Journal of Biodiversity and Environmental Sciences (JBES)
ISSN: 2220-6663 (Print) 2222-3045 (Online)
Vol. 6, No. 5, p. 269-280, 2015
http://www.innspub.net

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RESEARCH PAPER

OPEN ACCESS

Surface water quality assessment in Gilan Province, Iran

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Article published on May 23, 2015

Key words: Hydrogeochemistry, Irrigation water quality, Surface water, Gilan province.

Abstract

Surface water in Gilan province is assessed in order to determine its hydrogeochemistry and irrigation water quality using 55 water samples. In this regard, concentration of major ions and physicochemical parameters including $\mathrm{Ca^{2+}}$, $\mathrm{Mg^{2+}}$, $\mathrm{Na^{+}}$, $\mathrm{K^{+}}$, $\mathrm{HCO_3^-}$, $\mathrm{Cl^-}$, $\mathrm{SO_4^{2-}}$ and $\mathrm{CO_3^{2-}}$ pH, EC and TDS were determined. The average content of the major cations and anions follow as: $\mathrm{Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}}$and $\mathrm{HCO_3^- > SO_4^{2-} > Cl^- > CO_3^{2-}}$, respectively. Hydrogeochemical composition of surface water is a mixture of water types including $\mathrm{CaMgHCO_3}$, mixed CaMgCl and NaCl. Nonetheless, themajority of the samples has$\mathrm{CaMgHCO_3}$water type. Hence, alkaline earths and strong acid anions exceed alkalis and weak acid anions, respectively. Based on Gibbs diagrams and ionic ratios, weathering of silicate minerals is the main process controlling the surface water chemistry. Saturation indices (SIs) indicate that dissolution of carbonate minerals also plays an important role in regulating the surface water chemistry. Although sodium percentage (Na%), sodium adsorption ratio (SAR), electrical conductivity (EC), total dissolved solids (TDS) and permeability index (PI) in most of the samples are below the standard, nonetheless, residual sodium carbonate (RSC) and Total hardness (TH) indicate significant irrigation water unsuitability and hence thenecessity for caution and future study.

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Introduction

Intensive developments of industry, agricultural production and ever intensive urbanization have led to the increase in number of pollutants and the amount of wastewater which pollute water flows. On the contrary, the need for water of satisfying quality continuously grows. A big amount of agricultural, municipal and industrial wastewater discharges to water bodies around the world. The discharging of degradable wastewater in water bodies result in decrease in water quality generally and particularly DO (Dissolved Oxygen) concentrations (Nakhaei*et al.,*2010). Disposal of municipal, agricultural and industrial wastewater into the rivers with little or no treatment prior to discharge is a common practice in many developing countries. This has caused a serious concern over the deterioration of river water quality (Hadgu*et al.,*2014).

Recently, pollution has become a serious concern for human life due to the industrial burst in the world. And, the rivers are the main choices to hold and bear the responsibility of pollutants, especially in the developing countries (Akter*et al.,*2014).

The concerns over surface water quality are gradually emerging due to the disposed location of industrial units and the adverse effects on surrounding land and aquatic environment, as well as subsequent impacts on the system of the local community (Islam *et al.,*2011).

Surface water resources such as rivers are among the most vulnerable water bodies to contamination. Rivers play important role in transporting domestic and industrial wastewaters and non-point source pollutants (Singh *et al.,*2004). The quality of surface water is largely affected by physical, chemical and biological processes such as weathering of rock minerals, climate and amount of precipitation. Anthropogenic activities (domestic and industrial wastewaters, land reclamation, atmospheric deposition, irrigation return flow, etc.) can also degrade surface water quality and impair its use for drinking, industrial and agricultural uses. To characterize and control the surface water suitability regular monitoring programs seem important (Simeonov *et al.,*2004). Hence, the monitoring of surface water quality parameters is subjected as one of the most effective approaches to assess the environmental status of water resources, and also to set up the environmental protection policies.The main objective of this study is to evaluate surface water hydrogeochemistry and its suitability for irrigation water use.

Materials and methods

Study area

Gilan province is situated in north latitudes 36 34 and 38 27 and east longitudes 48 53 and 50 34, and is bounded by republic of Azerbayjan and Caspian Sea on the north, Mazandaran and Caspian Sea on the east, Ardabil on the west, and Qazvin and Zanjan on the south (Fig. 1.a). Gilan covers an area 14711 km^2 and includes 16 townships (Fig. 1.a) and contains 0.9% of the total area in Iran. The study area experiences the climate of very humid and sultry in the east (near to Caspian Sea) and mild and humid in the center and west. The relative humidity is 80%, varying between 55% in July and 98% in October, being the most humid province in Iran. Average annual temperature is 15.8 ˚C, ranging from 7.5 ˚C in winter and 24 ˚C in summer. Rasht, the capital of the province, is internationally known as the "City of Silver Rains" and within Iran as the "City of Rain". Average annual rainfall is 1402 mm, with a minimum 40.2 mm in July and maximum 2302 mm in October. According to the latest census in 2013, the population of Gilan is 2480874, which 61% is urban and the rest rural. Agriculture and forest activities are the most important professions in the study area.

