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Hydrochemistry of groundwater and its assessment for irrigation purpose in coastal Jeffara Aquifer, southeastern Tunisia

Belgacem Agoubi · Adel Kharroubi · Habib Abida

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Abstract Groundwater is of a paramount importance in arid areas, as it represents the main water resource to satisfy the different needs of the various sectors. Nevertheless, coastal aquifers are generally subjected to seawater intrusion and groundwater quality degradation. In this study, the groundwater quality of the coastal Jeffara aquifer (southeastern Tunisia) is evaluated to check its suitability for irrigation purposes. A total of 74 groundwater samples were collected and analyzed for various physical and chemical parameters, such as, electrical conductivity, pH, dissolved solids (TDS), Na, K, Ca, Mg, Cl, HCO_3, and SO_4. Sodium adsorption ratio, magnesium adsorption ratio, Sodium percentage, and permeability index were calculated based on the analytical results. The analytical results obtained show a strong mineralization of the water in the studied aquifer. TDS concentrations range from 3.40 to 18.84 gL^{-1}. Groundwater salinity was shown to be mainly controlled by sodium and chloride. The dominant hydrochemical facieses are Na–Cl–Ca–SO_4, mainly as a result of mineral dissolution (halite and gypsum), infiltration of saline surface water, and seawater intrusion. Assessment of the groundwater quality of the different samples by various methods indicated that only 7% of the water, in the northwest of the study area, is considered suitable for irrigation purposes while 93% are characterized by fair to poor quality, and are therefore just suitable or unsuitable for irrigation purposes.

Keywords Hydrochemistry · Coastal aquifer · Geostatistics · Groundwater · Tunisia

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Introduction

The southeastern Tunisia, on the Mediterranean Sea, is characterized by semi-arid to arid climate. In this dry region, where surface waters are very scarce or absent, groundwater represents the main source of water used to supply the ever growing needs of the domestic, agricultural, and industrial sectors. The shallow water is exposed to various anthropogenic and natural constraints, such as, urbanization, agricultural development, and very high evaporation rates. The study area recognizes an imbalance of its ecosystem, which resulted in a rapid increase of the groundwater salinity. The coastal Jeffara aquifer is not deep enough to be protected against salinity and pollution effects, which are further accentuated by continuous evaporation.

The most serious and obvious problem is the rapid depletion of groundwater resources of this shallow aquifer, which is being over-exploited at an alarming rate. The socioeconomic consequences of groundwater resources depletion are dramatic since groundwater will become too expensive for use in agriculture and, as a result, regional agricultural economies based on groundwater irrigation are doomed to collapse if the water resources are not adequately controlled.

Geostatistical assessment of hydrochemical variables is an important tool in spatial analysis of groundwater chemistry. Geostatistics designates the statistical study of natural phenomena which can often be characterized by a distribution in space of one or more variables (EC, pH, total dissolved solids (TDS), and major ions). These variables are called regionalized variables (Journel and Huijbregts 1978; Olea 1999).

Few studies in the literature dealt with the geostatistical assessment of groundwater quality data based on different irrigation indices (e.g., Kooveei et al. 2005; Shi et al. 2005; Assaf and Saadeh 2009; Monego et al. 2010; Soares 2010). Kooveei et al. (2005) used geostatistical analysis for the assessment of the water quality of the Sarchahan Plain Aquifer in Iran and reported that geostatistical analysis of EC and Cl distributions showed the influence of the Sarchahan diapir on the groundwater quality. Shi et al. (2005) assessed temporal and spatial variability of soil salinity in a coastal saline field and indicated that geostatistical techniques were used to assess spatial variability and temporal stability of soil salinity in a coastal tideland area in China. Assaf and Saadeh (2009) conducted a geostatistical assessment of groundwater nitrate contamination in the upper Litani Basin in Lebanon. Monego et al. (2010) examined the applicability of geostatistical modeling to obtain valuable information to assess the environmental impact of sewage outfall discharges and suggested that geostatistical techniques can help to obtain more precise predictions and hence to quantify more accurately dilution. Finally, Soares (2010) used geostatistical methods for the characterization of polluted sites and reported that geostatistics provide robust and accurate answers to the solution of monitoring and characterization of soil and water assessment.

The main objective of this study is to evaluate the suitability of groundwater from coastal Jeffara aquifer for rrigation use. Geochemical data are presented over standard graphical charts and diagrams in order to

