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Groundwater irrigation quality mapping using geostatistical techniques in Amol–Babol Plain, Iran

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Abstract Groundwater is acknowledged to be a reliable source for agricultural activities in arid and semi-arid regions. An assessment of the suitability of groundwater for agricultural usage was carried out on the Amol–Babol Plain, Iran, where agriculture is the dominant economic activity. Groundwater samples were collected from 154 wells during the wet and dry seasons in 2009. The sodium percentage, sodium adsorption ratio, residual sodium carbonate, magnesium hazard, and Kelly's ratios were used as indicators for the water quality. Geostatistical technique of ordinary kriging method was used to create spatial distribution maps. The thematic maps of salinity hazard, sodium adsorption ratio, and sodium percentage indicated an increasing trend of concentration from the western and southern areas to the east and north-east of the plain. The maps also show that the groundwater quality decreases gradually from the west and south sides to the north-eastern side. There is also no significant change in seasonal variation of water quality parameters.

Keywords Irrigation water · Ordinary kriging · Geostatistical · Amol–Babol · Iran

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Introduction

Groundwater is the most reliable water resource, especially in arid and semi-arid regions like Iran (Jalali 2007; Neshat et al. 2013). Agriculture is a dominant activity on the Amol–Babol Plain in the north of Iran, in which 85 % of the area is covered by agricultural land. The large expanse of agricultural land, which is used to provide food for the growing population, is highly dependent on the availability of irrigation water. Moreover, thousands wells have been constructed by farmers to supply groundwater for irrigation. Over-extraction of groundwater had presented several problems, such as reduced well yield, and saline water intrusion (Khashogji and Maghraby 2013). The quality of irrigation water directly affects the physical and chemical structure in soil and has a significant influence on crop production (Simsek and Gunduz 2007). The poor quality of irrigation water may be attributed to the high concentration of ions and trace elements, such as heavy metals in the soil and water. An excessive content of ions and trace elements may affect the fertility of the soil (Nishanthiny et al. 2010). Groundwater quality can be affected by numerous types of human activity such as agricultural, residential, industrial, and municipal activities (Nas and Berktay 2010). The variety and extent of groundwater chemical composition could also be influenced by natural processes such as evaporation, cation exchange, dissociation of minerals, mixing of water, rock weathering, and human activities (Appelo and Postma 1993). The geochemistry of soil (Zuane 1990) and the geological history of rocks (Walton 1970) have a significant impact on the chemical contamination of groundwater. Therefore, any groundwater suitability assessment for agriculture should include their chemical composition (Khodapanah et al. 2009). Groundwater consists of major cations and anions, such as sodium (Na^+), calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}), chloride (Cl^-), sulfate (SO_4^{2-}), and bicarbonate (HCO_3^-), which directly influence the water quality.

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Ions in water may accumulate in the soil and subsequently degrade the quality of water which will have a damaging effect on agricultural production (Simsek and Gunduz 2007). Several researchers calculated chemical indices, such as sodium percentage (Na%), sodium adsorption ratio (SAR), residual sodium carbonate (RSC), magnesium hazard (MH), and Kelly's ratio to understand the water quality and utilitarian aspects of groundwater for irrigation (Adhikary et al. 2011; Ramesh and Elango 2012; Vasanthavigar et al. 2012; Al-Taani 2013). However, better results may be obtained by analyzing chemistry of all the anions and cations rather than their individual parameters (Hem 1985). One of the important requirements to undertake irrigation quality assessment is to produce a specialised map to identify areas under pollution threat. Irrigation water quality mapping has been proposed as a valuable tool for the spatial distribution of assessment of the quality index parameters and also for making a comparative evaluation map (Adhikary et al. 2011). Combination of Geographic Information System (GIS) and geostatistical analysis are becoming an important tool for environmental geochemistry studies (Pradhan 2009; Ayazi et al. 2010; Manap et al. 2012, 2013). Geostatistic is a technique that enables the analysis and prediction of continuous variables that are distributed in space and time (Delgado et al. 2010). A geostatistical techniques of kriging considers the spatial correlation between the sample points and is used for mapping spatial variability (Uyan and Cay 2010). Groundwater quality varies over time, the role of temporal variation in groundwater quality parameters has been assessed in many studies (Enwright and Hudak 2009; Elci and Polat 2010; Kannel et al. 2008). Seasonal variation of water quality data assessment is complicated and requires statistical analysis of long-term data monitoring of the data (Elci and Polat 2010). As the groundwater is the main source of irrigation for the Amol–Babol Plain, the suitability of water quality should be studied in greater detail. The application of geostatistic to understand the spatial variation in groundwater irrigation quality is crucial for management of water resources for agricultural usages especially in the Amol–Babol Plain. Thus, the main objective of this study is to determine the groundwater quality for the purpose of irrigation, and to identify and classify groundwater quality zones in the Amol–Babol Plain based on geostatistical techniques and agricultural parameters.

Materials and methods

Study area

The Amol–Babol Plain is located in the northern region of Mazandaran Province, in the north of Iran. The area lies between latitudes 36° 16′ and 36° 47′ N and longitudes 52° 9′ and 52° 59′ E, covering an area of approximately 1,822 km^2 (Fig. 1b). The altitude of the study area ranges from below sea level near the Caspian Sea on the northern side to 970 m near the Alborz Mountains on the southern side. The significant drainage features of the Amol–Babol Plain are the Haraz, Babol and Talar Rivers (Fig. 2). The climate is semi-arid with an average annual rainfall of about 870 mm (Mazandaran 2010) of which 40 % falls during the rainy season and 16.8 % falls during the dry season. The moderate temperature is around 25 °C in the summer and 6 °C in the winter (Shahbazi and Esmaeli-Sar 2009). The most significant economic activity is agriculture. The cultivation of rice covers around 62 % of the land followed 12 % of citrus orchard, and crops, such as wheat, barley, beans and corn covers about 10 %. Only 25 % of the cultivated area is devoted to semi-aquatic and dry land (Fakharian 2010). Almost all of the domestic water and around 30 % of the irrigated water supply for agriculture are from groundwater. From the hydrogeological points of view, the Amol–Babol Plain consist of an unconfined aquifer that covers 94 % of the total plain, and a confined covers 50 % of the plain.

The average thickness of alluvial deposits is around 90 m. The thickness varies from 10 m in the northern region to 200 m inthe Haraz homogenous sediment layer on the western and southern side of the plain. There are approximately 6,634 deep and 61,496 shallow wells in the aquifers. The water abstraction from Amol–Babol aquifers during 2008 to 2009 period was about 302 million m^3 (Fakharian 2010; Table 1). The groundwater level contours indicate that the general groundwater flow direction in the aquifer is from the southern (Alborz Mountains) to the northern side (Caspian Sea). The highlands in the southern region of the study area consist of Permian limestone, shale and marl of Drood, Ruteh and Nesan Formations (Aghanabati 2004).

The northern side of the Alborz Mountains consists of early Jurassic sediment layers of sandstone, siltstone, and coal seams and late Jurassic limestone. Quaternary deposits of unconsolidated clay and sandy sediments are found in the central area and on the north side of the plain (Fig. 2). River alluvial, normally accrued by the weathering process has formed the Haraz homogenous alluvial fan on the western side of the study area near Amol City, and the Talar heterogeneous alluvial fans on the eastern side of the Amol–Babol Plain (Jamab 1995). The heavy discharge rates of the Haraz and Babol Rivers had washed fossil saline water between the sediment layers to the Caspian Sea, and prevented seawater intrusion of the coastal aquifer (Fakharian 2010). In the north-eastern area, fossil saline water is still existed due to the weak discharge rate of the Talar River.