Geologic setting

The western Alborz range on the south and Talesh Mounts on the north and west as huge barriers have surrounded Gilan. At Pleistocene, the morphology of Gilan was significantly changed by tectonics, climatic changes and erosion. The Recent sediments along with river, delta and coastal deposits and samples of older rock units cover most sectors of Gilan, indicating unstable nature of Gilan. The basement is mainly composed of volcanic igneous rocks (andesitic, basaltic and dacitic lavas and tuffs), regional metamorphic rocks (green schist and amphibolite schist facies, phyllite, meta-volcanic rocks, marble, serpentinite) and sedimentary rocks (limestone, sandstone, conglomerate, marl, shale, siltstone and coal) along with old and new terraces and alluviums (Fig. 1.b).Hydrologically, Gilan province is situated in Caspian Sea catchment area. The direction of surface water flow is towards Caspian Sea, thereby water flows from the highlands in the west to lowlands in the east (Fig. 1.c).

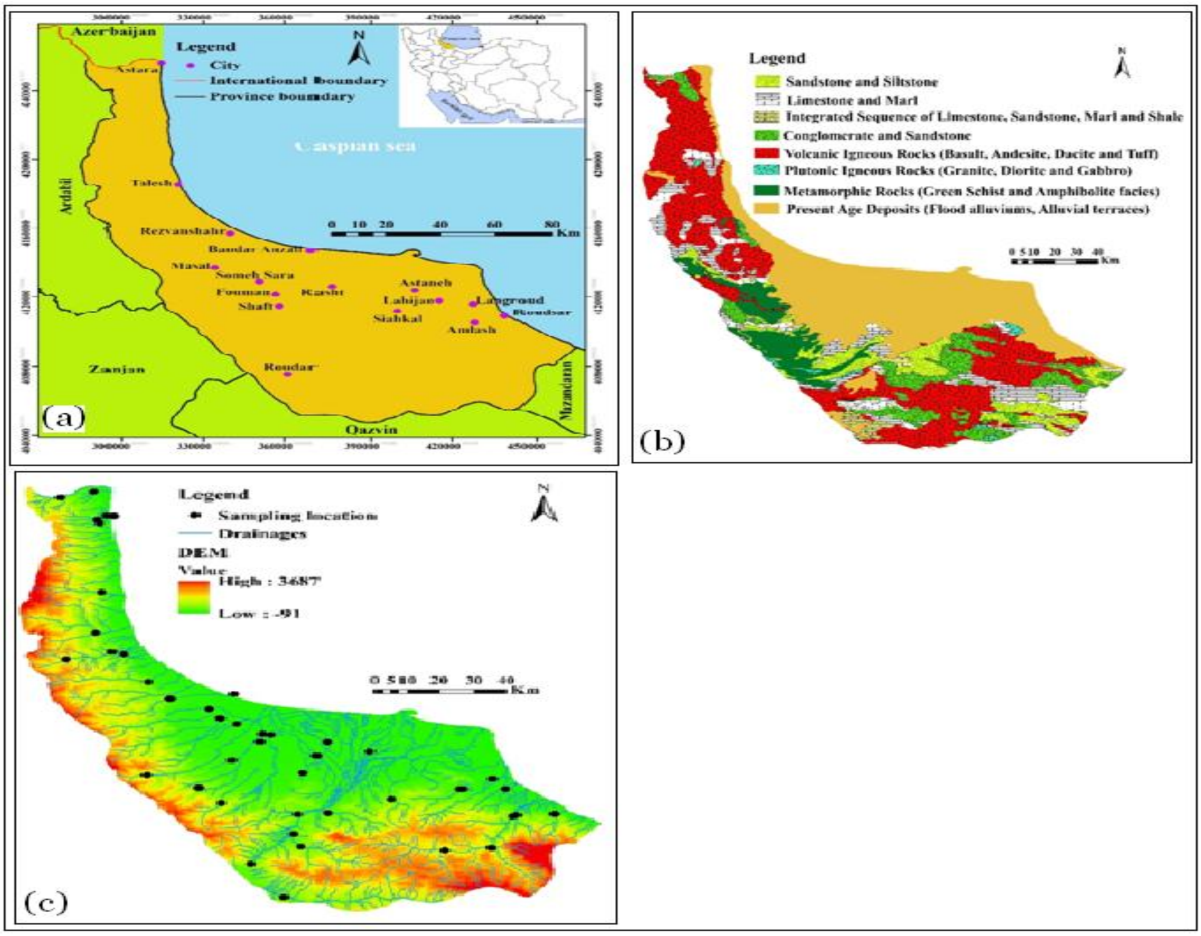

Fig. 1. a) Location of Gilan province, b) Lithology of the study area and c) sampling sites position along with digital elevation model (DEM).

Sampling and analysis

Sampling was carried out from 55 surface water samples in August 2013. Dry and clean bottles prewashed with diluted HNO_3(1:1) and rinsed three times with the sampling water were used to collect samples. Electrical conductivity (EC) and pH were measured at the site using standard portable instruments. The collected samples were instantly labeled, refrigerated and carried to Gilan regional water organization lab, and then retained at a temperature of 4˚C prior to analysis. Concentration of major ions was identified using the reference analytical methods (Table 1). TDS were also measured by evaporating pre-filtered samples to dryness.

Results and discussion

Physicochemical properties of the surface water The data were checked for normal distribution using

Kolmogorov–Smirnov and Shapiro-Wilk tests. Only HCO_3^- and pH are normally distributed ($\text{sig.} > 0.05$), while the significance level for the rest in both tests is lower than 0.05 and thus the data are non-normally distributed (Table 2). Therefore, the non-parametric tests was applied to statistically assess the data. Descriptive statistics of the analyzed data including minimum, maximum and mean is presented in Table 3. Average content of the major cations and anions are in the order of $Ca^{2+} > Na^+ > Mg^{2+} > K^+$and $HCO_3^- > SO_4^{2-} > Cl^- > CO_3^{2-}$, respectively.

