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Original Research Paper

Hydrochemistry of the Groundwater from Coastal Aquifer in Amol-Ghaemshahr Region, Mazandaran Province, North Iran

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ABSTRACT

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Key Words: Hydrochemistry Coastal aquifer Groundwater, GIS Mazandaran province Piper diagram Gibb's plot Present study is an attempt to understand the hydrochemical characteristics of groundwater in Amol-Ghaemshahr region, Mazandaran province in North Iran. Groundwater samples were randomly collected from 77 wells in Amol-Ghaemshahr plain having different depths, varying from 2.4 m to 198 m. The physico-chemical parameters such as pH, electrical conductivity (EC) and total dissolved solids (TDS) were measured in addition to major cation and anion concentrations. The abundance of major ions is as follows: $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and $HCO_{3}^{-} > Cl^{-} > SO_{4}^{-2-} > NO_{3}^{-}$. Thematic maps pertaining to pH, TDS, EC, Cl⁻, NO_{3}^{-} , SO_{4}^{-2-} and Na⁺ were presented in Geographical Information System (GIS) based maps. Different classes in thematic maps were categorized as desirable, permissible and unpermissible based on WHO standards for drinking purposes. The chemistry of water samples from coastal aquifer was interpreted by using classical Piper diagrams. The study indicates that Ca-Mg-HCO₃ and Ca-Mg-Cl are the dominant hydrochemical facies followed by Na-Cl and Ca-Mg-SO₄ facies. Gibb's plot reveals that the mechanisms responsible for controlling chemical composition of the groundwater are both rock-water interaction and evaporation.

INTRODUCTION

Water is universal solvent and freshwater is required for human activities and development. Occurrence of freshwater as surface water and groundwater bodies cater to the demand of all sectors. Coastal aquifers store fresh groundwater under continual risk of seawater intrusion, and overall water quality of such aquifers generally is influenced by landward movement of saltwater (Karahanoglu 1997). Evaluation of the chemistry of water in coastal aquifers identifies the variation in the quality of water and facilitates the authorities to adopt the remedial measures in ensuring the availability of acceptable quality of water for drinking and irrigation purposes.

Study area, located in Mazandaran province, North Iran, extends from 36°15' N to 36°45'N and 52°15'E to 53°E and includes Amol-Ghaemshahr along E-W and Caspian coast in the north and Alborz mountain in the south (Fig. 1). It covers approximately 2300 km².

Amol-Ghaemshahr plain is known for paddy fields, fruit gardens and citrus orchards. The Amol-Ghaemshahr coastal area receives freshwater inflow from a number of rivers and streams rising on the humid northern slope of the Alborz mountains located in the southern part of the study region. Amol-Ghaemshahr plain is thus, covered with alluvial materials of Tertiary and Quaternary sediments, consisting of rhythmically bedded fluvial-deltaic sediments of several large river systems such as Aleshroud, Haraz, Garmroud, Babolroud, Talar and Siahroud. Groundwater occurs under confined and unconfined conditions within the Tertiary and Quaternary alluvial soils (Khairy et al. 2012). Investigations carried out elsewhere in Iran on the chemical and physical properties of surface water indicate anthropogenic impacts on stream water quality (Marofi & Joneidi Jafari 2003, Jamshidi et al. 2012) and also on groundwater quality (Taher-Shamsi & Moussavi 2003, Khorsandi & Alaei Yazdi 2004, Jalali 2007, 2010). Gholami et al. (2008) worked on the modelling of alluvial and karst springs discharge in the Mazandaran region. This paper aims at describing the hydrogeochemisty in the Amol- Ghaemshahr area on the basis of physico-chemical properties of groundwater. Another objective of this study is to understand the factors controlling the chemistry of the groundwater in the study area.

MATERIALS AND METHODS

Groundwater samples were collected in two polyethylene bottles at 77 groundwater sampling sites (Fig. 1) from bore wells. Physico-chemical parameters, such as temperature, electrical conductivity (EC) and pH were measured in the field immediately after the collection of the samples using portable field meters. The preservation of the samples have been done according to published procedures by adding 65% of HNO₃ until the pH is 2 for major cations and other bottle stored cool at 4°C for major anions. Standard methods were

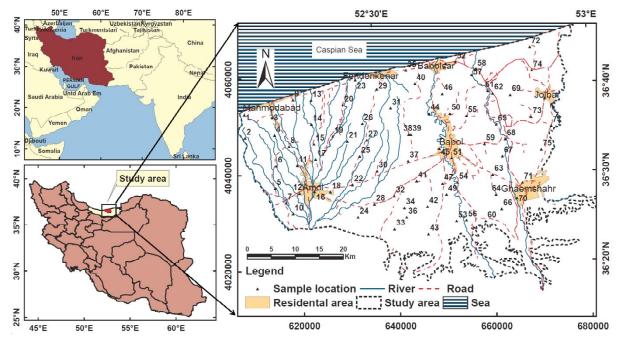


Fig. 1: Study area map with location of wells.

adopted for the analysis of the water samples (APHA 1995).

