Groundwater Quality Assessment in North of Iran: A Case Study of the Mazandaran Province

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Abstract: Mazandaran province is located on the southern coast of Caspian Sea (46,656 km^2), Iran. Irrigated agriculture in this region may exert serious pressure on groundwater resources. The aim of this study is to evaluate physicochemical characteristics in shallow (5-15 m) and deep groundwater (30-60 m) of 88 domestic wells over a seven-year period. The cluster analysis is used to know about interrelation of the similar characteristics of 88 sampling sites, which is formed based on three major clusters. In each cluster the principle characteristics were determined using factor analysis. Obtained results showed that the groundwater quality in this region is critical. Detection level of nitrate ranged from 20 to 137 mg l^{-1}, demonstrated a 83% of the observations exceeding the critical level of 50 mg l^{-1}. Further deterioration of the groundwater quality with agricultural development in this area can be expected if no mitigation strategies are developed.

Key words: Mazandaran province · Groundwater quality · Nitrate · Cluster analysis · Factor analysis

INTRODUCTION

Groundwater quality comprises the physical, chemical and biological qualities of groundwater. Temperature, turbidity, color, taste and odor make up the list of physical water quality characteristics. Since most groundwater is colorless, odorless and without specific taste, there is typically most concern with its chemical and biological qualities. Generally, groundwater quality depends on the quality of recharged water, atmospheric precipitation, inland surface water and subsurface geochemical processes [1]. Groundwater resource assessments and sustainability considerations are of utmost importance in the arid and semiarid regions, where water is commonly of critical economy and social significance. Intense agriculture and urban development cause high demand on groundwater resources in arid and semi-arid regions and also these resources at greater risk to contamination. Groundwater is the primary source of water for domestic, agricultural and industrial uses in many countries and its contamination has been recognized as one of the most serious problems in Iran [2]. Temporal changes in the origin and constitution of the recharged water, hydrologic and human factors, may cause periodic changes in groundwater quality. Sustainability of a natural resource

such as ground water is often a difficult and elusive subject [1]. Naturally, ground water contains mineral ions. These ions slowly dissolve from soil particles, sediments and rocks as the water travels along mineral surfaces in the pores or fractures of the unsaturated zone and the aquifer. They are referred to as dissolved solids. Some dissolved solids may have originated in the precipitation water or river water that recharges the aquifer. A list of the dissolved solids in any water is long, but it can be divided into three groups: major constituents (sodium, calcium, bicarbonate, etc), minor constituents (potassium, iron, carbonate, etc) and trace elements (aluminum, arsenic, copper, etc) [3]. Intrusion of seawater into the inland aquifers due to the over-exploitation of groundwater along the coastal area is an environmental issue than can cause groundwater pollution [4].

Iran, area about 1648000 km^2, is located on the Mediterranean-Himalayas-Indonesia crumpled belt. About one-fourth of its population is allocated in the agricultural sector. Groundwater has been extensively exploited for irrigation use and is considered as a durable and reliable water source for domestic use, especially by the rural population. Many deep and shallow wells have been constructed by farmers to supply the water demands for irrigation, resulting in water table decline during recent

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years. Mazandaran is located in the north of Iran and on the southern coast of the Caspian Sea. It is one of the most densely populated provinces in Iran. In this study area, groundwater is one of the nation's most important natural resources and provides drinking water for more than 3/4 of the population. Groundwater in Mazandaran is currently under serious pressure. The irrigated agricultural in Mazandaran is also reported to have negative impacts on groundwater quality [5, 6].