Table 1. Experimental methods used to determine major ions concentration.

Parameter	Method
Sodium	Flame photometry
Potassium	Flame photometry
Calcium	Flame photometry
Magnesium	Flame photometry
Chloride	$AgNO_3$ titration
Sulfate	Spectrophotometry
Bicarbonate	Titrimetry
Carbonate	Titrimetry

Factor analysis (FA)

Factor analysis aims to reduce dimensionality and explain as much information included in the data as possible in the least possible components (Johnson and Wichern,1992; Reimann *et al.*,2002). FA for the variables EC, TDS, TH, pH, Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-} and CO_3^{2-} was carried out with principal component analysis (PCA) to identify favorable number of principal components (PC) using IBM SPSS 20. On the basis of eigenvalues >1, the first three components explain 82.63% of cumulative variance (Table 4).

The variables EC, TH, TDS, Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-} and Cl^- have positive factor loadings in PC 1 and explain 55.45% of the total variance. The constituents from PC 1 are possibly derived from the identical source, and/or undergo the same geochemical processes. PC 2 which is comprised of HCO_3^- and pH explains 17.39% of the total variance. This means that the surface water pH is primarily influenced by HCO_3^-, due to the buffering effect of HCO_3^-. PC 3 is characterized by high positive CO_3^{2-} factor loading and accounts for 9.78% of the total variance.

Table 2. Statistical tests used to determine normality of the data.

Variables	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Ca^{2+}	0.137	55	0.012	0.912	55	0.001
Mg^{2+}	0.128	55	0.024	0.883	55	0.000
Na^+	0.335	55	0.000	0.564	55	0.000
K^+	0.333	55	0.000	0.440	55	0.000
HCO_3^-	0.094	55	0.200*	0.959	55	0.060
SO_4^{2-}	0.243	55	0.000	0.670	55	0.000
Cl^-	0.389	55	0.000	0.537	55	0.000
TDS	0.251	55	0.000	0.738	55	0.000
EC	0.233	55	0.000	0.739	55	0.000
pH	0.062	55	0.200*	0.976	55	0.334
CO_3^{2-}	0.536	55	0.000	0.182	55	0.000

*. This is a lower bound of the true significance.

a. Lilliefors Significance Correction.

Hydrogeochemical facies

Hydrochemical facies indicate environmental processes and/or evolution pattern of a water body. Similarities and differences among surface water samples is generally displayed by Piper (1944) diagrams. Hence, the samples with similar qualities are plotted in common groups and show the same hydrogeochemical process. Piper diagram (Fig. 2.) reveals that the Surface water in Gilan is characterized by three hydrogeochemical facies. Hydrogeochemical composition of surface water is characterized by $CaMgHCO_3$, mixed $CaMgCl$ and $NaCl$ water types. However, majority of the samples fall in the fields of $CaMgHCO_3$, indicating the dominant water type in the study area. Therefore, alkaline earths ($Ca^{2+}$and Mg^{2+}) and strong acid anions (Cl^- and SO_4^{2-}) exceed alkalis (Na^+ and K^+) and weak acid anions (HCO_3^- and CO_3^{2-}), respectively. The dissolution of calcite, dolomite and Ca, Mg-bearing silicates in the geological Formations are significantly responsible for the predominance of alkaline earths. Calcium and magnesium can be released into the water regarding the following reactions and lead to simultaneous hardness in the surface water:

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^-$$

$$Ca, Mg(CO_3)_2 + H_2O + CO_2 = Ca^{2+} + Mg^{2+} + 2HCO_3^-$$

Table 3. Descriptive statistics of the variables.

Parameters	Mean	Min.	Max.
Ca^{2+} (mg/l)	46.4	14.0	116.2
Mg^{2+} (mg/l)	12.3	1.8	38.9
Na^+ (mg/l)	25.9	2.1	188.7
K^+ (mg/l)	1.8	0.4	19.9
HCO_3^- (mg/l)	158.2	49.4	317.3
SO_4^{2-} (mg/l)	40.2	4.3	194.0
Cl^- (mg/l)	38.5	3.6	283.6
CO_3^{2-} (mg/l)	0.1	0.0	3.0
TDS (mg/l)	290.0	71.8	1114.0
EC (µmho/cm)	442.2	114.0	1769.0
TH (mg/l)	166.5	42.5	450.2
pH	7.3	6.7	8.0

Processes controlling water chemistry

Physical, chemical and biological processes, geological structure and mineralogical composition of host rocks, and also anthropogenic activities such as domestic and industrial wastes, excessive use of agrochemicals and release of septic tank effluents can effectively influence the surface water chemistry (Appelo and Willemsen, 1987;Liu *et al.*,2014). To identify natural processes controlling groundwater chemistry in the region Gibbs (1970) ratios were computed via the following equations:

$$\text{Gibbs ratio 1 (for cations)} = \frac{Na^+ + K^+}{Na^+ + K^+ + Ca^{2+}}$$

$$\text{Gibbs ratio 2 (for anions)} = \frac{Cl^-}{Cl^- + HCO_3^-}$$

Gibbs ratios 1 and 2 vary between 0.99-1.00 and 0.01-0.67, respectively. Plotting the data on Gibbs diagrams (Fig. 3.) which were constructed by TDS versus $(Na^+ + K^+)/(Na^+ + K^+ + Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ shows that majority of the samples lie in the field of rock weathering dominance. It indicates that hydrogeochemistry is notably affected by carbonate and silicate minerals dissolution. Few samples fall in the field of evaporation-crystallization dominance.