The study area map was prepared from the soft copy of the topographic map published by the National Cartographic Centre of Iran produced on a scale 1:25000. The topographic map was updated using Landsat ETM+ images. The produced map was digitized and isoline/spatial variation/zonation maps were prepared using ArcGIS 9.3 version software. Microsoft Excel was used to transport data to ArcGIS project.

RESULTS AND DISCUSSION

The hydrochemistry of groundwater samples of the study area with its range, average and WHO standards (1993, 2004) are presented in Table 1.

Physico-chemical characteristics: The pH of the groundwater samples in the study area varies from 6.8 to 8.3 with an average value of 7.4, thus indicating it to be mildly alkaline. Among the different locations, there is an increasing trend of pH values toward the coast (Fig. 2a) and the southern part of the study area with pH less than 7 characterize the preferential recharge areas.

The electrical conductivity (EC) of water is due to the presence of various dissolved solids. In the study area, the EC ranges between 681and 4310 μ S/cm at 25°C with an average of 1334 μ S/cm. Permissible values of EC (between 500 and 1500 μ S/cm) are found in most part of the study area whereas in the N-E part (Fig. 2b), the samples show higher values of EC (>1500 μ S/cm) for drinking needs. This shows that EC increased significantly from 681 to 4310

 μ S/cm which may possibly be due to the saline water incursion. For agricultural uses, the N-E part of the study area, which is proximal to coast, show relatively higher values of EC and belong to doubtful to unsuitable class for irrigation purposes.

Fig. 2c shows the aerial distribution of the total dissolved solids (TDS) in the study area. Values of TDS content range between 436 mg/L and 2888 mg/L. According to World Health Organization (WHO 1996) specification, water containing less than 500 mg/L of dissolved solids is desirable, 500-1500 is permissible and >1500 is unpermissible for drinking purposes. Large part of the groundwater of the study area is having permissible TDS values and only in a limited area (Fig. 2c), the groundwater was found unpermissible for drinking purposes. Higher values of TDS (>1500 mg/L) and EC are recorded in the N-E part of the study area. Based on TDS values, groundwater samples in the study area varied from fresh (TDS <1000 mg/L) to brackish (TDS >1000 mg/L) in nature (Freeze & Cherry 1991, WQA 2012). Nearly 20% of the study area is covered with brackish, while the groundwater of the rest of the area is freshwater.

Total hardness (TH) exhibits a minimum content of 115 to a maximum of 1040 mg/L with an average of 426.23 mg/L. The spatial distribution of hardness (Fig. 3f) shows higher concentrations towards the northeastern part.

Cation chemistry: The major sequence of cations dominance in groundwater of the aquifer in the investigated area has the order $Ca^{2+} > Na^+ > Mg^{2+} > K^+$. The major cation