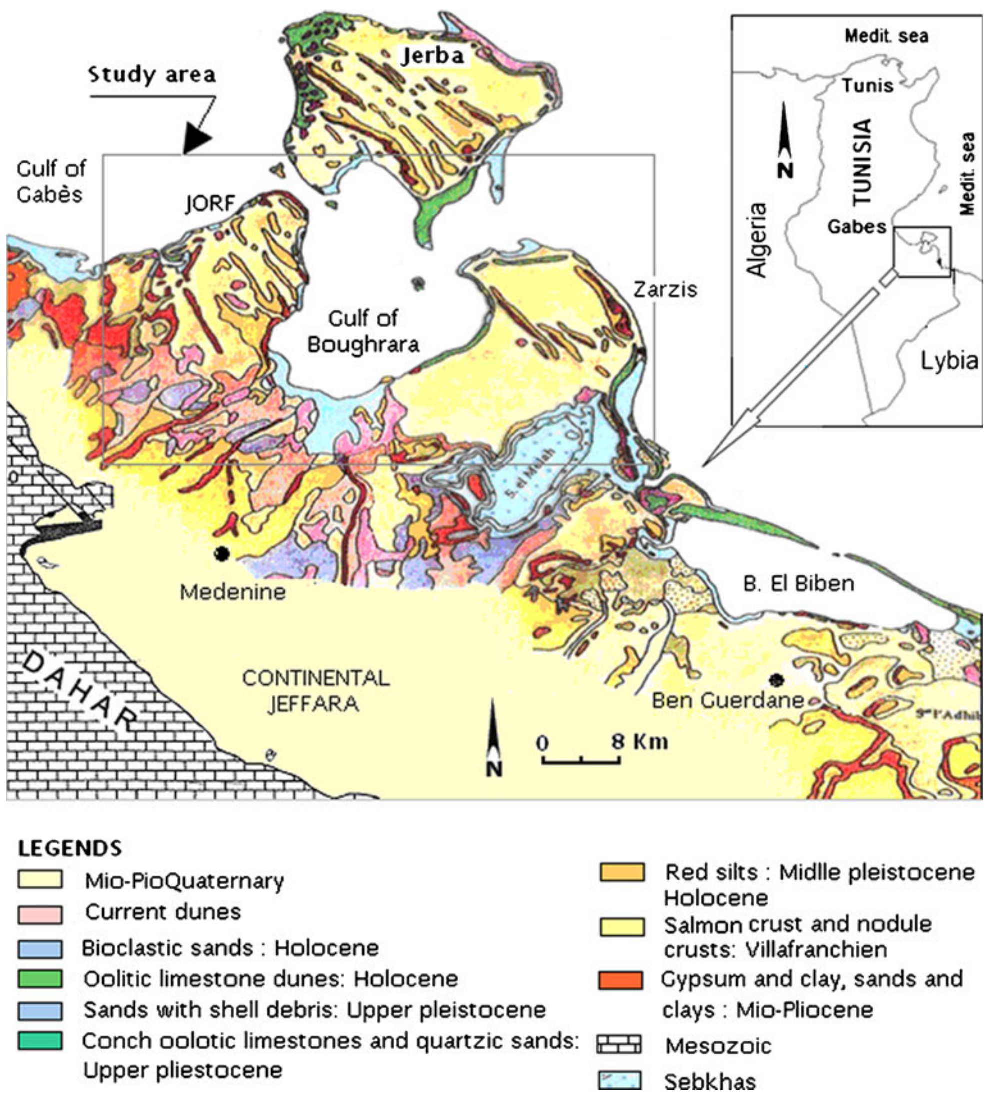

Fig. 1 Location map and geological settings of the coastal Jeffara plain (after Jedoui 2000)

recognize the various hydrochemical types or facieses of the groundwater. Geostatistical tools are also used to map the spatial variability of the groundwater quality. This may help in the long run to support new and more efficient remedial measures to combat the deterioration of water quality.

Materials and method

Study area and hydrogeological setting

The study area is located in southeastern Tunisia on the Mediterranean Sea. The average mean annual rainfall is about 200 mm/year, implying a problem of water shortage for drinking and irrigation uses, which prevailed for many years. In this area, due to the shortage of surface waters, most of water demands for irrigation and drinking are met from ground water resources.

Relative humidity ranges from 43% to 84%, and temperature varies from 10°C in winter to 45°C in summer. The wind is 42% from NE and NW. The rainfall is irregular and varies significantly from a year to another. Its average ranges from 43 to 200 mm (Ouessar et al. 2004; OSS 2005).

The geological map of southeastern Tunisia (Fig. 1) shows two principal geological provinces. The Jeffara plain, filled up by a thick Neogene sequence. It represents a collapsed block that extends eastward into Libya and the Pelagian basin. It was formed during the Late Cretaceous and Cenozoic by extensional faulting (Jedoui 2000; Bouaziz et al. 2003). The Dahar Mountain which separates the Jeffara plain in the East from the Sahara Platform.

The geological formations are of alternating continental and marine origin. A marine, superior Permian represents the oldest submerging layers and the most recent ones are of the recent quaternary age. In between, appear strata of different ages, which are generally declining northward (Bouaziz et al. 2003). In the coastal Jeffara, the Upper Miocene aquifer is represented by a thick impermeable layer of marl and gypsum, which limits water infiltration. The Miocene aquifer is a deep confined system. The coastal shallow aquifer is logged in continental Mio-Pliocene. The Mio-Pliocene bedrock is formed by alternating deposition of gypsum, clay, and sand (sandstone). All these clastic deposits alternate with evaporite deposits, which represent the final stage of a great continental cycle (Jedoui 2000; Bouaziz et al. 2003).

Located between the sea and the desert, this zone has promoted a socioeconomic importance. Fertile soils and easy access to water resources have contributed to the development of irrigation schemes covering almost the entire coastal area of Jorf and Akara-Zarzis region.