Table 4. Factor analysis using PCA method.

Parameters	Component		
	1	2	3
Cl^-	0.962	0.106	-0.061
TDS	0.955	0.269	0.025
Na^+	0.930	0.095	-0.134
EC	0.911	0.222	0.092
SO_4^{2-}	0.864	0.220	-0.144
TH	0.805	0.501	0.210
Ca^{2+}	0.770	0.381	0.335
K^+	0.682	-0.228	0.152
Mg^{2+}	0.677	0.581	-0.042
pH	-0.005	0.890	-0.081
HCO_3^-	0.455	0.565	0.441
CO_3^{2-}	-0.087	-0.040	0.860
Total Variance	55.450	17.390	9.780

Saturation indices are usually used to evaluate the equilibrium degree between surface water and minerals. The thermodynamic controls on the water composition which has equilibrated with various minerals can be predicted by the calculation of the mineral equilibrium (Deutsch,1997). Comprehending Changes in minerals saturation state is important to distinguish the different stages of hydrochemical evolution and help determine which geochemical reactions are responsible for regulating water chemistry (Langmuir *et al.*,1997; Coetsiers and Walraevens, 2006). Hence, the saturation state of the groundwater was distinguished with respect to major carbonate minerals (calcite, aragonite and dolomite) and evaporites (halite, gypsum and anhydrite) using the hydrogeochemical equilibrium model, Phreeqc via the following equation (Parkhurst and Appelo,1999):

$$\mathrm{SI} = \log\left(\frac{\mathrm{IAP}}{\mathrm{Ksp}}\right)$$

where SI is the saturation index, IAP is the ion activity product and K_{sp} is the solubility product of a specific solid phase at given temperature. Figure 4 illustrates the saturation states of carbonate and evaporate minerals. Regarding carbonate minerals majority of the samples are plotted above the saturation line $(\mathrm{SI} > 0)$ while evaporate minerals mostly fall under the saturation line ($\mathrm{SI} < 0$). Hence, carbonate minerals primarily undergo precipitation process while evaporate minerals are mainly dissolved. Evaporate minerals such as gypsum and anhydrite gradually and without precipitation dissolve along the water flow, leading to increase in the content of calcium and thus decrease in the content of HCO_3^- and CO_3^{2-} by precipitation of carbonate minerals. Hence, Evaporites are difficultly saturated due to lack of enough Ca^{2+} in a hydrological system. It can thus be explained that carbonate minerals play an important role in controlling surface water chemistry in Gilan.

Table 5. Classifications presented for irrigation water parameters.

Index	Range	Water Class	Samples (%)
Na%	< 20	Excellent	60.01
	20-40	Good	23.63
	40-60	Permissible	10.9
	60-80	Doubtful	5.45
	> 80	Unsuitable	0
SAR	< 10	Excellent (S1)	83.64
	18-Oct	Good (S2)	9.09
	18-26	Doubtful (S3)	5.45
	> 26	Unsuitable (S4)	1.81
RSC (meq/l)	< 1.25	Good	1.81
	1.25-2.5	Doubtful	16.36
	> 2.5	Unsuitable	81.82
TDS	< 1000	Fresh	98.18
	1000-3000	Slightly saline	1.82
	3000-10000	Moderately saline	0
	10000-35000	High saline	0
TH	< 75	Soft	14.55
	75-150	Moderately hard	38.18
	150-300	Hard	38.19
	> 300	Very hard	9.09
EC	< 250	Excellent	18.18
	250-750	Good	67.27
	750-2000	Permissible	14.54
	2000-3000	Doubtful	0
	> 3000	Unsuitable	0
PI	≤ 25%	Critical	1.81
	25% - 75%	Unsuitable	5.45
	≥ 75%	Acceptable	92.74

Compositional relations of the major ions

The chemical composition of groundwater is influenced by several factors such as the mineralogical composition and physical properties of host rock(s), residence time of groundwater contacting with aquifer matrix and the nature of recharge water (Dudeja *et al.*,2011). The compositional relations among aqueous species can well be understood using ionic ratios.

The relation of Na^+ and Cl^- can easily be identified based on Na^+/Cl^- ratio. Figure 5 shows that the samples mostly fall below the equiline (halite dissolution line). Hence, dissolution of halite cannot significantly affect the surface water chemistry. Reverse cation exchange might be a possible process for the samples falling below the equiline. The additional content of chloride can also be derived from anthropogenic sources including irrigation return flow and industrial wastes. The samples lying above the equiline the cation exchange reactions can be a probable process which leads to bind calcium and magnesium on minerals adsorption sites and simultaneous increase in concentration of sodium and potassium.

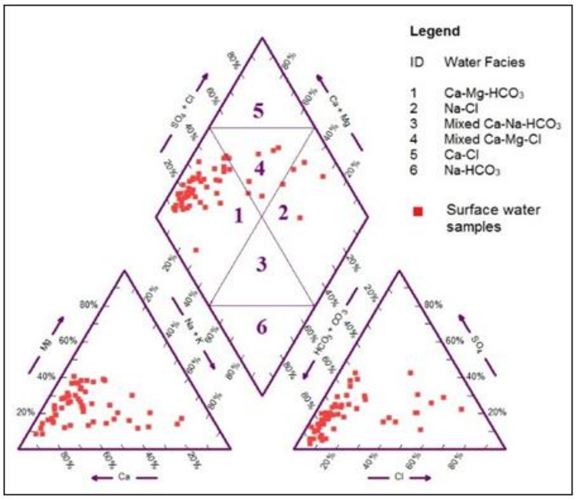

Fig. 2. Piper diagram showing hydrogeochemical facies in the study area.