Sample collections and preparations

Groundwater samples were collected from 154 wells during October and November (wet season), and May and June (dry season) in 2009. The temperature, pH, electrical conductivity

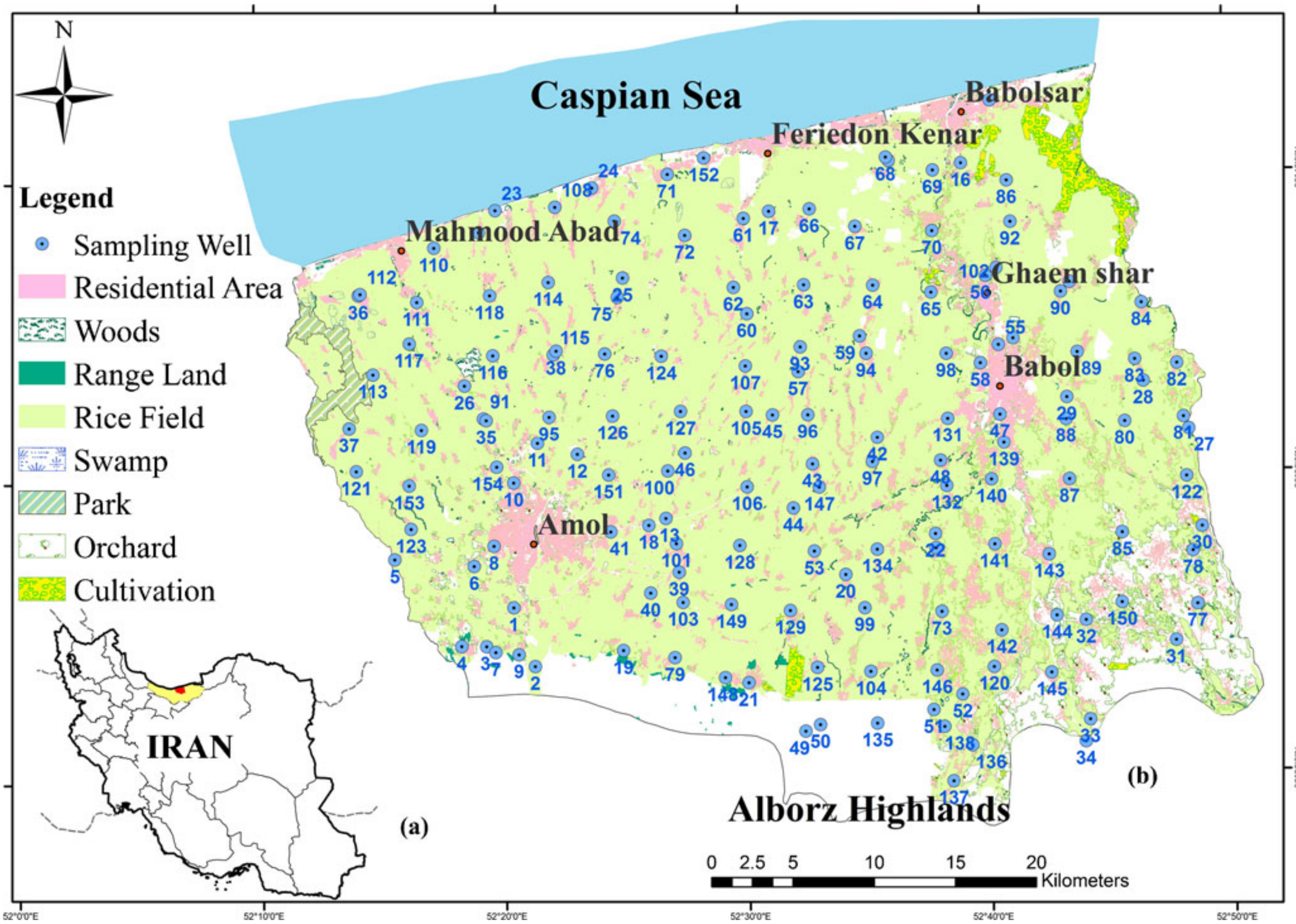

Fig. 1 **a** Map of Iran and **b** land use scheme of the Amol–Babol Plain (Fakharian 2010)

(EC), and total dissolved solids (TDS) were measured immediately after sampling using a multi-parameter WP600 series meter. The water samples were collected after 10 min of pumping, transferred into acid-washed polyethylene bottles (APHA 2005; New Zealand S 1998a), and stored for less than 24 h at 4 °C before being transferred to the laboratory. The concentration of potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), nitrate (NO_3^- as N), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-) were analyzed following the standard methods (APHA 2005). The major cations of Ca^{2+} and Mg^{2+} were determined by titrimetry, sodium and potassium by flame photometry. Bicarbonate values were measured by acid titration, chloride concentration by $AgNO_3$ titration and sulfate was determined by spectro-photometer. Quality controls and quality assurance were applied to obtain reliable data by checking the blank samples and a calibration curve was constructed for the elements. The accuracy of the results was checked by calculating the ionic balance errors (Eq. 1) (Appelo and Postma 1993), which were within ±5 %.

$$\text{Error of ion balance} = \frac{\sum \text{cation} - \sum \text{anion}}{\sum \text{cation} + \sum \text{anion}} \times 100 \qquad (1)$$

Geostatistical analysis

ArcGIS 9.3 (ESRI 2003) and geostatistical analyst extension were used for the kriging estimations, and generation of distribution maps. The ordinary kriging (OK) method is an optimal geostatistical technique, that can be applied for mapping groundwater quality where observations near to each point are more similar than those far away (Sajil Kumar et al. 2011). In this method, the regionalized variable is assumed to be stationary and is expressed as Eq. 2:

$$z(x) = \mu + \varepsilon(x) \qquad (2)$$

Where μ is an unknown constant and is generally considered as the mean of the attribute values, and $z(x)$ is the attribute value at any location x with stochastic residual $\varepsilon(x)$ with zero mean (Adhikary et al. 2010). One of the advantages of the kriging method is that it presents the possibility of interpolation of the estimation error of the regionalized variables where there is no initial measurement (Uyan and Cay 2010). This feature offers a measure of the estimation precision and reliability of the spatial variable distribution (Leuangthong et al.