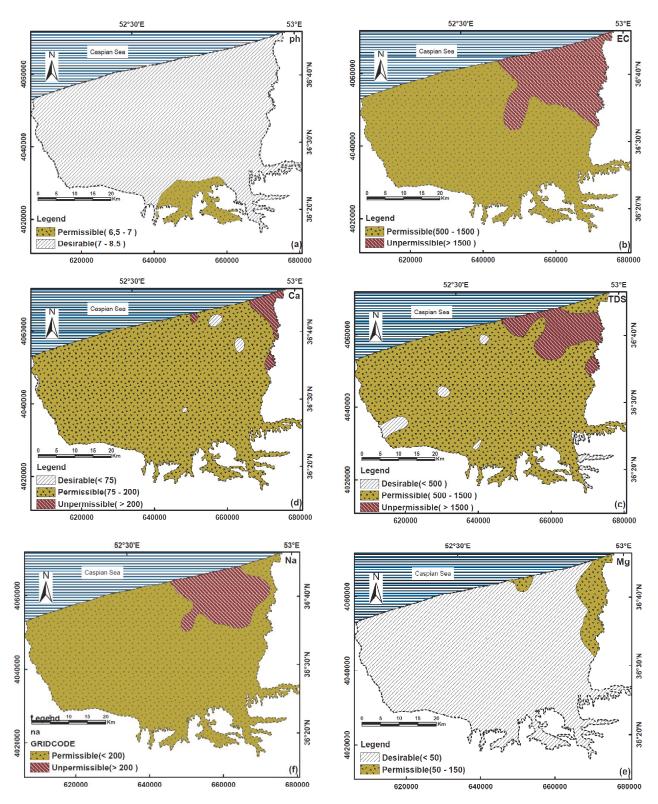


Fig. 2: Zonation map of pH(a), EC(b), TDS(c), Ca(d), Mg(e) and Na(f) for the groundwater samples in the study area.

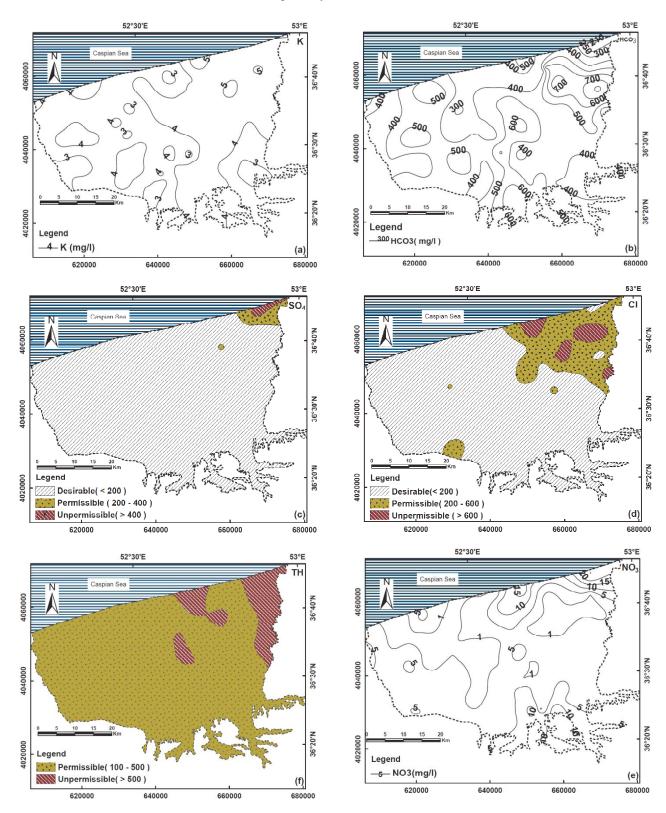


Fig. 3: Isoline map of K(a), HCO₃(b), NO₃(e), and zonation map of SO₄(c), Cl(e) and TH(f) for the groundwater samples in the study area.

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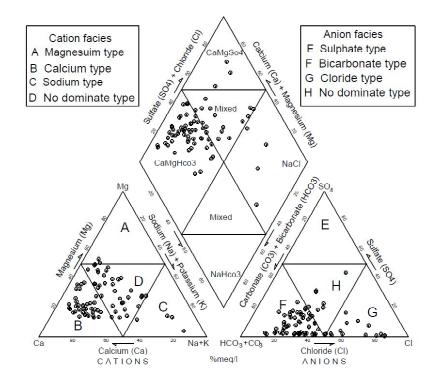


Fig. 4: Piper diagrams for classification of groundwater quality in the Amol-Ghaemshahr aquifer, north Iran.

Table 1. C	Comparison	between th	ne ranges of	compositions of	ground	lwater in t	the stud	y area and	WHC) standa	rd for	drinking	water
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Parameters	Range	Average	WHO (19	96 &2004)	No. of samples within		
			DL	PL	permissible limits (n=77)		
рН	6.8-8.3	7.39	7-8.5	6.5-9.2	77		
EC (µs/cm)	681-4310	1334.48	500	1500	61		
TH (mg/L)	115-1040	426.23	100	500	65		
TDS (mg/L)	436-2888	878.49	500	1500	70		
$Ca^{2+}(mg/L)$	38.07-228.44	125.49	75	200	74		
$Mg^{2+}(mg/L)$	4.86-114.23	27.49	50	150	77		
Na ⁺ (mg/L)	9.2-747.17	106.32	-	200	67		
$K^+(mg/L)$	2.35-5.47	3.95	-	12	77		
$HCO_3^{-}(mg/L)$	244.07-817.63	458.10	-	-	-		
SO_4^{2-} (mg/L)	4.8-436.8	54.86	200	400	76		
CL (mg/L)	21.27-1074.22	158.43	200	600	72		
NO_3 (mg/L)	0.12-24.61	2.96	45		77		