The Ca^{2+}/SO_4^{2-} ratio can be used to well know Ca^{2+} and SO_4^{2-} relation. $Ca^{2+} - SO_4^{2-}$scatter diagram (Fig. 6.) reveals that majority of the surface water samples are plotted below the equiline (gypsum dissolution line). This means that dissolution of calcium sulfate minerals such as gypsum and anhydrite is primarily not responsible for supplying calcium and sulfate. Hence, Ca^{2+} and SO_4^{2-} are not involved in the identical geochemical processes(Hounslow,1995). Ca^{2+} can undergo a calcite precipitation and/or a Ca^{2+}/Na^{+} ion-exchange between clay minerals and water, while sulfates are majorly found as a dissolved species (Desbarats,2009). The additional sulfate content in the surface water also might be derived from anthropogenic sources such as irrigation return flow containing agrochemicals.

The $(Ca^{2+} + Mg^{2+})/HCO_3^-$ ratio superior to 0.5 is usually used to display $Ca^{2+} + Mg^{2+}$ and HCO_3^- relation. Based on Figure 7, most of the samples fall below the calcite and dolomite dissolution line, suggesting that calcite and dolomite cannot be a primary source regulating Ca^{2+}, Mg^{2+} and HCO_3^- chemistry. Weathering of silicate minerals along with reverse cation exchange might control the excess concentrations of HCO_3^-. Figure 8 also shows the relation of $Ca^{2+} + Mg^{2+}$ and $HCO_3^- + SO_4^{2-}$ for the samples. The $(Ca^{2+} + Mg^{2+})/(HCO_3^- + SO_4^{2-})$ ratio will be one, and also the data will be plotted along and/or on the 1:1 line if Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-} are derived from the dissolution of calcite, dolomite and gypsum. All of the samples lie below the line. Hence, silicate dissolution and/or cation-exchange process can occur.

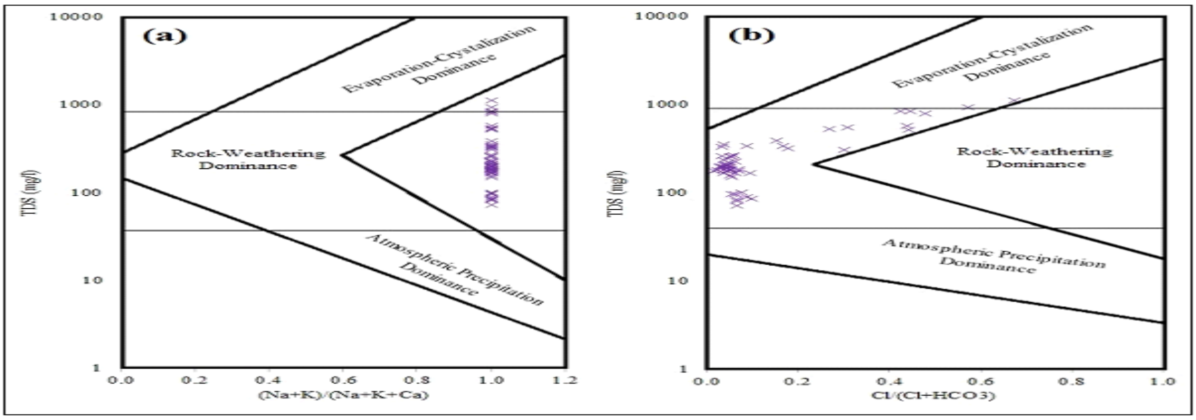

Fig. 3. Gibbs diagrams constructed by TDS as a function of a)$(Na^{+} + K^{+})/(Na^{+} + K^{+} + Ca^{2+})$ and b) $Cl^{-}/(Cl^{-} + HCO_3^{-})$.

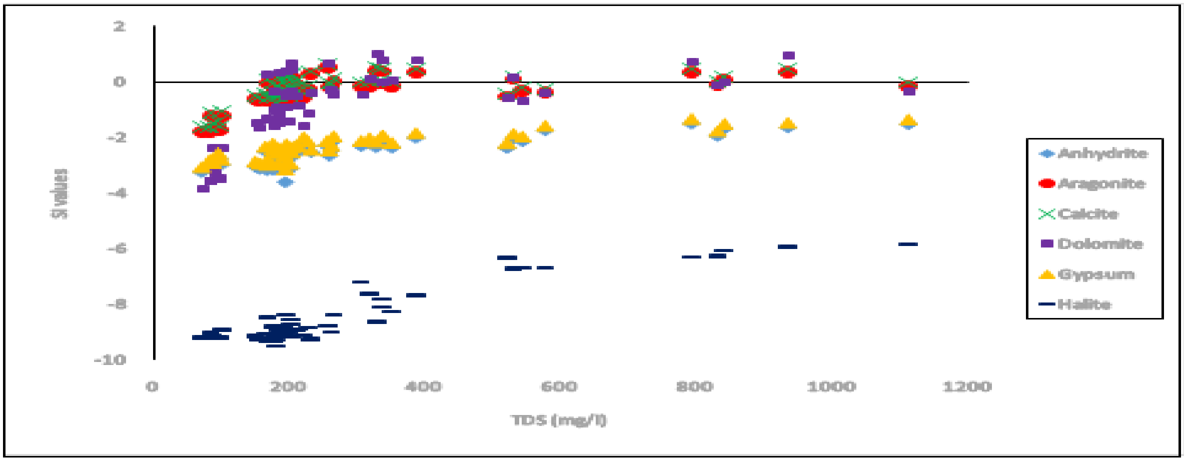

Fig. 4. Saturation indices (SIs) of major carbonate and evaporate minerals.