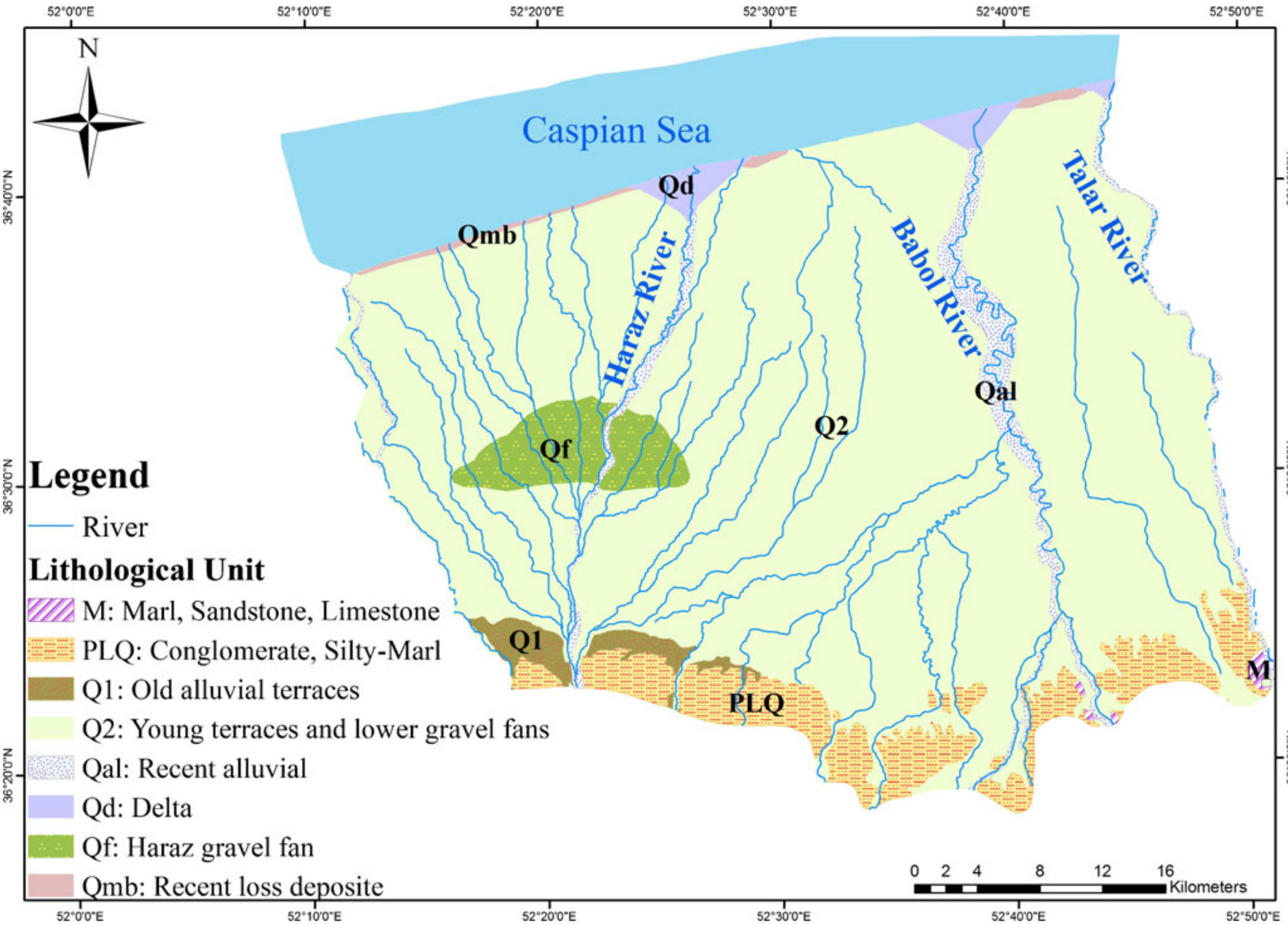

Fig. 2 Geology map of Amol–Babol Plain (Fakharian 2010)

2004). The experimental variogram measures the average degree of dissimilarity between an un-sampled point and a nearby point, to represent the autocorrelation at different distances. The correlation is site specific and should be used with caution in different areas. The values of the experimental semivariogram were calculated from the measured data using the measure of moment approach (Eq. 3; Matheron 1965):

$$\gamma\ (h) = \frac{1}{2\ n\ (h)} \sum_{i=1}^{n\ (h)} [z(x_i + h) - z(x_i)]^2 \qquad (3)$$

Table 1 Total abstraction from groundwater from 2008 to 2009 (Fakharian 2010)

Water resource	Number	Annual discharge (MCM*)	Percent (%)
Spring	142	19.5	5.3
Wells	68,130	342	94
Qantas	2	0.85	0.7
Total	68,274	302.15	100

*Million Cubic Meters

Where γ (h) is the semivariogram and is expressed as a function of the magnitude of the lag distance, n (h) is the number of observation pairs for x_i and (x_i+h) and z (x_i) is the variable at location x_i.

Data exploration

Kriging provides the best interpolation results if the data are normally distributed. The preliminary step of geostatistical analysis is to determine the normality of data. If the data are not normal or skewed, transformation should be undertaken to normalize the data (ESRI 2003). Residual sodium carbonate (RSC) and magnesium hazard (MH) showed a normal distributed, whereas, EC, sodium percentage, sodium adsorption ratio, and Kelly's ratio are not normally distributed. Therefore, a log transformation was applied for these variables to conform them to a normal distribution. Trend analysis was undertaken to determine the presence of any large-scale trends. If a global trend is present, the trend needs to be removed to make the data stationary and improve prediction errors (Adhikary et al. 2011). However, the trend analysis did not show any significant global trend for all parameters. Therefore, it was not necessary to remove the trend prior to the estimation.

Semivariogram fitting

Semivariance is a measure of the degree of spatial dependence between samples. The semivariogram is a function that relates the semivariance of the data points to the distance (ESRI 2003). Eleven different functions of circular, spherical, tetraspherical, pentaspherical, exponential, Gaussian, rational quadratic, hole effect, and K-Bessel. J-Bessel and stable semivariogram models were evaluated in this study. The suitable models for fitness on the experimental variogram were assessed by cross-validation (Mehrjardi et al. 2010). In order to ensure the predictability of the theoretical model, prediction performances were tested for all models (Jalali 2007). Cross-validation helps to find which model provides the best prediction. An accurate model is recognized by the mean error (ME) and mean standardized error (MSE) being close to zero; the root mean square error (RMSE) and average standardized error (ASE) as small as possible and the root mean squared standardized error (RMSSE) close to one (ESRI 2003). If the average estimated prediction standard errors are close to the root mean square, prediction error from cross-validation one can be confident that the prediction standard errors are appropriate (ESRI 2003). After using different models for different irrigated water quality parameters and based on the cross-validation results, it was found the exponential, Gaussian and K-Bessel were the most accurate models to be used in the study area (Table 2). The nugget-sill ratio represented as a percentage can be applied in the classification of the spatial dependency of groundwater quality parameters (Uyan and Cay 2010). The nugget variance (C_0) represents the level of random variation within the data (Cynthia et al. 2000).

The sill (C_0+C) shows the asymptote of the curve where the structural variance attains its maximum value because it remains constant (Delgado et al. 2010). The range indicates the lag distance at which the semivariogram reaches the sill value (Cynthia et al. 2000). If the ratio is less than 25 %, then the variable has strong spatial dependence; if the ratio is between 25 % and 75 %, the variable has moderate spatial dependence, and if greater than 75 %, the variables show weak spatial dependence (Ahmadi and Sedghamiz 2007). In the study area, the nugget–sill ratio indicates that except for the SAR and Na% parameters in the dry season, which show strong spatial dependency, other variables represent moderate dependency in the dry and wet seasons (Table 3).

Statistical analysis

The statistical distribution of groundwater quality data was tested using the one-sample Kolmogorov–Smirnov (K-S) test (Helsel and Hirsch 2002). The K-S test is based on a simple way to quantify the difference between the observed and expected distribution. The data normality distribution can be tested to confirm the results of data exploration analysis using geostatistical technique (Table 4). If p value>α (α=0.05), then it presents no difference between the data distribution (normal distribution), and if the p value<α, then the data could be non-normally distributed at the 95 % confidence level.

K-S test should be performed prior to the use of statistical methods to consider the role of seasonal variation on the quality of irrigation water. The paired sample *t test* was applied to the data that were normally distributed (Helsel and Hirsch 2002) and the sample size number must be greater than 30 samples in each group (Elci and Polat 2010). Non-parametric tests, such as the Wilcoxon rank test, were applied for non-normally distributed data, instead of the parametric test, such as the paired sample *t test* (Helsel and Hirsch 2002). In the application of both tests, if the p value<α (α=0.05), it indicates that there is a significant difference between the concentration of data over two seasons. Otherwise, if the p value>α, it indicates that there is no significant difference between data concentration in the both seasons.

Table 2 Cross-validation results for ordinary kriging method

Season	Parameters	Best fit model	ME	MSE	RMSE	ASE	RMSSE
Dry	Salinity index	K-Bessel	-3.98	-0.0213	370.4	348.3	1.088
	SAR	K-Bessel	-0.045	0.8876	-0.077	0.817	1.097
	Na%	Exponential	0.0719	-0.0058	14.13	14.83	0.999
	RSC	Exponential	-0.0007	-0.0000	3.461	3.195	1.084
	MH	Exponential	0.2836	0.01735	11.19	12.76	0.891
	Kelly ratio	K-Bessel	0.0879	-0.1138	1.314	0.722	1.447
Wet	Salinity index	K-Bessel	-7.29	-0.0183	435.7	383.8	1.064
	SAR	K-Bessel	-0.1131	-0.0483	2.608	2.941	1.001
	Na%	Gaussian	0.0978	-0.0001	14.45	16.31	0.919
	RSC	K-Bessel	-0.0581	-0.0147	3.726	3.769	0.989
	MH	Exponential	0.0195	0.0012	12.27	12.15	1.010
	Kelly ratio	Exponential	-0.0299	-0.0591	0.642	0.588	1.148

Table 3 Best-fitted variogram models of irrigated water quality and their parameters

Season	Parameters	Nugget (C_0)	Sill (C_0+C)	(C_0/C_0+C)*100	Range (km)
Dry	Salinity index	0.0631	0.1381	45.6	49.3
	SAR	0.2373	0.9372	25.1	40.8
	Na%	0.0769	0.3172	24.2	19.3
	RSC	8.4318	12.355	65.4	35.5
	MH	0.0522	0.0846	61.4	19.3
	Kelly ratio	0.4282	0.9772	43.1	32.1
Wet	Salinity index	0.0715	0.1695	42.2	49.6
	SAR	0.2574	0.8701	29.5	34.3
	Na%	0.1809	0.2915	62.1	17.4
	RSC	10.015	14.597	68.5	14.5
	MH	100.10	131.91	75.8	47.1
	Kelly ratio	0.3219	0.8484	37.9	27.6

Irrigation groundwater quality map construction

The irrigation quality maps were created to represent a general view of suitability of the groundwater for agricultural activities. The maps were produced by overlying interpolation maps of the salinity index, SAR, Na%, RSC, MH, and Kelly's ratio from the results of the kriging method. Overlay analysis is a common, widely used method for analyzing and evaluating geospatial data in the GIS environment. The advantage of the overlay method is its ability to match files for the same geographic area, which enable visualization of the interactions among the different data. The spatial integration for final irrigation water quality mapping was carried out using ArcGIS spatial Analyst extension.