DL - Desirable limit; PL - Permissible limit

concentrations (Ca²⁺, Na⁺, Mg²⁺ K⁺) in most of the groundwater samples are below the WHO (1996, 2004) for drinking water standards (Fig. 2d-f). The concentration of calcium ion (Ca²⁺) ranges between 38.1 and 228.4 mg/L with an average of 125.5 mg/L. The concentration of Mg²⁺ in water ranges from 4.9 to 114.2 mg/L with an average of 27.5 mg/L. The basement rocks of Alborz mountains consist of sedimentary sequence of carbonate, siliciclastic (sandstone-shale), and volcanic rocks (Mehdi Alavi 1996, Jon Davidson

et al. 2004, Maurizio Gaetani et al. 2009). The concentration of Ca^{2+} and Mg^{2+} in the investigated area is mostly related to the dissolution of carbonate and silicate rock particles. In addition to the above sources, the possibility of dissolution of Ca and Mg from the organic matter cannot be ruled out as all horizons of detrital material in the study area have common or abundant sea shells (Dewan & Famouri 1964). Sodium ion is considered as one of the most important ions in natural water. The source of sodium in water depends on

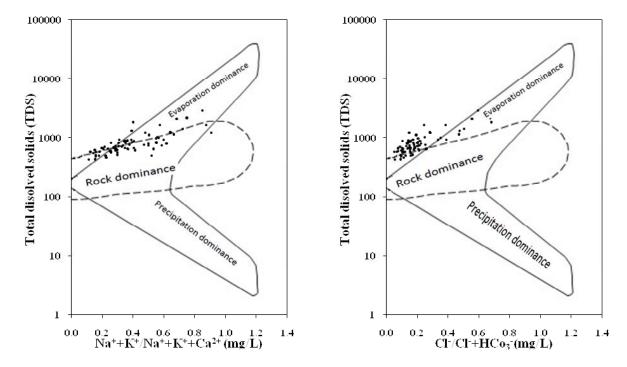


Fig. 5: Gibb's diagram showing the mechanism controlling the chemistry of groundwater.

the rock type through which the water moves. The main source for the presence of most sodium ions (Na⁺) in the natural water is the release of soluble products during the weathering of plagioclase feldspars which are typical constituents of many igneous rocks in Alborz mountain. The value of Na⁺ ranges between 9.2 and 747.2 mg/L with an average of 106.3 mg/L. Potassium content is lower than sodium. From the zonation maps (Fig. 2d-f), it is evident that higher concentrations of calcium, magnesium and sodium are found in the groundwater samples of the N-E part of the study region. The natural sources of potassium in water are the minerals of local igneous rocks such as feldspars, mica and sedimentary rocks as well as silicate and Na bearing clay minerals through reverse cation exchange reactions (Howari & Banat 2002). In the investigated water, the potassium content ranges between 2.3 and 5.5 mg/L. The spatial variation of potassium is shown in Fig. 3a.

Anion chemistry: Concentration of HCO_3^{-1} is highest in all the groundwater samples followed by Cl⁻, SO_4^{-2} and NO_3^{-1} in the order of decreasing abundance. The values of bicarbonate in the groundwater of the study area range from 244.1 to 817.6 mg/L with an average value of 458.1 mg/L (Table 1). The spatial variation of bicarbonate in the groundwater samples of the study area is provided in Fig. 3b. Chloride showed much variations and its content in groundwater varies from 21.3 to 1074.2 mg/L. Chloride concentration in 14 groundwater samples exceeds the permissible limit of 1000 mg/L of WHO standards (WHO 2004) for drinking purposes. The natural processes such as weathering, incursion of sea water and irrigation drainage return flow are possibly responsible for chloride content in the groundwater. Sulphate concentrations in the region range from 4.8 to 436.8 mg/L. Sulphate ion concentration may also probably been derived from either saline water or from the application of fertilizers as sulphate and gypsum bearing sedimentary rocks have not been reported from the study region. The sulphate ion concentration is higher only in two groundwater samples when compared with WHO standards (WHO 2004). The zonation maps of chloride and sulphate are illustrated in Fig. 3c and Fig. 3d. From the diagrams, it is evident that the quality of groundwater in most part of the study area is desirable for drinking purposes based on chloride and sulphate concentrations. However, the N-E part of the study area fall under permissible to unpermissible categories. Nitrate was detected in groundwater samples and its concentration was found to vary from 0.1 to 24.6 mg/L which is below the maximum permissible limit of 45 mg/L prescribed by WHO (2004). The isoline map (Fig. 3e) shows the spatial variation of nitrate in the study area.