The Ca^{2+}/Mg^{2+} ratio was used to understand the effect of silicates dissolution. The ratios higher than 2 indicate weathering of silicate minerals (Katz *et al.*,1997) while the ratios lower than 2 suggest more proportion of carbonate minerals dissolution (Mayo and Loucks,1995). From Figure 9 it can be explained that silicates dissolution is the major process controlling the surface water chemistry in the study area. As well as if silicates dissolution is the main process average TDS should be less than 500 mg/l (Hounslow,1995). Most of the samples have a TDS value lower than 500 mg/l, thereby mean TDS value is 290 mg/l (Table). The abundance of igneous rocks in the study area (especially in the west and south) suggests that silicate weathering might occur based on the following reactions:

1) $2NaAlSi_3O_8 + 9H_2O + 2H_2CO_3 = Al_2Si_2O_5(OH)_4(\text{Kaolinite}) + 2Na^+ + 2HCO_3^- + 4H_4SiO_4$

2) $CaAl_2Si_2O_8\ (\text{Anortite}) + 2CO_2 + 3H_2O = Al_2Si_2O_5(OH)_4(\text{Kaolinite}) + Ca^{2+} + 2HCO_3^-$

3) $2KMg_3AlSi_3O_{10}(OH)_{10}\ (\text{Biotite}) + 14CO_2 + 15H_2O = Al_2Si_2O_5(OH)_4(\text{Kaolinite}) + 2K^+ + 6Mg^{2+} + 14HCO_3^- + 4H_4SiO_4$

5) $Mg_2SiO_4\ (\text{Olivine}) + 4H_2CO_3 = 2Mg^{2+} + 4H_4SiO_4$

6) $CaMgFeAl_2Si_3O_{12} + 6CO_2 + 5H_2O = Al_2Si_2O_5(OH)_4(\text{Kaolinite}) + Ca^{2+} + Mg^{2+} + Fe^{2+} + 6HCO_3^- + SiO_2$

All the reactions are acid consuming and thus have a pH buffering effect. The producing HCO_3^- in the reactions of silicate minerals weathering leads to high content of HCO_3^- in the water resources of Gilan.

Irrigation Water quality

The excess dissolved ions content might affect physicochemical soils and plants characteristics including lowering the osmotic pressure, disrupting plant metabolism and changes in the structure, permeability and aeration of soil. Therefore, irrigation water quality notably depends on content of the dissolved ions. Irrigation water quality is evaluated by investigation of EC, TDS, SAR, Na%, RSC, TH and PI. EC is a good measure of salinity hazard to crops. Growth and development of crops can be influenced by salinity from different ways including specific ion toxicity, nutritional disorders and osmotic effects (Lauchli and Epstein,1990).

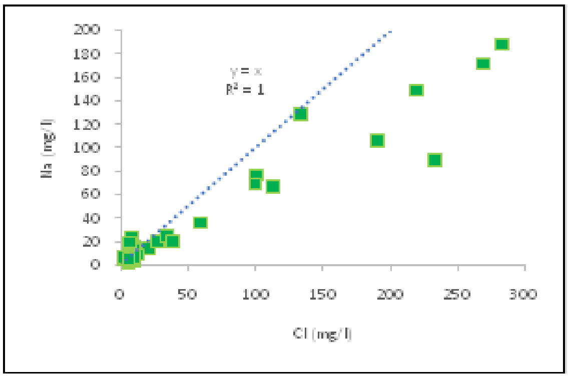

Fig. 5. Scatter plot of sodium versus chloride.

The excess content of salts in water causes formation of saline soil. The effect of TDS and EC on salinity of the water samples was assessed by Wilcox (1955) and Stewart and Kantrud (1971) classifications (Table 5). Based on EC classification, water quality in 85.45% of the samples is excellent to good. TDS value in 98.18% of the samples is <1000 and thus fresh for irrigation uses.

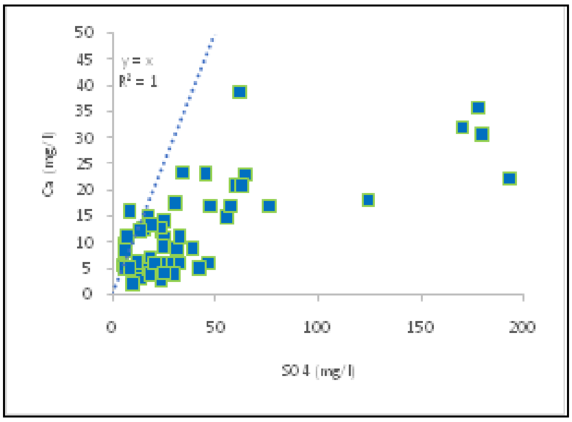

Fig. 6. Scatter plot of calcium versus sulfate.