Results and discussion

Statistical summary

The water quality standard of the Food and Agriculture Organization (FAO 1994) was used as the basis for the water quality evaluation for agricultural purposes in this study (Table 5). The pH values in the groundwater samples mostly vary within the ranges of 6.4 to 7.8 and 6.3 to 7.8 during the dry and wet seasons respectively. The groundwater pH values of most of the samples are within the permissible limit of 6.5–8.5 (FAO 1994). Less than 3 % of the samples show pH values lower than the water standard, which may indicate the slightly acidic situation of groundwater due to the carbonate bedrock in some parts of the study area. The values of electrical conductivity and TDS are mostly attributed to the geochemical process, such as ion exchange, evaporation, silicate weathering, rock water interaction and also anthropogenic activities (Ramesh and Elango 2012). The EC values range from 618 to 3168 μs/cm and from 624 to 4378 μs/cm in the dry and wet seasons, respectively (Table 5). In the dry season, 0.6 %, and in the wet season 1.94 % of the samples show that the EC value exceed the permissible limit of 3,000 μs/cm (FAO 1994) in the study area. The TDS means concentration is 2,459 mg/l in the dry season, but increases to 3,122 mg/l in the wet season. Although, the mean values of the EC are lower than the FAO (1994) standard limit of 2,000 mg/l, 1.27 % and 3.89 % of the samples represent TDS values above the permissible limit in the dry and wet seasons, respectively.

Magnesium is in the range of 7 to 310 mg/l and 5 to 100 mg/l in the dry and wet seasons, respectively. As evident from the results, around 11.4 % of the samples for the dry season and 11.0 % of the samples for the wet season exceed the desirable

Table 4 Kolmogorov–Smirnov test for data distribution

Parameter	EC		SAR		Na%		RSC		MH		Kelly ratio	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Mean	1,179.6	1,202.3	2.629	2.608	29.30	30.34	2.28	3.08	46.50	42.85	0.608	0.504
Std. deviation	446.7	558.1	2.893	3.912	17.62	16.47	3.44	3.75	12.10	12.39	1.405	0.689
P-value*	0.040	0.002	<0.0001	<0.0001	0.000	0.007	0.059	0.603	0.848	0.899	0.000	0.000
Data distribution	Non-normal		Non-normal		Non-normal		Normal		Normal		Non-normal	

*α=0.05

Table 5 Groundwater quality and their comparison with irrigation water standard (FAO 1994)

		Descriptive statistics of dry season				Descriptive statistics wet season				Irrigation water standard
Parameters	Union	Min.	Max.	Mean	Std. Deviation	Min.	Max.	Mean	Std. Deviation	
pH	–	6.41	7.86	6.94	0.28	6.3	7.8	6.8	0.22	6.5-8.4
EC	μS/cm	618.5	3,168	1,156.6	439.19	624.3	4,378	1,188.9	532.1	3,000
TDS	Mg/l	359.8	2,459	845.92	335.72	414.2	3,122	880.31	409.45	2,000
K^+	Mg/l	1.00	172	12.941	21.033	1.00	110	20.816	21.704	2.00
Mg^{2+}	Mg/l	7.00	310	41.42	26.163	5.00	100	37.727	16.287	60
Ca^{2+}	Mg/l	11.00	200	77.293	29.517	11.0	190	84.019	34.533	400
HCO_3^-	Mg/l	10.00	1,000	400.37	150.56	20.0	1,350	512.2	219.05	610
SO_4^{2-}	Mg/l	0.00	175	81.515	42.553	0.00	175	88.013	41.683	1,240
Cl^-	Mg/l	22.00	475	176.38	113.35	34.0	490	188.78	114.18	1,063
Na^+	Mg/l	10.04	568.64	76.345	88.382	10.07	574.3	76.797	89.25	920

limit of 60 mg/l (FAO 1994). The major source of magnesium in the groundwater is the ion exchange of minerals in rocks and soils by water (Aghazadeh and Asghari 2010). The Mg/Ca ratio is lower than 5 in the most parts of study area, which indicate that the groundwater is affected by dissolution of limestone and dolomite in the study area.

The potassium concentration in groundwater mostly increases by the weathering of potash silicate minerals, the application of potash fertilizers and the usage of surface water for irrigation (Jain et al. 2010). The mean values of K^+ vary between 12.9 mg/l in the dry season to 20.8 mg/l in the wet season. Both values exceed the FAO (1994) guidelines for the maximum admissible limit of 2 mg/l. The nitrate concentration ranges from 0.1 to 39.4 mg/l in the dry season and from 0.01 to 20.00 mg/l in the wet season. Among the 154 sampling wells, 6.5 % of samples in the dry season and 7.1 % samples in the wet season show nitrate concentration above the standard limit of 10 mg/l (FAO 1994). In areas with intensive irrigation activities similar to the Amol–Babol Plain, irregular utilization of fertilization significantly influences the groundwater quality by the direct input of potassium and nitrate from fertilizers and sewage ponds to groundwater.

The existence of shallow wells (depth<10 m), especially in coastal area, could play an important role in the increase of the K^+ and NO_3^- concentration in the groundwater. The bicarbonate concentration varies from 10 to 1,000 mg/l in the dry season and from 20 to 1,350 mg/l in the wet season, which is more than the 610 mg/l suggested by the FAO (1994) irrigation water quality standard. Natural processes, such as the dissolution of carbonate minerals and dissolution of the atmospheric and soil CO_2 could be the source of HCO_3^- in the groundwater (Jeong 2001). The mean concentration of chlorides in the groundwater during the dry season is 176.3 mg/l, which increases slightly to 188.7 mg/l during the wet season. In both seasons, the mean values of Na^+ and Cl^- are under the permitted limits 920 Mg/l and 1,063 Mg/l (FAO 1994), respectively. Silicate weathering, seawater intrusion and fossil saline water could possibly be the sources of the Na^+ and Cl^- in the study area.

Mapping groundwater quality for irrigation purpose

Salinity hazard/salinity index

The most influential water quality criterion on crop productivity is the salinity index, which can be computed using the electrical conductivity values (Ravikumar et al. 2011). The salts usually originate from the dissolved minerals in the groundwater or from a high saline water table (Simsek and Gunduz 2007).

Groundwater samples are mostly in classes II and III (moderate to high salinity) in the both seasons (Table 6). Moderate salinity is not harmful to agricultural activities. However, high salinity groundwater can be considered for the irrigation of moderate and high salt-tolerant crops (Ravikumar et al. 2011). Three samples in the dry season and one sample in the wet season are categorized as class I , which is appropriate for high salt-tolerant crops. None of the samples are classified in classes,   and I , which are unsuitable for irrigation.

Water with an EC value lower than 700 μs/cm is considered as excellent to good quality for irrigation purposes (Table 6). Approximately, 12.7 % and 11.6 % of the water samples are classified as good quality in both seasons. The spatial distribution maps show that this class is situated in a limited area southwest of Amol City in the west of the plain, in both seasons (Fig. 4a, b). The majority of the samples (around 83 % in both seasons) are considered as water with permissible quality, which covers a wide area in the southern, western and northern sides of the plain (Fig. 3).