The application of different multivariate statistical techniques helps the interpretation of complex data matrices to better understand the water quality [7]. Cluster analysis (CA) is a simple approach for classification of groundwater quality into two or more mutually exclusive unknown groups based on combinations of interval variables [8]. The purpose of CA is to discover a system of organizing observations. On the other hand, cluster analysis, allows many choices about the nature of the algorithm for combining groups. Each choice may result in a different grouping structure. Factor analytic (FA) is another multivariate statistical technique. The main applications of FA techniques are: (1) to reduce the number of variables and (2) to detect structure in the relationships between variables, that is to classify variables. Therefore, factor analysis is applied as a data reduction or structure detection method [7]. In the present study, groundwater quality survey in Mazandaran province has been performed using two multivariate techniques (CA and FA) during 2000-2006 within the irrigated agricultural land. Actually, this study assessed the state of groundwater qualities, the spatial variations and investigated the influential factors of water quality along the study area in order to provide the basis for future management strategies

MATERIALS AND METHODS

Study Area: The study area extends between latitude 35° 46' and 36° 58' north and longitude 50° 21' and 54° 8' east. It is bordered clockwise by Golestan, Semnan and Tehran provinces (Fig. 1). Mazandaran province is geographically divided into two parts: the coastal plains and the mountainous areas. In plain intensive large-scale agricultural activities is practiced using irrigation. The Alborz Mountains is covered by forest. The province enjoys a moderate, semitropical climate with an average temperature of 25°C in summer and about 6°C in winter. The average annual rainfall observed over a period of 20 years (1985-2005) is 936 mm. Rainfall occurs mainly in the wet period, with maximum quantity in November and December. The population of the province has been steadily growing during the last 50 years. According to the census of 1996, the population of the province was 2,602,008 of which 45.89% were registered as urban dwellers and 54.1% as villagers [5].

Data and Statistical Analysis: In this study for spatial assessment groundwater quality of Mazandaran province, the quality and quantity data of 150 wells were provided from Water Resources Management Organization (WRMO) of Iran. Then 88 wells with long and complete information were selected. The selected wells are involved: Ramsar-Chaloos 17 wells, Noshahr-Noor 11 wells, Amol-Babol 19 wells, Joibar-Ghaemshahr 10 wells, Sari-Neka 20 wells, Behshahr-Bandaregaz 11 wells. A matrix of 88 wells × 12 quality parameters was obtained during a 7-year (2000-2006) monitoring program. The groundwater parameters includes electrerical conductivity (EC), total dissolved solid (TDS), pH, nitrate (NO_3^-),

Fig. 1: A Schematic Showing Studying Area

bicarbonate (HCO_3^-), chlorine (Cl^-), sulfate (SO_4^{-2}), calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium (Na^+), potassium (K^+) and sodium absorption ratio (SAR).

Information on the temporal and spatial trends of the water quality should help in the decision-making process, particularly in developing countries, where there is insufficient data. There is a certain difficulty in handling and interpretation of large sets of water quality data using conventional statistics. A number of simple but powerful chemometric techniques, such as cluster analysis, help to find statistically important factors in data variability and thus improve conclusions in environmental impact studies [9].

In order to homogenize different expressions for different parameters, i.e. mg l^{-1}, µS cm^{-1}, the initial data were standardized to a mean value of zero and a standard deviation of 1 [10]. After normalization of data, multivariable statistics techniques were used for statistical analysis of groundwater quality. Cluster analysis has proven useful in solving classification problems where the object is to sort cases or variables into groups, or clusters, such that the degree of association is strong between members of the same cluster and weak between members of different clusters [7]. In this study, CA was applied for the evaluation and grouping of the data set including 12 parameters (groundwater quality) of 88 different sampling sites during 7 years (2003-2006) (7392 observations). Hierarchical agglomerative CA was performed on the normalized data set by means of the Ward's method, using squared Euclidean distances as a measure of similarity in order to group 88 sampling sites into distinct hydrochemeical groups that have different groundwater quality characteristics. The Ward's method uses an analysis of variance approach to evaluate the distances between clusters in an attempt to minimize the sum of squares (SS) of any two clusters that can be formed at each step. Ward's method, also known as minimum variance clustering, is a widely used type of agglomerative cluster analysis which is reported as effective in several studies [7].