High content of sodium leads to lose water quality and develop alkaline soil. SAR and Na% were computed as follow:

$$\mathrm{Na\%} = \frac{\mathrm{Na^+} + \mathrm{K^+}}{\mathrm{Ca^{2+}} + \mathrm{Mg^{2+}} + \mathrm{Na^+} + \mathrm{K^+}} \times 100$$

$$\mathrm{SAR} = \frac{\mathrm{Na^+}}{\sqrt{\frac{\mathrm{Ca^{2+}} + \mathrm{Mg^{2+}}}{2}}}$$

Based on SAR classification (Richards, 1954) majority of the surface water samples (83.64%) have excellent irrigation quality (Table 5). Wilcox (1955) classification based on Na% shows that the surface water samples (60.01%) mainly lie in excellent irrigation quality. Salinity and alkalinity hazards of soil can well be known using Wilcox and USSL diagrams. Plotting the data on Wilcox diagram (Fig. 10.) displays that 14.54% of the samples fall in the fields of doubtful and unsuitable while most samples have good to permissible quality for irrigation purposes. On the basis of USSL diagram (Fig. 11.), the samples fall in the various classes including C1S1 (14.54%), C2S1 (69.12%), C2S4 (1.81%), C3S2 (5.45%), C3S3 (3.63%) and C3S4 (5.45%). Most of the surface water samples fall in C2S1 (medium salinity and low alkalinity) which indicate irrigation water suitability for about all crops and soils. Medium salinity waters are especially appropriate for crops irrigation on coarse textured soils having fine permeability. It is much considerable that the usage of saline water for irrigation is solely under specific circumstances such as cultivation of salt-tolerate crops.

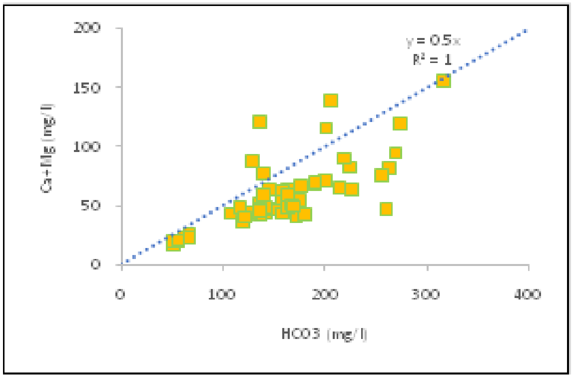

Fig. 7. Scatter plot of calcium and magnesium versus bicarbonate.

PI, proposed by (Doneen, 1966) is also an index to assess irrigation water suitability which is calculated via the following equation:

$$\mathrm{PI} = \frac{\left(\mathrm{Na^+} + \sqrt{\mathrm{HCO_3^-}}\right)}{\left(\mathrm{Na^+} + \mathrm{Mg^{2+}} + \mathrm{Ca^{2+}}\right)} \times 100$$

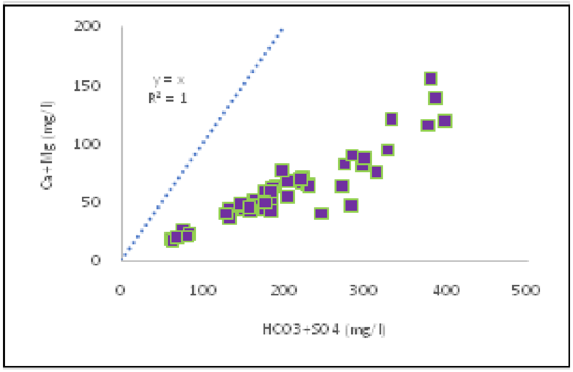

Fig. 8. Scatter plot of calcium and magnesium versus bicarbonate and sulfate.

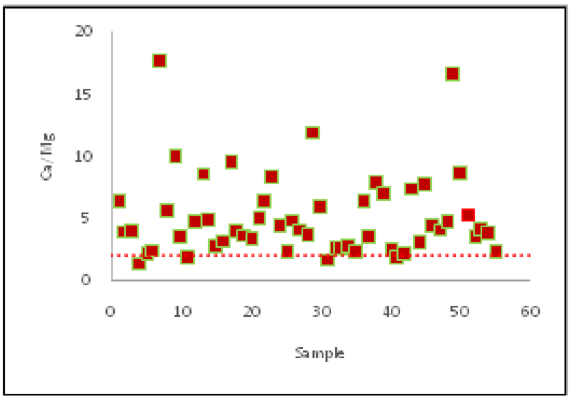

Fig. 9. $\mathrm{Ca^{2+}/Mg^{2+}}$ratio as a function of the samples.

Based on PI classification (Table 5), PI value in most of the water samples (92.74%) is greater than 75% which suggests irrigation water suitability.