No significant variation in the water salinity had been observed in the central area using both seasons (Fig. 4a, b). About 3.8 % of the samples in the dry season and 5.1 % of the

Table 6 Classification of waters based on EC (Handa 1969)

EC (μs/cm)	Water salinity	Percentage		
		Dry season	Wet season	p value*
0-250	Low (excellent quality)	–	–	
251-750	Medium (good quality)	12.73 %	11.68 %	
751-2,250	High (permissible quality)	83.43 %	83.11 %	
2,251-6,000	Very high	3.82 %	5.19 %	
6,001-10,000	Extensively high	–	–	0.783
10,001-20,000	Brines weak concentration	–	–	
20,001-50,000	Brines moderate concentration	–	–	
50,001-100,000	Brines high concentration	–	–	
>100,000	Brines extremely high concentration	–	–	

*Wilcoxon signed rank test, $\alpha=0.05$

samples in the wet season belong to very high class of salinity. The areas with very high water salinity extend to the north-eastern side of the plain where the fossil saline water trapped between the sedimentary layers and sediments is effectively delineated with true resistivity ranges of 1–5 Ω/m and small grain size heterogeneous layers (Fakharian 2010).

Based on the Wilcoxon signed rank test, the p value for EC concentration is 0.783; this is significantly greater than $\alpha=0.05$, which indicates that there is no difference between dry and wet seasons for electrical conductivity concentrations in the study area.

Sodium adsorption ratio (SAR)

Another significant water quality factor that influences the soil permeability is the sodium adsorption ratio (SAR). The sodium hazard in the irrigation water is measured by the relative concentration of major cations, such as Na^+, Ca^{2+}, and Mg^{2+} (Khodapanah et al. 2009). SAR is calculated using the following equation (Hem 1985):

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \quad (4)$$

Where, all ionic concentrations are represented in meq/l.

A high concentration of SAR leads to the development of an alkaline soil (Nishanthiny et al. 2010). The soil will be hard and compact when dry and increasingly impervious to water penetration (Nishanthiny et al. 2010). Therefore, the physical structure of soil will degrade becoming unsuitable for plant growth. Todd

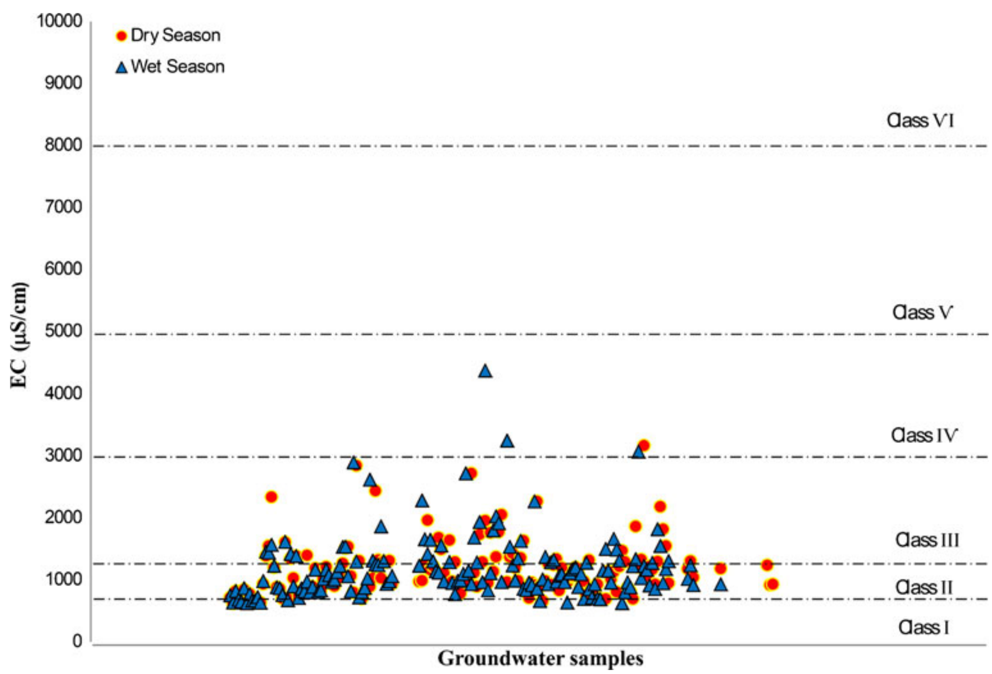

Fig. 3 Salinity index for the groundwater samples of Amol-Babol Plain

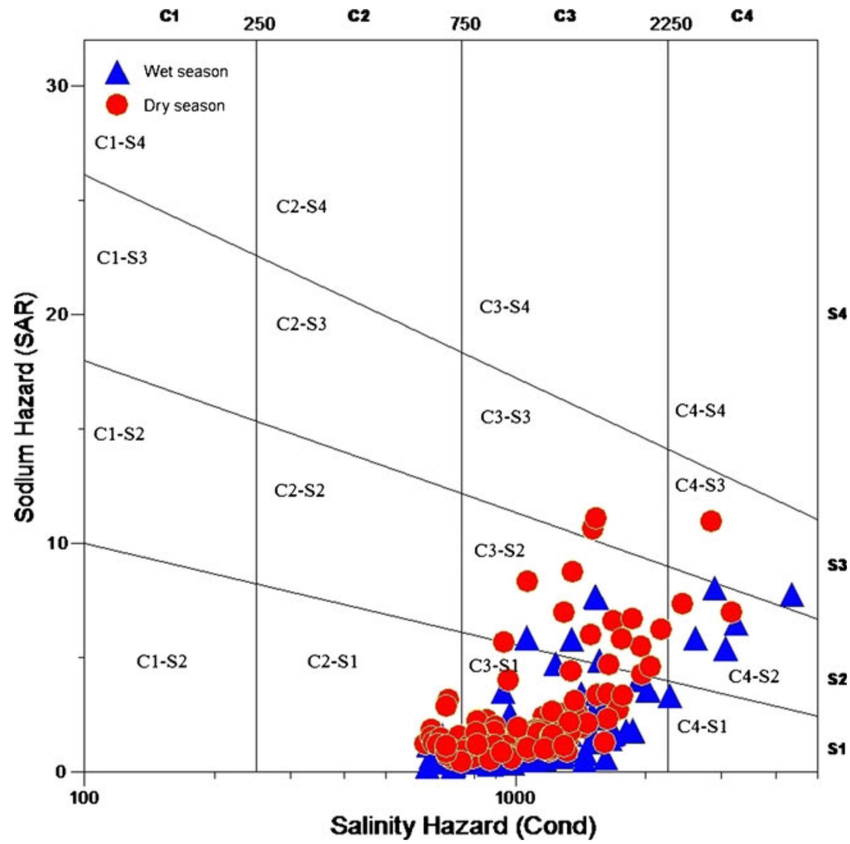

Fig. 4 US salinity hazard diagram (after Richards (1954))

(1959) suggested a classification for SAR concentrations in groundwater for irrigation purposes (Table 7).

During the dry season, the SAR concentration of all groundwater samples is classified as excellent in terms of water quality (Table 7). In the wet season, the majority of samples are classified as excellent, except for two samples that belong to the good category. The results of the Wilcoxon signed rank test show that the seasonal change of SAR is insignificant, with 95 % confidence between both seasons in the Amol–Babol Plain. The SAR concentration exhibits a similar trend as that for the salinity index. There is a gradual increase in the SAR values from the western and southern parts to the north-eastern side of the plain. The excellent to

Table 7 Classification of waters based on SAR values (Todd 1959)

SAR value	Water quality	Percentage		*P*-value*
		Dry season	Wet season	
< 10	Excellent	100 %	98.70 %	
10-18	Good	–	1.30 %	
19-26	Doubtful	–	–	0.103
26 <	Unsuitable	–	–	

*Wilcoxon signed rank test, α=0.05

good water quality is distributed across an extensive part of the study area.