Table 1 Basic statistics of the groundwater chemical composition

Variable	Unit	Min	Max	Mean	SD	Skewness
EC	ms cm^{-1}	3.63	24.2	8.02	3.08	2.35
pH	–	6.65	7.91	7.64	0.17	−3.26
TDS	g L^{-1}	3.40	18.84	6.58	2.44	2.17
Na^+	mg l^{-1}	225	3,726	959.18	522.47	2.42
K^+	mg l^{-1}	14	432	71.7	113.89	4.98
Ca^+	mg l^{-1}	64	1,032	492.6	209.83	−0.09
Mg^+	mg l^{-1}	30.9	720	296.4	132.6	0.82
Cl^-	mg l^{-1}	335	7,029	1,845	1,024.41	2.28
SO_4^{2-}	mg l^{-1}	38	3,408	1,841.08	610.53	−0.23
HCO_3^-	mg l^{-1}	13	512	200.6	101.20	1.11
SAR	–	2.26	24.88	8.46	3.74	1.54
%Na	–	21.29	79.78	44.82	10.15	0.28
MAR	–	21.09	94.59	50.89	17.23	0.38
PI	–	1.36	4.50	2.56	0.75	0.73

SAR sodium adsorption ratio, *%Na* sodium percent, *MAR* magnesium adsorption ratio, *PI* permeability index, *SD* standard deviation

Data sampling and analysis

Seventy-four groundwater samples were collected from the examined aquifer. The considered hand-dug wells are used

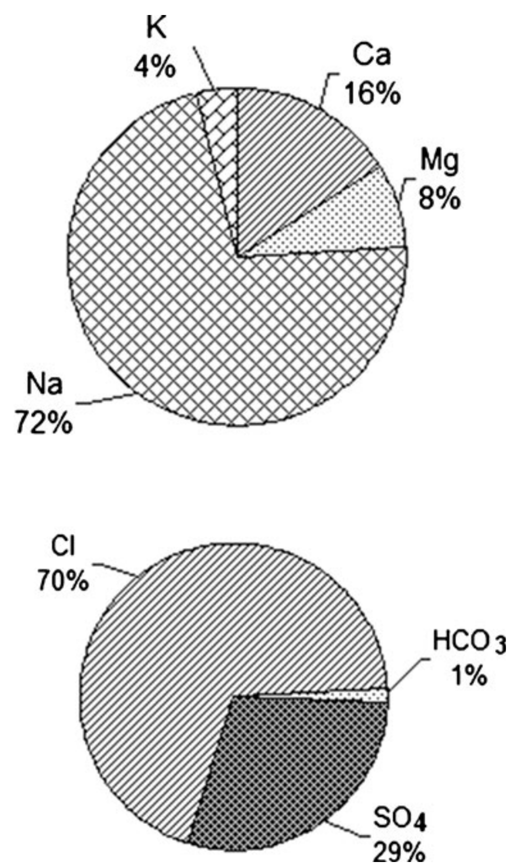

Fig. 2 Pie diagram for major ions

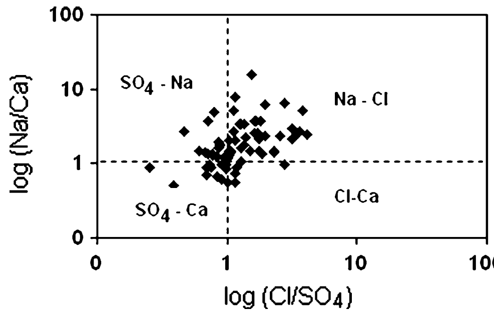

Fig. 3 Geochemical facies distribution of groundwater from Jeffara coastal aquifer

for domestic, agricultural, and domestic/agricultural purposes and were found uniformly distributed over the study area. Groundwater sampling was performed in March 2009. The

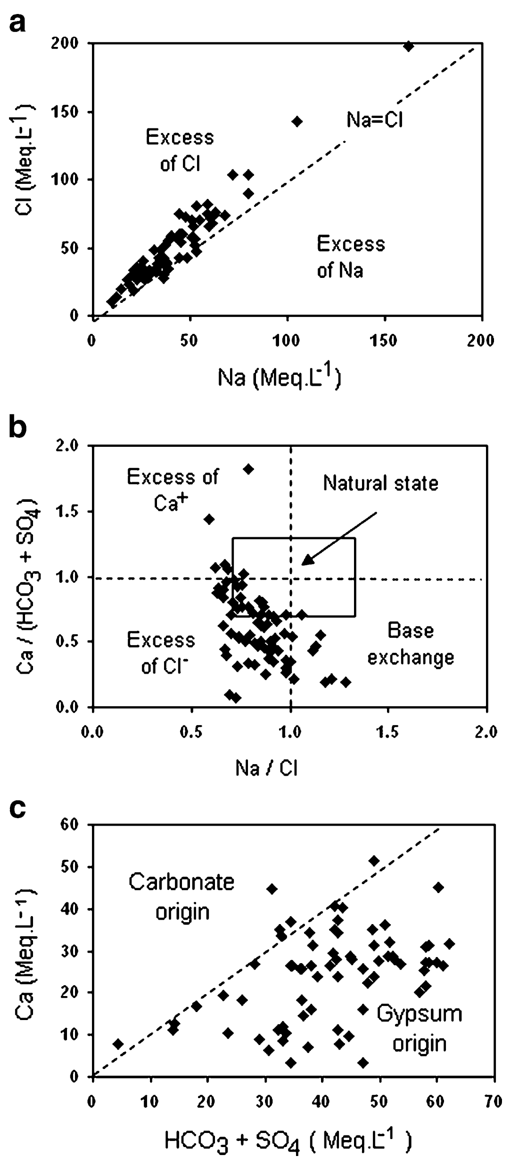

Fig. 4 **a** Relationship between Cl and Na, **b** $Ca/(HCO_3+SO_4)$ versus Na/Cl, and **c** Ca versus HCO_3+SO_4