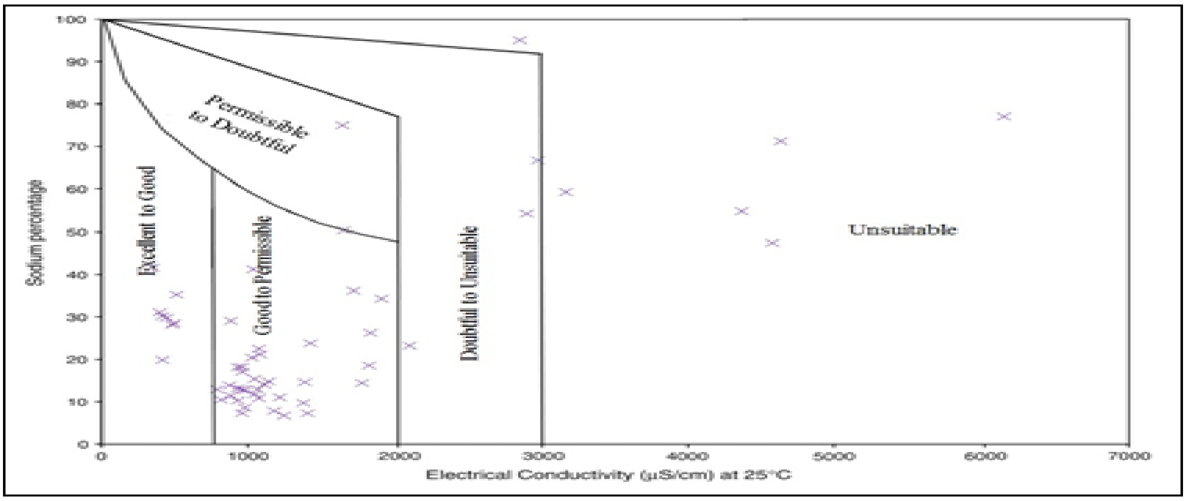

Fig. 10. Wilcox diagram constructed by sodium percentage versus EC.

The excess concentration of HCO_3^- and CO_3^{2-} in water and reaction with Ca^{2+} and Mg^{2+} of in soil solution causes Ca, Mg-bearing carbonate minerals precipitation, resulting in the dominance of sodium adsorbed on clay surfaces and enhancing exchangeable sodium percentage in the soil. This contributes increase in sodium hazard and consequent problems such as reducing soil permeability (Todd and Mays,2005). RSC index was calculated via the following equation to indicate the hazardous carbonate and bicarbonate effects on irrigation water quality

$$RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+})$$

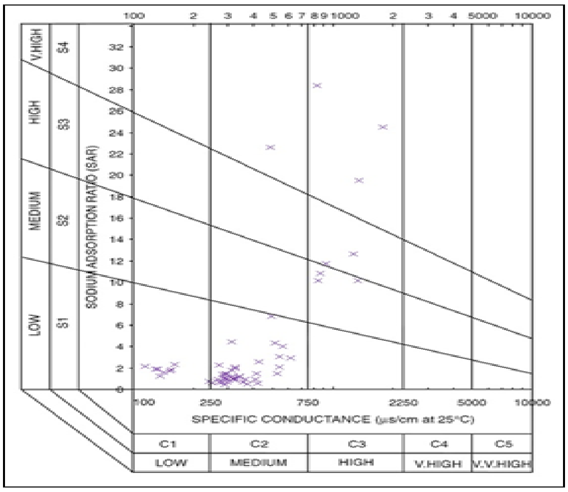

Fig. 11. USSL diagram constructed by SAR versus EC.

From the Table 5, it can be interpreted which RSC value in 81.82% of the samples is greater than 2.5, in meq/l, reflecting unsuitable water quality for irrigation uses. The soil irrigation with the water having high RCS causes high pH and infertility of the soil regarding sodium carbonate deposition as shown via the black color of the soil (Eaton, 1950).

A hard water is featured by high alkaline earths concentration. Alkaline earths exceeded alkalis as was shown by Piper diagram. Therefore, identification of water hardness because of its impacts on irrigation water quality seems important and was calculated via the following equation (Todd, 1980):

$$TH = 2.497Ca^{2+} + 4.115\ Mg^{2+}$$

TH values range from 42.53 to 450.18 for the surface water samples (Table 5). Majority of the samples (76.37%) lie in moderately hard and hard water classes, while 14.55% of the samples have soft water quality. Hence, surface water in Gilan is mainly hard. Hard water may result in deposition of carbonate minerals and encrustation on water supply distribution systems. The excess deposited carbonates might also affect media pH and reduce sodium content available to the plants (Robbins,2010).

Conclusion

This study indicates that natural processes mainly control surface water chemistry in Gilan province. However, some sites are significantly impacted by anthropogenic factors such as application of agricultural fertilizers. The weathering of various lithological formations, plays a crucial role in providing ions content of the surface water. The mean concentration of the major cations and anionsare in the order of $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$and $HCO_3^{-} > SO_4^{2-} > Cl^{-} > CO_3^{2-}$, respectively. Piper diagram shows that $CaMgHCO_3$is the major hydrogeochemical facies. As well alkaline earths ($Ca^{2+}$and Mg^{2+}) and strong acid anions (Cl^{-} and SO_4^{2-}) exceed alkalis (Na^{+} and K^{+}) and weak acid anions (HCO_3^{-} and CO_3^{2-}), respectively. Gibbs plots and ionic ratios diagrams illustrate that the weathering of silicate minerals is the primary natural process regulating the surface water chemistry. Nevertheless, the dissolution of carbonate minerals also can influence hydrogeochemistry of the area as was shown by saturation indices, thereby majority of the samples are oversaturated with respect to calcite, dolomite and aragonite while evaporites including anhydrite, gypsum and halite mainly display unsaturation status. The investigation of residual sodium carbonate (RSC) and Total hardness (TH) reflect crucial irrigation unsuitability of the surface water in majority of the samples. However, sodium percentage (Na%), sodium adsorption ratio (SAR), electrical conductivity (EC), total dissolved solids (TDS) and permeability index (PI) mostly are below the standard levels. Hence, there is a need for the exact and comprehensive monitoring and managing the surface water resources in the polluted sites. The proper management programs can be considered as an efficient tool for preserving the precious water resources.

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