Based on the U.S. Salinity diagram classification of irrigation water (1954), the salinity hazard for groundwater is classifiedas high to medium (Fig. 4). Most of the water samples belong to the C3–S1 group, representing the high salinity/low sodium type, which is detrimental to crops (Khodapanah et al. 2009). About 13 samples (8.28 %) in the dry season and 11 samples (7.14 %) in the wet season are in the category of C2–S1, indicating the medium salinity/low sodium type of irrigation water. Groundwater belonging to this class can be used for irrigation activities without any salinity control. 6.30 % and 5.19 % of water samples are in the C3–S2 class in the dry and wet seasons, respectively, indicating the high salinity/medium sodium water type. This class cannot be used on soil with restricted drainage (Ravikumar et al. 2011). Approximately two samples from the dry season and four samples from the wet season belong to the C4–S2 class. High salinity/high sodium (C3–S3) and very high salinity/high sodium is unsuitable for irrigation without special management practice, but could be utilized for salt tolerant plants on permeable soils with special management practice (Khodapanah et al. 2009), around three samples in the dry season and one sample in the wet season belong to these classes.

Table 8 classification of waters based on sodium percent (Wilcox 1955)

Na%	Water quality	Percent		P-value*
		Dry season	Wet season	
<20	Excellent	36.9 %	27.9 %	
20-40	Good	45.03 %	50.0 %	
40-60	Permissible	10.19 %	11.0 %	0.435
60-80	Doubtful	7.0 %	7.7 %	
>80	Unsuitable	0.6 %	0.6 %	

*Wilcoxon signed rank test, α=0.05

Sodium percentage

The concentration of the sodium in irrigation water is also known as the sodium percentage. The sodium percentage has been used to classify the chemical composition of the groundwater. Excess sodium in water will change the soil structure and reduce soil permeability (Nishanthiny et al. 2010). Sodium in high concentrations tend to be absorbed by clay grains, displacing Mg^{2+} and Ca^{2+}, which reduces the permeability of soils (Ravikumar et al. 2011). The sodium percentage can be calculated using Eq. 5 (Wilcox 1955):

$$Na\% = \frac{(Na^+ + K^+) \times 100}{Ca^{2+} + Mg^{2+} + Na^+ + K^+} \quad (5)$$

Where, all ionic concentrations are represented in meq/l.

Statistically, the seasonal change in sodium percentage concentrations is not significant in the study area. The Wilcox (1995) classification of groundwater samples indicates that 36.9 % and 27.9 % of samples belong to the excellent water quality category (Table 8 and Fig. 5). This group of samples is mostly concentrated on the western part of the plain, where Amol City extends onto the Haraz alluvial fan. In the Haraz alluvial fan, geophysical investigation showed high true resistivity (around 200 Ω/m) and high natural underground drainage, which leads to the leaching of ions in the discharge area and decreases groundwater salinity on the western side of the Amol–Babol Plain. About 45.0 % and 50.0 % of water samples in the dry and wet seasons are in the category of good to permissible for irrigation purposes. The spatial variation shows that the northern, north-western and some parts of the south and center of the plain are prone to good to permissible concentrations of Na% in the groundwater (Fig. 6).

It is observed that around 7.0 % of samples are classified as doubtful to unsuitable for irrigation activities in both seasons and about 2.5 % of the wells have an unsuitable quality for irrigation water in the Amol–Babol Plain. The doubtful to unsuitable zones are distributed in a few areas in the center of the plain in the

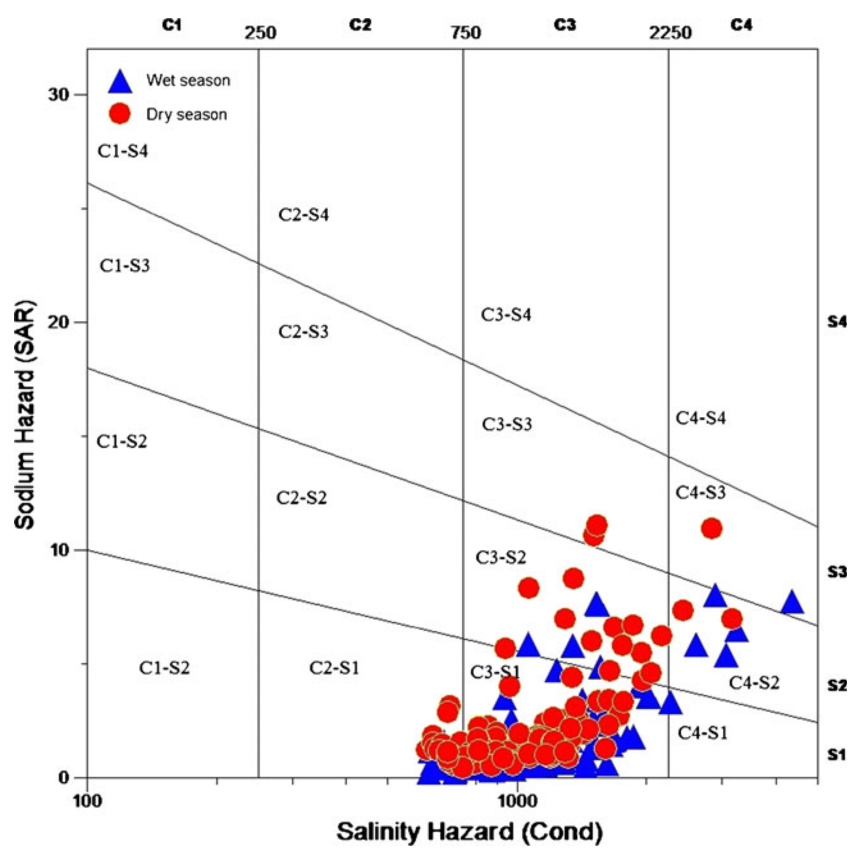

Fig. 5 Suitability of groundwater for irrigation in Wilcox diagram

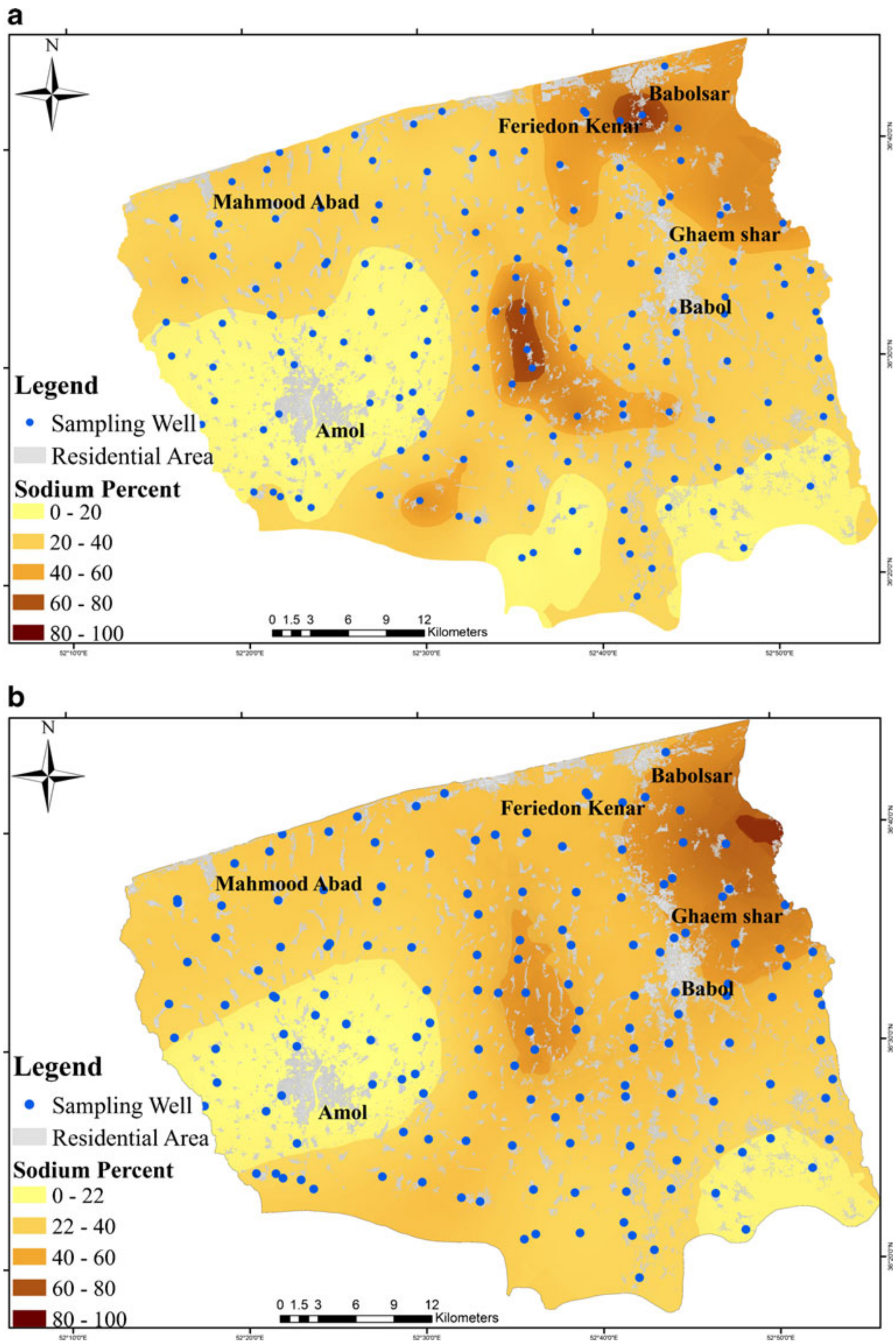

Fig. 6 Spatial distribution of sodium percent **a** dry season and **b** wet season