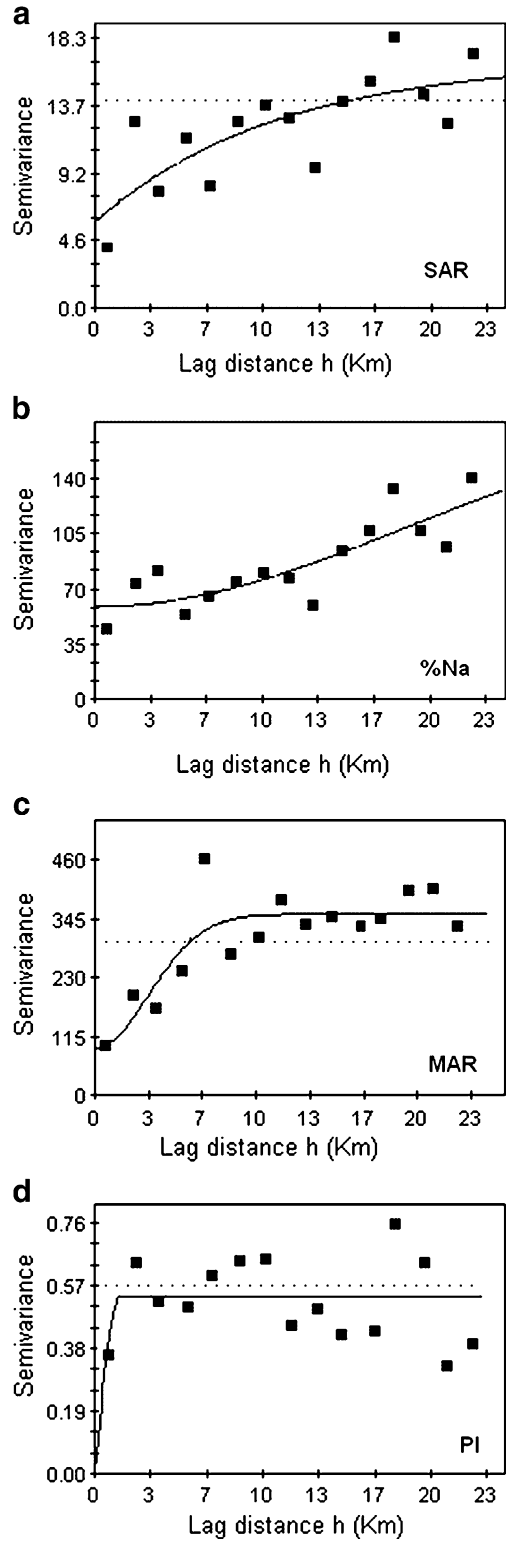

Fig. 5 Omni-directional experimental semivariograms and the cross-validation: **a** sodium adsorption ratio, **b** percentage sodium, **c** magnesium adsorption ratio, and **d** permeability index

coordinates and altitude of each sampled point were measured using eXplorist XL GPS Magellan. Electrical conductivity (EC), pH, and TDS were measured in the field using a multi-parameter (C933 Multi-Parameter) Analyzer. The major ions were analyzed using Ionic Chromatography (Methrohm 850 Professional IC).

Groundwater hydrochemical composition

Geochemical properties and principles that govern the behavior of dissolved chemical constituents in groundwater are referred to as hydrogeochemistry (Obiefuna and Sheriff 2011). The chemical composition of groundwater is related to the solid product of rock weathering and changes with respect to time and space. Therefore, the variation on the concentration levels of the different hydrogeochemical constituents dissolved in water determines its usefulness for domestic, industrial and agricultural purposes. In this way, Pie diagram and major ions relationship such us Na/Ca versus Cl/SO_4, Ca versus HCO_3+SO_4, Cl versus Na, and Ca/(HCO_3+SO_4) versus Na/Cl were established in order to identify groundwater mineralization process.

Irrigation water quality generally varies depending upon the types and quantities of dissolved salts. Thus, water suitability for irrigation use is determined not only by the total amount of dissolved solids but also by the kind of salt (Sarkar and Hassan 2006). According to Sarkar and Hassan (2006) and Obiefuna and Sheriff (2011), the irrigation water quality is judged by four accepted criteria: (1) TDS, (2) relative proportion of sodium to other cations, expressed by sodium adsorption ratio (SAR), (3) chlorine (Cl^-) or/and boron contents, and (4) residual sodium carbonate.

