cl of samples at different locations.

Relict seawater entrapped in these sediments during the Holocene transgression may cause the elevated Na^+ and Cl^- concentrations mainly in deeper aquifers. High NH_4^+ dissolved concentrations ranging maximum of 4.4 mg/l are observed in shallow samples. Sources of NH_4^+ may be fertilizer, decay of buried organic matter or from latrines at nearby villages.

Conclusion:

The hydrochemical analysis of both surface and groundwater in the Gallikos river basin has provided useful information on water quality. Surface water quality deterioration is apparent and is mainly attributed to anthropogenic pollution. Groundwater samples collected from boreholes drilled near the river are found to be affected by surface water pollution, as river seepage is a main aquifer recharge mechanism.

The groundwater in the study area is classified into type, the $Na-Cl$ type. The major ion trends are $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $Cl^- \rightarrow SO_4^{2-} \rightarrow HCO_3^-$. Agricultural activity i.e., use of chemical fertilizers, land-use pattern and extended groundwater abstraction for agriculture cultivation are important factors influencing both aquifer chemistry and accumulation and mobility of As from soil to groundwater. Potential salinization sources in the study area are mainly presence of paleo-brackish water and agricultural effluents.

The area is located far from the coast and seawater intrusion. Many of the solutes present in the groundwater can influence adsorption of As. Adsorption of As by metal oxyhydroxides mainly, Fe-oxyhydroxides and clay minerals is likely to be a major control on the transport of As in groundwater and are mobilized under Fe and SO_4^{2-} -reducing conditions. Microbial oxidation of organic matter and reductive dissolution of Fe and Mn-oxyhydroxide are the important processes to mobilize. The highest bacteriological pollution was found in 22 locations where MPN coli $>1000/100$ m/L and high pollution was found in 22 locations where MPN coli is between 105 and 13500 $1000/100$ m/L in R2 of Dalaki river.

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