dry season and extend to the north-eastern side in both seasons (Fig. 6).

Residual sodium carbonate (RSC)

The residual sodium carbonate (RSC) is a valuable parameter that has a significant effect on the suitability of water for irrigation uses (Adhikary et al. 2011). The bicarbonate hazard is generally described in terms of RSC. Water with a high concentration of HCO_3^- shows a tendency for calcium and magnesium to participate as the water in the soil becomes highly concentrated (Nishanthiny et al. 2010; Ravikumar et al. 2011). Therefore, the RSC was analyzed to determine the hazardous effect of HCO_3^- and CO_3^{2-} on the irrigation water

Table 9 Groundwater quality based on RSC (after Richard (1954))

RSC (epm)	Water quality	Percent		P-value*
		Dry season	Wet season	
< 1.25	Good	33.75	31.16	
1.25-2.50	Doubtful	22.29	16.23	0.057
2. 50 <	Unsuitable	43.94	52.59	

*Pried sample *t-test*, α=0.05

quality (Sadashivaiah et al. 2008; Ramesh and Elango 2012). The RSC is calculated by the following formula (Eq. 6; Eaton 1950):

$$RSC = \left(CO_3^{2-} + HCO_3^{-}\right) - \left(Ca^{2+} + Mg^{2+}\right) \tag{6}$$

Where, all ionic concentrations are expressed in meq/l.

About 69 samples (43.94 %) in the dry and 81 samples (52.59 %) in the wet seasons show an RSC value of more than 2.50, indicates that the groundwater is unsuitable for irrigation (Table 9). This is probably due to the influence of carbonate rock dissolution, especially in the highland areas in the southern side of the study area (Fig. 2). The interpolated image reveals that the central part of the plain (between Amol and Babol Cities) shows RSC values of unsuitable concentration, in both seasons (Fig. 7).

The results of the paired sample *t test* show that the *p* value for RSC is close to the confidence threshold of 0.05, which indicates the borderline significance of seasonal changes in the study area. Therefore, the high concentration of RSC in groundwater could reflect the nature of the geological formation (especially related to Permian and Jurassic limestone formations) with which it has been in contact. Around 22.29 % and 16.23 % of water samples belong to the doubtful category in the dry and wet seasons, respectively.

The other 53 water samples (33.75 %) in the dry and 48 samples (31.16 %) in the wet seasons belong to the good category in the Amol–Babol Plain. The areas extending to the Haraz alluvial (western side) and Tallar alluvial (eastern side) are under good to doubtful RSC concentrations for both seasons (Fig. 7).

Magnesium hazard (MH)

Magnesium and calcium are necessary ions for plant growth but a high concentration of Mg^{2+} affects the soil aggregation and friability, and may decrease the crop production (Ravikumar et al. 2011). A high concentration of Mg^{2+} is usually because of the presence of exchangeable Na^{+} in irrigated soils. Equation 6 has been suggested by (Doneen 1964) for specifing the magnesium hazard for irrigation water:

$$MH = \frac{Mg^{2+}}{Mg^{2+} + Ca^{2+}} \times 100 \tag{7}$$

In Amol–Babol Plain, around 38.2 % of samples in the dry season and 28.6 % of samples in the wet season showed a MH ratio of more than 50.0 %, indicating its harmful effect on crop yield. The study shows that this class covers a wide area in the east and north-east sides of the plain and limited area on the western side, in both seasons. The remaining samples include 61.8 % and 71.4 % in the dry and wet seasons, respectively, which shows MH ratio below 50 % indicating the suitability of water for irrigation uses. The paired sample *t test* was applied to identify the role of seasonal variation in the MH concentration in the study area. Since the *p* value is close to the α value (p value=0.041, α=0.05), it could be concluded that the magnesium hazard is influenced by seasonal changes. However, the exact reason for the MH concentration is still unknown.

Kellyś ratio

Kelly's ratio (Kelly 1940, 1951; Paliwal 1967) classifies irrigation water quality based on the level of Na^{+}, Mg^{2+}, and Ca^{2+}. The proposed KR value for irrigation water is given by Eq. 9:

$$KR = \frac{Na^{+}}{Ca^{2+} + Mg^{2+}} \tag{9}$$

Where, all the ionic concentration is represented in meq/l.

A Kelly's ratio of more than one represents an excess level of Na^{+} in water and unsuitable for irrigation purposes. Therefore, water samples with a ratio of less than 1 are suitable for irrigation usage. In the study area, around 80 % of samples in both seasons present KR<1, indicating that the water is suitable for irrigation. The remaining samples, which include 20 samples (12.7 %) for the dry season and 18 samples (11.7 %) for the wet season, show a KR of more than one in the Amol–Babol Plain. For the Kelly's ratio data, the *p* value is greater than the α value (p=0.982>0.05). Therefore, the seasonal difference is not statistically significant.

Irrigation groundwater quality map

The irrigation groundwater quality map shows that the groundwater quality decreases gradually from the west and south sides of the area to the east and north-eastern part of the Amol–Babol plain (Fig. 8). Suitable water quality covers