A geostatistical approach for water assessment quality

Prior to any geostatistical estimation, the semivariogram or the covariance must be determined from the regionalized variable data. Semivariograms are the basic geostatistic tools for visualizing, modeling and exploiting the spatial autocorrelation of a regionalized variable. The spatial correlation between values at different locations is determined through calculation of semivariograms, where the semi-variance $\gamma(h)$ is plotted as a function of the distance (h) between sampling points. The functional relationship shows the measure of how a variable Z changes in value between site x and ($x+h$) at distance h (lag h). Experimental semivariogram and experimental covariance were computed based on Eqs. 1 and 2, respectively.

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \left(Z(x) - Z(x+h)\right)^2 \quad (1)$$

$$C(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \left[\left(Z(x) - \overline{Z}(x)\right)\left(Z(x+h) - \overline{Z}(x)\right)\right] \quad (2)$$

where $C(h)$ is the experimental covariance, $\gamma(h)$ is the experimental semivariogram, $Z(x)$ is the measured value of a regionalized variable Z at location x, $Z(x+h)$ is the measurement value of the variable Z at location ($x+h$), $\overline{Z}(x)$is the sample mean of the random variable x, and N is the number of pairs of the variable $Z(x)$ at location points separated by the same distance h.

Spatial estimation of a regionalized variable can be done by a kriging procedure. Kriging provides a means of interpolation to determine parameter values at non-sampled locations, using knowledge about spatial relationships (the semivariogram) in the data set. Kriging is based on the regionalized variable theory and provides not only an interpolated estimate for a given location, but also a variance estimate of the interpolated value. Kriging refers to the process of estimating variable values at locations, where no measurements are available. Given the assumption of normality, the value at a location x_0, $Z(x_0)$, is estimated as a weighted average of measured values as follows (Eq. 3):

$$Z^*(x_0) = \sum_{i=1}^{n} \lambda_i Z(x_i) \quad (3)$$

In which $Z^*(x_0)$ is the kriged value at location x_0, $Z^*(x_i)$ is the known value at location x_i, $\lambda_1, \ldots, \lambda_n$ are a set of weights obtained by solving the ordinary kriging system.

Table 2 Variographic parameters of the groundwater chemical composition from coastal Jeffara aquifer

	Model	Sill	Range	Nugget	N/S	Z-Z*	σ	MSPE
CE (ms cm^{-1})	Exponential	6.00	1.86	0.4	7%	0.106	1.116	0.00130
pH	Exponential	0.03	2.53	0.0004	1%	0.0045	0.107	0.00058
TDS (g L^{-1})	Exponential	10.08	2.44	1.08	11%	0.15	1.426	0.00144
%Na	Gaussian	187	26.52	58.4	31%	−0.002	0.216	−0.00013
SAR	Exponential	16.84	10.88	5.84	35%	0.09	1.62	0.00076
MAR	Gaussian	353.6	4.70	91.30	26%	−0.014	6.04	−0.00003
PI	Spherical	0.54	1.51	0.001	0%	0.003	0.504	0.00008

N nugget, *S* sill, *MSPE* mean standardized prediction error

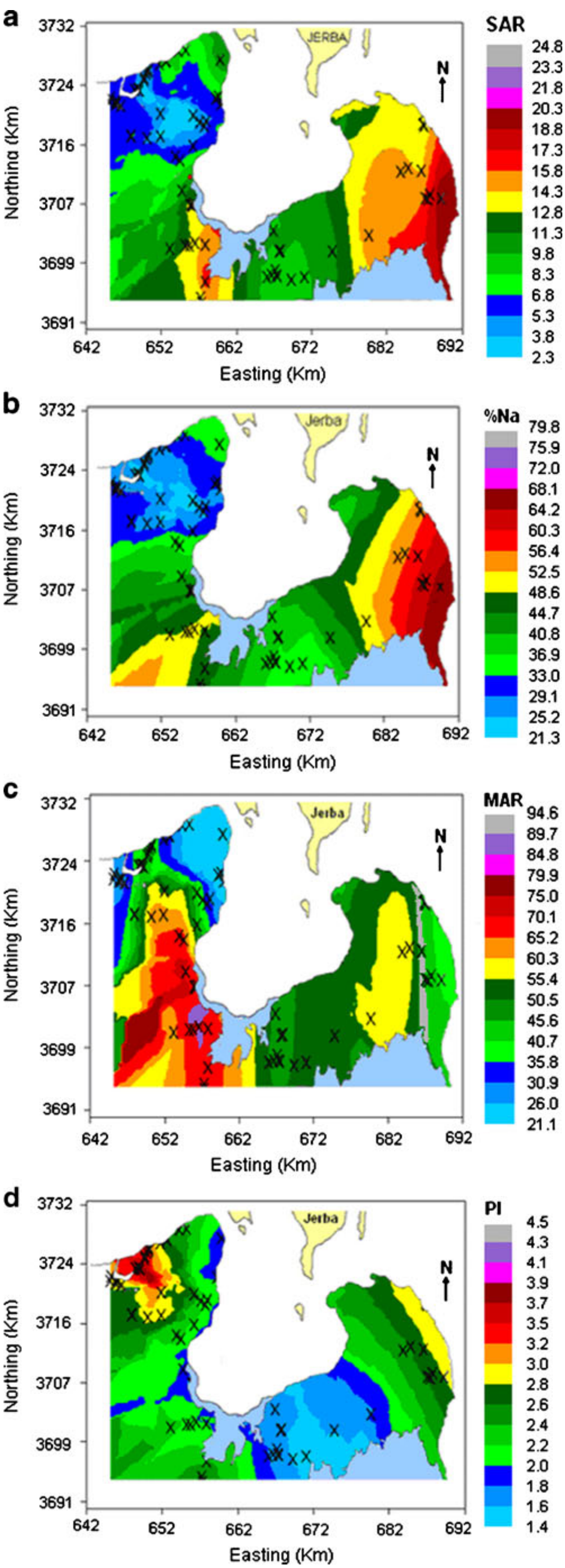

Fig. 6 Spatial trend maps produced by ordinary kriging: **a** sodium adsorption ratio, **b** percentage sodium, **c** magnesium adsorption ratio, and **d** permeability index (in March 2009)