Regarding multivariate analysis, factor analysis is a widely known as a statistical technique, witch enables us to extract the underlying common factors that control behavioral patterns and its primary purpose is data reduction and summarization. In the present work, factor analysis, which is a correlation-oriented method, was applied to extract and understand a small number of water quality factors from a large data set of many correlated variables in each homogenous cluster. All statistical analysis was used by STATISTICA 6.0 [11].

RESULTS AND DISCUSSION

Cluster Analysis: Study wells were distinct in 3 hydrochemical groups by cluster analysis. The number of wells in each cluster was shown in Table 1. So we can divide the study area into three zones. The number of wells in cluster I, cluster II and cluster III is 57, 36 and 5% of total study wells, respectively. The statistical summary (minimum, maximum, mean of values and standard deviation) of groundwater quality was presented in Table 2 for understanding the general quality of groundwater in each cluster during 7-year duration.

Variation in TDS in groundwater may be related to land use and also to pollution [12 and 13]. It is well-known that P, NO_3^-, SO_4^{2-}, Na^+ and Cl^- ions are mostly derived from agricultural fertilizers, animal waste and municipal and industrial sewage. These factors can be related to the total dissolved solid (TDS) variation and can be used to indicate the influence of human activities on the water chemistry [14]. The production of SO_4^{2-} has multiple origins, mainly from dissolution of sulphate minerals and anthropogenic sources. TDS in the study area has a great variation as shown in Table 2. The TDS is higher in cluster II and III than cluster I. This means that there are more cations and anions in the water indicating an increase in the water's electrical conductivity (EC). We can indirectly determine TDS concentration by measuring the water's electrical conductivity. At a high TDS concentration, water becomes saline. These results show

Table 1: The Number of Wells in Each Cluster

	Region						
	Ramsar-Chaloos	Noshahr-Noor	Amol-Babol	Joibar-Ghaemshahr	Sari-Neka	Behshahr-Bandaregaz	Total No.
Cluster I	17	11	10	3	4	6	51
Cluster II	-	-	9	5	14	4	32
Cluster III	-	-	-	2	2	1	5

Table 2: The Minimum, Maximum, Mean Values and Std. Dev. of the Quality parameters at Different Cluster during 2000-2006 (All units are mg l^{-1} except $\mu s.cm^{-1}$ for EC)

Variable	Custer I[*]				Custer II[**]				Custer III[***]			
	Mean	Min.	Max.	STD	Mean	Min.	Max.	STD	Mean	Min.	Max.	STD
SAR	1.6	0.5	17.2	2.4	2.5	0.6	9.7	2.0	2.50	1.010	6.40	2.18
NO_3^-	67.9	20.2	137.9	24.3	95.3	79.2	125.2	10.5	88.10	70.250	95.60	10.34
K^+	0.1	0.0	0.6	0.1	0.1	0.0	0.1	0.0	0.07	0.025	0.14	0.04
Na^+	3.1	0.7	46.3	6.5	4.9	0.7	20.7	4.6	5.30	1.300	14.61	5.30
Mg^{2+}	2.4	1.3	6.6	0.9	2.9	0.8	4.4	0.9	2.90	1.420	4.40	1.11
Ca^{2+}	3.7	2.2	8.2	1.2	4.5	1.5	6.4	1.2	4.30	2.370	5.87	1.35
SO_4^{2+}	1.4	0.4	8.1	1.4	2.4	0.3	6.3	1.4	2.10	0.540	3.82	1.19
Cl^-	2.2	0.3	46.9	6.6	3.4	0.3	17.0	3.8	3.80	0.480	12.30	4.86
HCO_3^-	5.6	3.3	8.1	1.2	6.5	2.4	10.5	1.7	6.70	4.100	8.90	1.78
pH	7.8	7.6	8.0	0.1	7.8	7.6	8.1	0.1	7.80	7.700	7.80	0.05
TDS	612.0	300.7	3942.6	528.0	809.5	201.4	2062.7	398.5	824.90	349.400	1641.00	488.10
EC	934.8	440.7	6181.0	834.9	1267.6	290.7	3237.6	636.9	1291.80	503.800	2566.50	776.05