Higher concentrations of Ca may be attributed to the surrounding sedimentary rocks/shells and significant amount of Na and Cl in groundwater may be attributed to evaporation as the depth to groundwater is shallow. Dominance of HCO_3^- and Ca^{2+} over Na⁺ and K⁺ combined in majority of

EC	TDS	Ca^{2+}	Mg^{2+}	Na^+	\mathbf{K}^+	HCO ₃ ⁻	SO_4^{2-}	Cl	NO ₃ -
1.00									
1.00	1.00								
0.46	0.46	1.00							
0.63	0.63	0.35	1.00						
0.93	0.93	0.17	0.41	1.00					
0.74	0.73	0.51	0.36	0.66	1.00				
0.51	0.51	0.19	0.18	0.52	0.59	1.00			
0.19	0.19	0.40	0.14	0.08	0.22	-0.12	1.00		
0.96	0.96	0.38	0.64	0.90	0.62	0.31	0.03	1.00	
0.16	0.16	0.40	0.12	0.05	0.14	-0.12	0.51	0.11	1.00
	$ \begin{array}{c} 1.00\\ 1.00\\ 0.46\\ 0.63\\ 0.93\\ 0.74\\ 0.51\\ 0.19\\ 0.96\\ \end{array} $	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} & & & & & & \\ 1.00 & & & & & \\ 1.00 & 1.00 & & & & \\ 0.46 & 0.46 & 1.00 & & & \\ 0.63 & 0.63 & 0.35 & 1.00 & & \\ 0.93 & 0.93 & 0.17 & 0.41 & 1.00 & & \\ 0.74 & 0.73 & 0.51 & 0.36 & 0.66 & 1.00 & & \\ 0.51 & 0.51 & 0.19 & 0.18 & 0.52 & 0.59 & 1.00 & \\ 0.19 & 0.19 & 0.40 & 0.14 & 0.08 & 0.22 & -0.12 & \\ 0.96 & 0.96 & 0.38 & 0.64 & 0.90 & 0.62 & 0.31 & \\ \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Table 2: Correlation matrix for different water quality constituents.

the groundwater samples may possibly indicate agricultural return flow as the prime source.

Hydrochemical facies: In order to understand the chemical characteristics of groundwater in the study region, results of the chemical analysis of the groundwater samples were plotted in Piper (1944) trilinear diagram (Fig. 4) using RockWorks/14 Complete software. Fig. 4 displays the classification of water as various chemical types on the Piper diagram. The dominant water types in the study area are in the order of Ca-Mg-HCO₃ > Ca-Mg-Cl > Na-Cl>Ca-Mg-SO₄. However, most of the samples fall in Ca-Mg-HCO₃ and a few in Ca-Mg-Cl, limited samples are clustered in Na-Cl and Ca-Mg-SO₄ segments. Dominance of Ca-Mg-HCO₃ facies suggests that the groundwater is freshwater. However, water types Ca-Mg-Cl, Na-Cl and Ca-Mg-SO₄ suggest the mixing of saline water caused from seawater contamination or mixing of brine water from underlying brine water bearing unconfined aquifer horizons.

The Gibbs ratio (Gibbs 1970) for the ions (Na/(Na + Ca) and Cl/(Cl + HCO₃) of groundwater samples were plotted against the respective values of TDS. The plots (Fig. 5) indicate that the groundwater samples of the study area overlap in the rock-water interaction and evaporation dominance categories. Recharge of the aquifers of the study area takes place by the river water and/or rain water and water table in most part of the study area is shallow. These factors might have caused the groundwater samples to fall in the overlapping zone of rock-water interaction and evaporation dominance categories.

A statistical correlation analysis was made to understand the interrelationship between chemical parameters and the same has been shown in Table 2. All the constituents are positively correlated with various degrees excepting $SO_4^{2^-}$ and NO_3^- with HCO_3^- . Very high positive correlation of Cl⁻ (0.96) and Na⁺ (0.93) and significant correlation of K⁺ (0.73) and Mg²⁺ (0.63), in addition to HCO_3^- (0.51) and Ca²⁺ (0.46) with TDS value suggest that these ions are the major contributors for TDS concentration in the groundwater. Strong positive correlation (0.90) between Na^+ and Cl^- indicate the influence of saline water on the chemistry of groundwater.

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