The nugget can be attributed to measurement errors or spatial sources of variation at distances smaller than the sampling interval or both (Assaf and Saadeh 2009). The range is the distance beyond which $\gamma(h)$ does not change significantly. A longer range indicates a stronger spatial continuity.

In order to assess groundwater quality for irrigation, SAR, sodium percentage (%Na), magnesium adsorption ratio (MAR), and permeability index (PI) were mapped using ordinary kriging techniques.

Sodium absorption ratio The sodium or alkali hazard potential in irrigation water may be expressed in terms of the SAR, which can be estimated by Eq. 4 given by Richards (1954), where all the ions are expressed in milliequivalents per liter:

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

There is a significant relationship between SAR values of irrigation water and the extent to which sodium is adsorbed by the soils. If water used for irrigation is high in sodium and low in calcium, the cation-exchange complex may become saturated with sodium (Sarkar and Hassan 2006). This can destroy the soil structure owing to dispersion of the clay particles.

Magnesium adsorption ratio Raghunath (1987) proposed the MAR ratio to characterize irrigation waters. The MAR is given by Eq. 5, in which all the ions are expressed in milliequivalents per liter:

$$\mathrm{MAR} = \frac{\mathrm{Mg}}{\mathrm{Ca} + \mathrm{Mg}} \times 100 \tag{5}$$

Waters with MAR>50 are considered to be harmful and unsuitable for irrigation use.

Sodium percentage EC and sodium concentration are very important in classifying irrigation water. Besides affecting the growth of the plants directly, salts also affect soil structure, permeability, and aeration, which indirectly affect plant growth (Singh et al. 2009). Wilcox (1955) Diagram uses %Na and EC values to classify irrigation water quality. Na% is calculated using Eq. 6, in which all the ions are expressed in milliequivalents per liter:

$$\%\mathrm{Na} = \frac{\mathrm{Na} + \mathrm{K}}{\mathrm{Ca} + \mathrm{Mg} + \mathrm{Na} + \mathrm{K}} \times 100 \tag{6}$$

Permeability index The permeability index was calculated according to Doneen (1964) and Raghunath (1987), as given by Eq. 7:

$$PI = \frac{Na + \sqrt{HCO_3}}{Ca + Mg + Na} \times 100 \quad (7)$$

All chemical elements here are expressed in equivalent per liter.

Finally, for practical interpretation of spatial development of salinity hazard in the study area, a kriged map based on Richards diagram (1954) will be presented. For each class, a number was attributed and the wells were numbered accordingly. This kind of map shows areas under different classes of vulnerability and risk groundwater resource degradation which leads to identify the areas needing immediate attention for remedial measures.

Results and discussions

Groundwater chemistry

Basic statistics of major ions concentrations, EC, pH, TDS, and evaluation parameters of water quality are summarized in Table 1. In general, pH is slightly acidic to alkaline in nature. It varies from 6.65 to 7.91 with a mean of 7.64. The EC values vary from 3.63 to 24.2 $S cm^{-1}$. TDS values vary between 3.40 and 18.84 $g L^{-1}$, with a mean of 6.58 $g L^{-1}$. The large variations in the EC, TDS, and ionic concentrations may be attributed to geochemical processes and hydrological conditions and seawater mixing.

Pie diagram (Fig. 2) shows that Na^+, Cl^-, SO_4^{2-}, and Ca^+ are the dominant ions composition of groundwater. The diagram also shows that chlorine and sodium ions are more abundant. Cl^- represents 70% of the cations while Na represents 72% of the anions. Therefore, there is possibility there is a possibility for further concentration increase due to dissolution of these elements (Na^+, Cl^+, Ca^+, and SO_4^{2-}) resulted from the dissolution of evaporate deposits of Mio-Pliocene and a potential local saltwater intrusion.