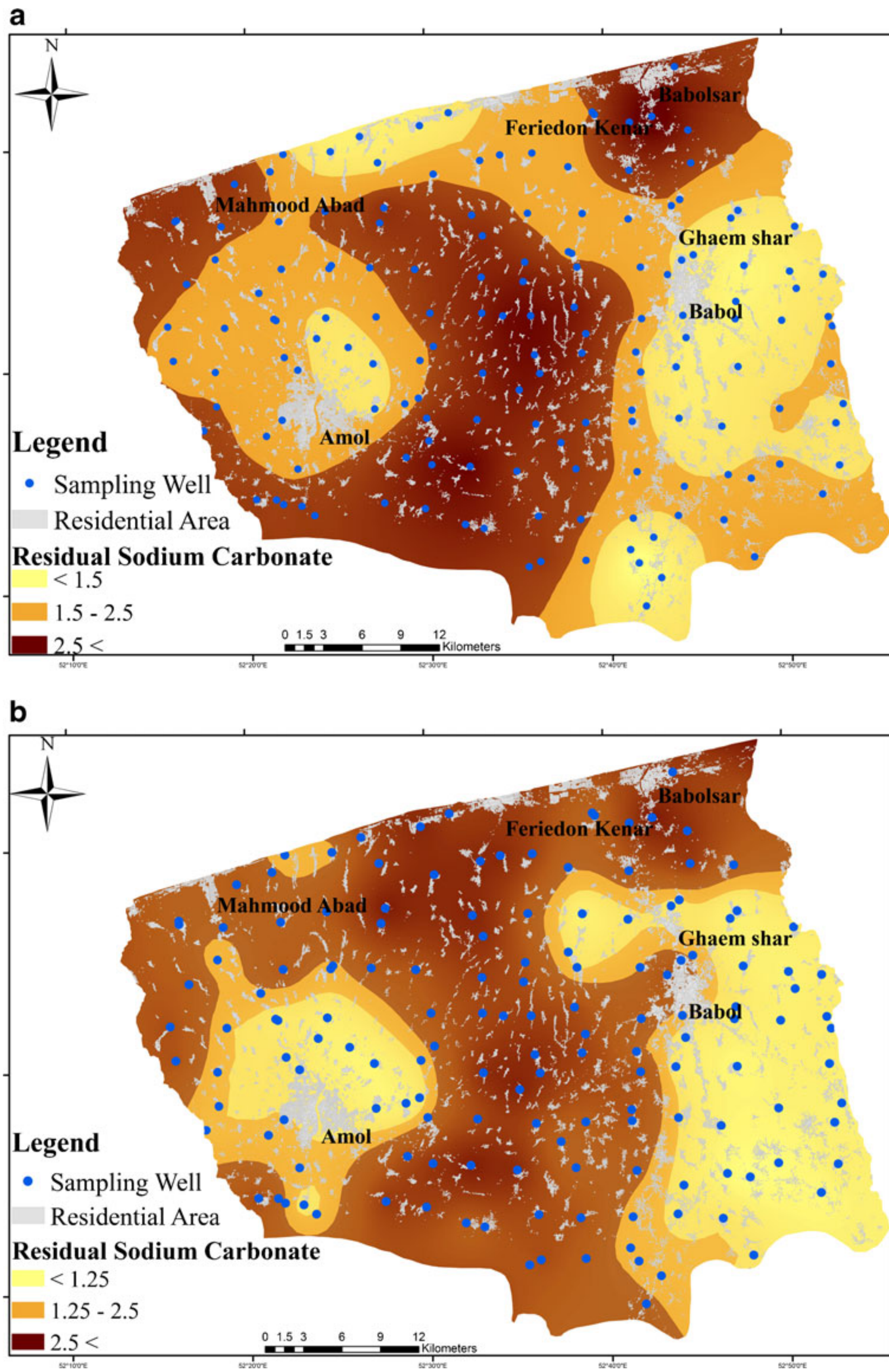

Fig. 7 Spatial distribution of RSC **a** dry season and **b** wet season

about 709 (39 %) and 700 km^2 (38.5 %) of the Amol–Babol Plain in the dry and wet seasons, respectively. Suitable water is found in the area around Amol City, which is situated on the Haraz homogenous alluvial fan, and also at the Alborz Highlands on the southern side of the plain (Fig. 8). Groundwater with moderate-suitability extends to about 928 km^2 (51.1 %) in the dry season and to 976 km^2 (53.7 %) in the wet season. Groundwater belonging to this group covers some areas on the northern, eastern and central side of the plain (Fig. 8). The unsuitable groundwater quality covers around 157 km^2 (8.6 %) and 165 km^2 (9 %) on the north-eastern side in the dry and wet seasons, respectively. In addition, the irrigation groundwater quality map shows that there is no significant variation of water quality during both seasons.

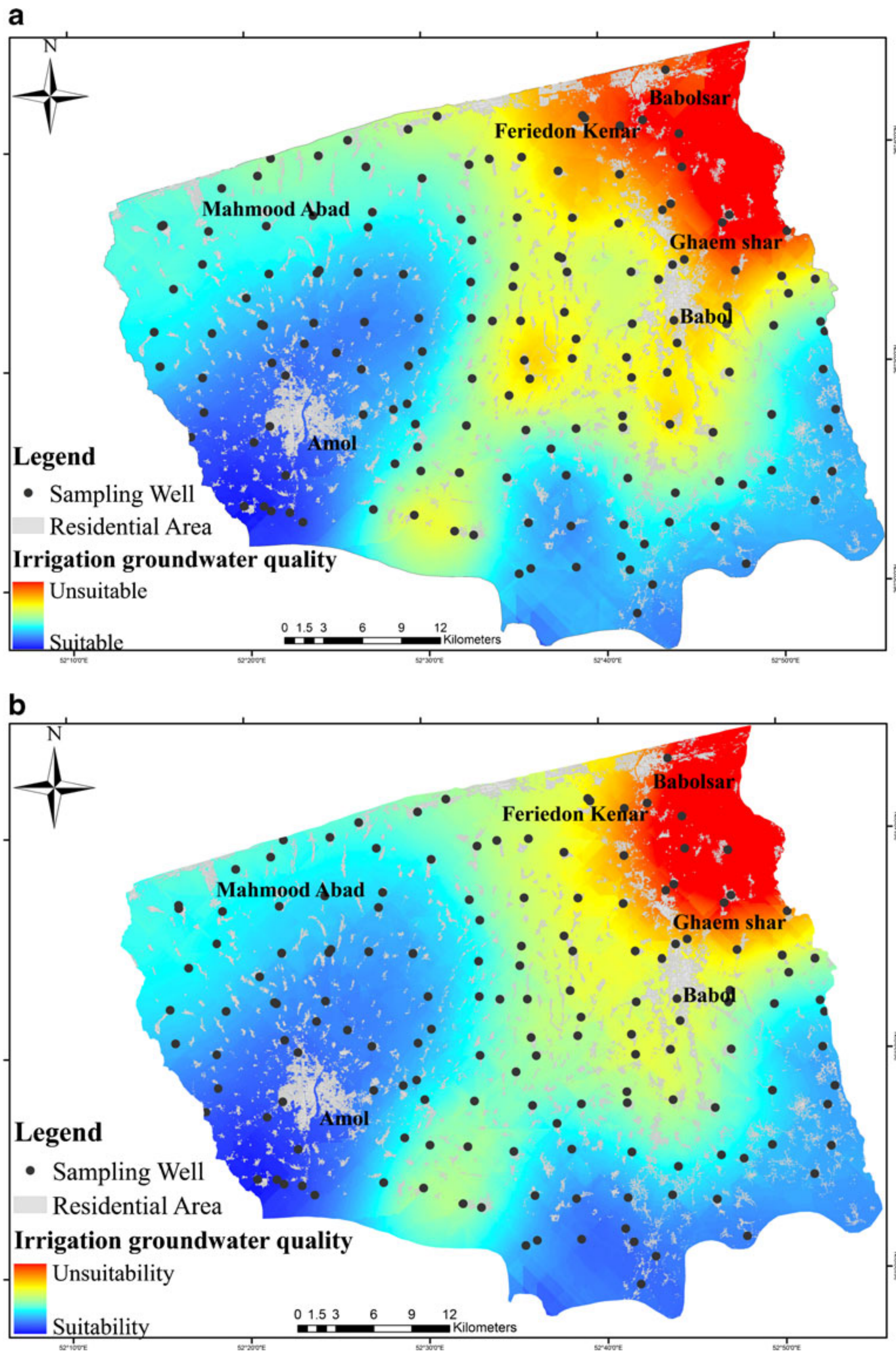

Fig. 8 Groundwater irrigation quality **a** dry season and **b** wet season

Conclusion

The hydro chemical investigation undertaken shows that most of the study area falls under the salinity hazard of medium and high, which is mostly distributed on the north and north east of the plain. This shows that the groundwater is subjected to seawater intrusion and fossil saline water. The delineated zones with high concentrations of RSC are mostly located on the southern and central sides of the plain where groundwater has been influenced by the dissolution of the carbonate rock formation of the Alborz Highlands. No SAR problem was observed in the sampling well during the study. From the Wilcox diagram, it is observed that most of the groundwater samples are in good to permissible limits in the wet and dry seasons in the study area.

The suitable to moderate-suitable irrigation water is mainly found in the western, southern and central parts of the study area. The most suitable groundwater quality extends to the Haraz alluvial fan on the western side of the plain. Generally, the groundwater quality decreases from the west and south sides to the east and north-eastern sides where the wells are located in or around layers of fossil saline water and heterogeneous sediment layers of Talar alluvial fan and the southern side of Babol City. It can be concluded that the seasonal changes for all parameters, except magnesium hazard are not statistically significant. However, the magnesium hazard and residual sodium carbonate values show borderline significant seasonal changes. Therefore, the concentration of these two parameters could be influenced by the amount of precipitation and evaporation during both seasons in the plain. Hence, lithology, seawater intrusion, and land use patterns mostly control the concentration of groundwater quality parameters and seasonal variation has a less significant role on the groundwater quality in the Amol–Babol Plain.

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