*: No. of wells = 51; **:No. of wells = 32; ***:No. of wells = 5

that the number of wells (with TDS more than 500) for cluster I, cluster II and cluster III are 53, 84 and 80%, respectively. Water with a TDS above 500 mg l^{-1} is not recommended for use as drinking water [14]. However, critical condition in cluster II and III are located in middle and east of the study area, respectively, in spite of this; groundwater is being used as drinking water in these areas. Water with a TDS above 1,500 to 2,600 mg l^{-1} (EC greater than 2.25 to 4 mmho cm^{-1}) is generally considered problematic for the irrigation use on crops with low or medium salt tolerance. There were no wells with TDS above 1,500 to 2,600 mg l^{-1} in cluster I and III. However, 20% of wells in cluster II are located in Sari-Neka and Amol-Babol regions that have TDS above 1,500 to 2,600 mg l^{-1}. Hussain *et al.* (2008) showed that agricultural activities have resulted in release of many dissolved solid so TDS level was found to be very high in eastern Saudi Arabia [8].

Nitrate concentration is another problem in each cluster. The range of NO_3^- is shown in Table 2. Within the soil mineral N pool, nitrate-N receives particular attention as it is dissolved through the soil solution and therefore it is extremely mobile. It can be easily incorporated in the plant biomass, but also leach from the root zone of the crops and it causes groundwater pollution [15]. Yammani *et al.* (2008) declare that in farmland area the high concentration of nitrate significantly related to the excess usage of fertilizers [4]. In comparison with the WHO's drinking water guideline of 50 mg l^{-1} for NO_3^-, 83% of wells showed higher concentrations. Nitrate levels situated between 20 and 137 mg l^{-1} in total study area, with 68% of the observations in cluster I and 100% of wells in cluster II and III are exceeding the critical level of

50 mg l^{-1}. High concentration of nitrate in the north area of Iran especially in Mazandaran province results from the extensive agriculture. Nitrate leaching from the root zone of irrigated crops may exert pollution pressures on groundwater bodies. Jalali and Kolahchi (2008) analysed 48 groundwater sample in Malayer, western Iran and found that 75% of the water samples showed nitrate concentration above the human-affected value (13 mg l^{-1}), while more than 12.5% exceeded the maximum acceptable level (50 mg l^{-1}) [16]. It could be expected that a great part of HCO_3^- originated from dissolution of carbonate rocks in the aquifer through the action of percolating waters enriched in CO_2 after being in contact with the atmosphere [2]. Thus, the dissolution of carbonate which releases Ca^{2+} into solution, yield water of type Ca-HCO_3^- as a final product. The concentration of HCO_3^- is same in each cluster, approximately. The relative concentrations of the cation occur in the order of $Ca^{2+}>Mg^{2+}>Na^+>K^+$ for cluster I and $Na^+>Ca^{2+}>Mg^{2+}>K^+$ for Cluster II, III. The relative concentrations of the anion occur in the order of $HCO_3^->Cl^->SO_4^{2-}$ for all clusters. Jalali (2008) found that the chemical composition of the groundwater are dominated by Ca^{2+}, Na^+, SO_4^{2-},Cl^- and HCO_3^- in Razan (west of Iran) where agriculture as main use [2]. Intrusion of seawater through the rock fractures is another cause for contamination of groundwater. Seawater and urban wastes which are the combined source of contamination exist in some wells at the area close to the coast. In this study area, the groundwater shows alkaline nature (pH 7.6-8.1).