The scatter-plot diagram (Fig. 3) presents the relationship between log (Na/Cl) and log (Cl/SO_4) where Na, Cl, and SO_4 are expressed in milliequivalents per liter. Figure 3 shows that most dominant ions are sodium and chloride. The high Na and Cl concentrations suggest that these ions have probably a common origin. The presence of Na^+ and Cl^- in natural water is attributed to the dissolution of halite. However, sodium chloride may have other origins (natural or anthropogenic). The scatter-plot diagrams (Fig. 4a, b) present the relationship between Cl–Na and $Ca/(HCO_3+SO_4)$–Na/Cl indicate a surplus of Cl. The evolution of the Na^+ concentration with that of Cl^- shows an excess of Cl^- level which is explained by the existence of another origin for chlorine other than halite. The chlorine content is mainly attributed to seawater intrusion. The plot of Ca versus HCO_3+SO_4 (Fig. 4c) shows

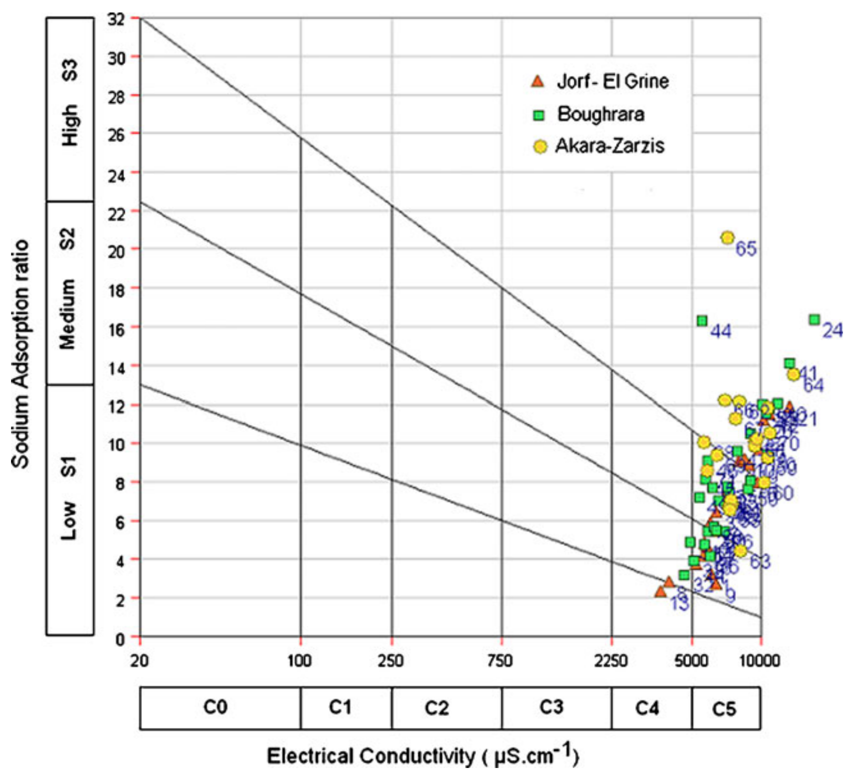

Fig. 7 Classification of groundwater from coastal Jeffara for irrigation use, based on Richards method

Table 3 Classification of the groundwater samples (based on Richards diagram)

Class of water	Number of hand-dug wells	Percentage of wells	Salinity hazard
C4S1	02	3%	Low SAR and medium EC
			Suitable for very high salt-tolerant crops
C4S2	03	4%	Low SAR and high EC
			Suitable for organic soils or coarse textured soils
C5S2	08	11%	Medium SAR and medium EC
			Groundwater can be used with chemical amendments in open soils and with excessive leaching.
C5S3	40	54%	Medium SAR and high EC
			Unsuitable for irrigation water
Out of range	21	28%	Very high SAR and very high EC
			Poor water quality

that the calcium contained in groundwater from coastal Jeffara aquifer has a gypsum origin. This finding suggests that the dissolution of gypsum. The plot of Ca versus HCO_3+SO_4 (Fig. 4c) shows that the calcium contained in groundwater from coastal Jeffara aquifer has a gypsum origin, implying a gypsum dissolution.

Geostatistical assessment of water quality

Variographic analysis of irrigation parameters is the first step of geostatistical assessment. Selecting a semivariogram model is an iterative process that involves calculating experimental semivariograms, fitting an alternative semivariogram, calculating an alternative ordinary kriging prediction and carrying out a cross-validation statistical analysis to assess the performance of the prediction phenomena (Assaf and Saadeh 2009). The semivariogram model was selected using two main evaluation criteria: Nugget/Sill ratio (Hani and Karimineja 2010) and the mean standardized prediction error (MSPE). According to Assaf and Saadeh (2009), the MSPE is defined as follows Eq. 8:

$$\mathrm{MSPE} = \frac{\sum_{i=1}^{n-1} \left(Z^*(x_i) - Z(x_i)\right)/\sigma^*(x_i)}{n-1} \tag{8}$$

In which $Z^*(x_i)$ and $\sigma^*(x_i)$ are the estimated value and standard error of the variable at location x_i, respectively, based on the other $n-1$ data points.

Figure 5 shows experimental variograms and fitted model for SAR, Na%, MAR, and PI. SAR, TDS, pH, and EC are fitted exponential, %Na and MAR are modeled Gaussian and PI is modeled spherical. Variographic parameters of irrigation parameters are summarized in Table 2. It shows that the MSPE values for the prediction models range from −0.00003 to 0.00144 and the Nugget/Sill ratio varies between 0% and 35%, implying thereby a relatively insignificant biases and a good estimation of prediction variability.

SAR and US salinity The kriged contour map of SAR in coastal Jeffara aquifer (Fig. 6a) shows a risk of mineralization almost all over the study area. The SAR values vary between 2.26 and 24.8. According to the Richards (1954) Reverside diagram, computed by DIAGRAMMES software (Simler 2009), in which the EC is taken as salinity hazard and SAR as alkalinity hazard. Figure 7 shows that water samples fall in the category C4-S1, C4-S2, C5-S2, and C5-S3. However, 55% fall outside the diagram, indicating a medium to high alkali water and high salinity. Classification of the groundwater samples from coastal Jeffara, based on Richards diagram, is shown in Table 3. It shows that 7% of the groundwater samples are suitable for salt-tolerant crops or organic soils; 11% can be used with chemical amendment in open soils and 82% are unsuitable for irrigation use.

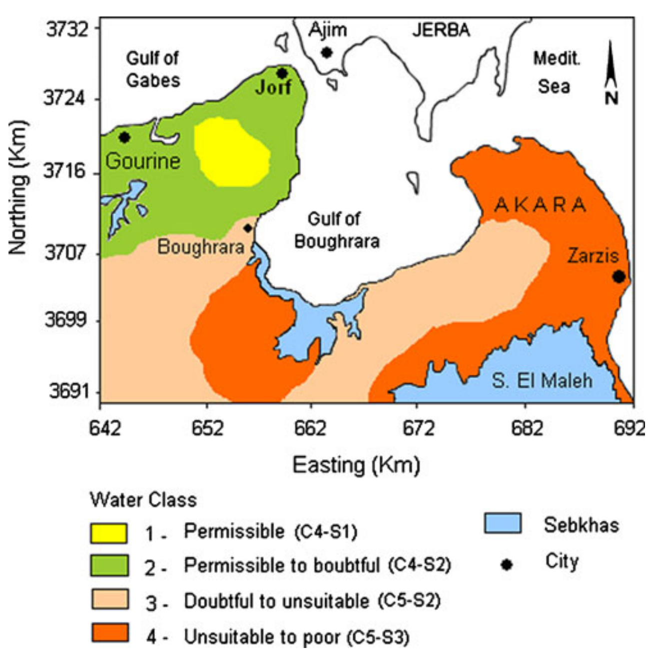

Fig. 8 Assessment map of groundwater for irrigation use based on Richards diagram

Sodium percentage Figure 6b shows that spatial development of sodium percentage was permissible in most of Jorf-Gourine and Boughrara area. However, the Akara-Zarzis region shows a permissible to doubtful groundwater. High Na% values in the Zarzis area are probably attributed to the contribution of sebkhat El Maleh in the south and seawater mixing in the eastern part of study area.

Magnesium adsorption ratio and permeability index In the analyzed waters from coastal Jeffara, 37 samples have MAR values exceeding 50%. Figure 6c shows that the groundwater from Jorf-Gourine is not harmful for irrigation and in Boughrara and Akara-Zarzis the analyzed groundwater is unsuitable. Permeability index ranges from 1.7 to 4.5. Figure 6d shows that the Jorf-Gourine has the lowest permeability index indicating that the groundwater from this area is good to permissible.

Mapping groundwater quality assessment for irrigation use

The ability of groundwater salinity hazard for irrigation use was mapped based on Richards diagram (Fig. 7). Numbers of 1 to 4 were assigned to C4-S1, C4-S2, C5-S2, and C5-S3 classes, respectively, and the wells were numbered accordingly. Ordinary kriging was then used to map the spatial development of groundwater suitability for irrigation use (Fig. 8). The map obtained clearly shows that only the central part of Jorf peninsula shows a permissible water class for irrigation use. Poor water quality, which is unsuitable for irrigation, is located in the Akara-Zarzis peninsula and in the border of the sebkhas. Waters from Boughrara and the eastern part of the Jorf Area range from permissible to doubtful. These waters can be used with special soils treatment and with plants showing salt tolerance.

The Jorf-Gourine Region (Northeastern part of the study area) is characterized by two water types: a good to permissible groundwater in the center and permissible water in most of the region. This is probably explained by the existence of a lenticular sheet formed by the Mio-Pliocene sands. The spatial variability of groundwater quality was shown to be affected by the nature of the geological formations, the sebkhas bordering much of the study area and seawater intrusion.

Conclusions

The groundwaters in the coastal Jeffara, southeastern Tunisia, have been evaluated for their chemical composition and suitability for irrigation uses. The interpretation of the hydrochemical data reveals that the groundwater of the Jeffara aquifer is highly saline, rich in Cl, Na, SO_4, and Ca. The sequence of the abundance of the major ions is in the following order $Cl > Na > SO_4 > Ca > Mg > K > HCO_3$. Ordinary kriging was used to map spatial development of salinity hazard parameters (SAR, MAR, %Na, and PI). Autocorrelations between the different studied parameters were obtained, which indicates that groundwater mineralization is controlled by several processes.

Richards diagram relating sodium adsorption ratio and electrical conductivity showed that 7% of the groundwater samples fall in the field of permissible for irrigation of organic soils or highly tolerant crops and 11% of the groundwater samples can be used with chemical amendment in open soils and 82% are unsuitable for irrigation use.

According to magnesium adsorption ratio, out of the 74 treated samples, 37 have MAR values exceeding 50%. Permeability index values range from 1.7 to 4.5 with a lowest value is in the central part of Jorf peninsula indicating that the groundwater in this area is of permissible to good quality for irrigation use.

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