Factor Analysis: In the present study, the factor analysis was used to reduce large number of variables in each

Table 3: The Results of Factor Analysis

	Factor 1	Factor 2	Factor 3	Factor 4
Cluster I				
Eigenvalue	8.13	1.790	1.500	1.100
Variance %	67.78	14.95	7.440	6.830
Cumulative of Variance %	67.70	82.70	90.17	97.00
Cluster II				
Eigenvalue	9.21	1.50	1.320	
Variance %	76.70	13.2	4.680	-
Cumulative of Variance %	76.70	89.9	94.66	-
Cluster III				
Eigenvalue	9.70	1.20	1.01	-
Variance %	81.30	10.1	8.00	-
Cumulative of Variance %	81.30	91.5	99.6	-

cluster to a few factors. The factor model used is expressed as:

$$X_j = \sum_{r=1}^{p} a_{jr} f_r + \varepsilon_j \qquad (1)$$

where, X_j is the expression level of n different variables from the jth microarray experiment, f_r is the rth common factors, p is the specified number of the factors, j is the random variation unique to the original variable X_j, a_{jr} is the loading of the jth variable on the rth factor and is the error for each microarray and it corresponds to the loading or weights on principal components. Varimax rotation was then adopted.

The results of the factor analysis are summarized in Table 3. According to Table 3 four factors are identified in cluster I (western area of Mazandaran province) which control groundwater quality. Factor 1 was accounted for 67.7% variance in the data. The variables present in this factor are sodium adsorption ratio (SAR), Na^+, Cl^- and TDS. This factor indicates ion exchange and the contribution of weathering process in the study area. Variables HCO_3^- and NO_3^- are considered as factor 2. Factor 2 was accounted for 14.9% of the total variance. Variable K^+ is considered as factor 3. Factor 3 was accounted for 7.4% variance in the data. Factor 2 and 3 may be attributed to leaching of fertilizer from soils in the study area. The pH is considered as factor 4 was accounted for 6.8% variance in the data (Table 3).

In the cluster II (middle area of Mazandaran province), three factors were found to be responsible for the variation in groundwater quality. Factor 1 was accounted for 76.7% variance in the data and includes SAR, Na^+ and Cl^-. This factor indicates ion exchange and the contribution of weathering process in the study area. Factor 2 includes the variables like HCO_3^-, Ca^{2+} and Mg^{2+}, was accounted for 13.2% variance in the data.

Associations between Ca^{2+}, Mg^{2+} and HCO_3^- suggest dissolution of calcite, dolomite and siderite. Factor 3 includes the variable pH was accounted for 4.6% variance in the data (Table 3).

Three factors are identified in cluster III (eastern of Mazandaran province) which control groundwater quality. Factor 1 was accounted for 81.3% variance in the data. The variables present in this factor are SAR, Na^+, Cl^- and TDS. The pH is considered as a Factor 2. Factor 3 has high loading for NO_3^- and was accounted for 8% variance in the data (Table 3). The substantial contribution of nitrate in the study area is considered to result from the application of agricultural fertilizers in excess of the land capability conditions. Yammani *et al.* (2008) used factor analysis for identification of influencing factors for groundwater quality variation. They found three factors including factor I (Ca^+, Na^+, Cl^-, SO_4^{2-} and NO_3^-), factor II (SiO_2, Mg^{2+} and HCO_3^-) and factor III (CO_3^{2-} and K^+). In present work, SO_4^{2-} was not as influencing factor for groundwater quality [4].

CONCLUSIONS

Groundwater quality was surveyed along the coast of Mazandaran province using multivariable analysis methods. Mazandaran province was divided to three groups according groundwater quality by cluster analysis. The number of wells in cluster I, cluster II and cluster III is 57%, 36% and 5% of total study wells, respectively. The relative concentrations of the cation occur in the order of $Ca^{2+}>Mg^{2+}>Na^+>K^+$ for cluster I and $Na^+>Ca^{2+}>Mg^{2+}>K^+$ for Cluster II and III. The relative concentrations of the anion occur in the order of $HCO_3^->Cl>SO_4^{2-}$ for all clusters. Factor analysis successfully allowed the characterization of groundwater quality as the delineating of zones where agriculture effluents were impacting the water. Nitrate contamination and TDS were the most important problem with using the groundwater for drinking water in this study area. The most prevalent forms of the groundwater pollution from non-point sources (NPS) are salt and nitrate contamination, which adversely affect approximately most of the wells.

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