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Hydrogeochemical characteristics and assessment of drinking water quality in Zeuss–Koutine aquifer, southeastern Tunisia

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Abstract Zeuss–Koutine aquifer, located in southeastern Tunisia, has been used intensively as a primary source to meet the growing needs of the various sectors. Detailed knowledge of the geochemical evolution of groundwater and water quality can enhance understanding of the hydrochemical system, promoting sustainable development and effective management of groundwater resources. To this end, a hydrochemical and statistical investigation was conducted. Groundwater samples have been collected from 13 wells from 1995 to 2005; to understand the sources of dissolved ions and assess the chemical quality of the groundwater. Results demonstrate that among the cations, only the mean concentrations of Na^+ exceed guideline values set by the World Health Organization (WHO). Regarding the analyzed anions, the concentration of SO_4^{2-} and Cl^- are above the WHO allowable concentrations. Total dissolved solids in most groundwater samples are greater than 1,000 mg l^{-1}, the limit set by the WHO, indicating slightly saline or moderately saline water. In general, a significant increase in the degree of water mineralization was observed in the direction of southwest to northeast following the regional flow direction. Calculated saturation indices show that all water samples were oversaturated with respect to aragonite, calcite, and dolomite, and undersaturated with respect to anhydrite, gypsum, and halite. Based on hydrochemical facies, two types of water predominate in the study area. The first is Ca–Na–SO_4–Cl in type and located in the southwest which corresponds to the recharge part of the aquifer. The second type is Na–Ca–Cl–SO_4 and located in the east, which corresponds to the discharge part.

Keywords Zeuss–Koutine aquifer · Drinking water quality · Hydrochemical facies · Saturation indices · Trend evolution · Multivariate statistical analysis

Introduction

Nowadays, in the current world, a sustainable socioeconomic development of every community depends much on the sustainability of available

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water resources. Water of adequate quantity and quality is required to meet growing household, industrial, and agricultural needs (Das et al. in press).

In arid zones, water is a rare and precious resource. The current situation of the water resources and their uses in Tunisia present stakes which are common to many areas of the Mediterranean basin: limited and already largely exploited resources to answer the growth of the needs, the increasing use of so-called nonconventional resources, a competition between sectoral uses of water, an increasing merchandising of the resources, and constraining climatic conditions which come to reinforce the tensions around water (Romagny et al. 2004).

The southern Tunisian region is semi-arid and arid with a mean annual rainfall of 100–230 mm and evaporation rates of 1,300–1,600 mm per annum, and the climatic water balance is almost negative year round (Ouessar et al. 2004). The average annual rainfall decreases from north to south from approximately 1,300 to less than 200 mm. In northern Tunisia, the population use dam water as a source of freshwater for agricultural and domestic purposes, whereas communities in the south, where surface waters are very scarce or absent, rely mainly on groundwater of variable quality for their domestic supplies.

Since groundwater represents the main source of water in the dry areas of Tunisia, as it is the case in many arid and semi-arid regions around the world, the aquifers have been massively pumped to meet the growing needs of the various sectors (drinking, industry, agriculture, aquaculture, tourism, etc.) during the last decades. The Zeus–Koutine aquifer, which extends over 920 km^2, is the first source for fresh water for drinking purposes. It has been pumped heavily since the early 1970s. In recent years, the overuse of groundwater has led to the lowering of groundwater levels and worsening its quality (OSS 2005). The quality of groundwater is equally important as that of quantity. Due to growing population, agriculture expansion, and urbanization, groundwater resource management has become increasingly important for sustainable development of these regions. It is therefore necessary to subject the water to routine quality analyses in order to assess its suitability for human consumption. An appropriate assessment of the suitability of groundwater for domestic water supplies requires that the concentrations of some health parameters (inorganic constituents) as well as esthetic parameters are compared with the World Health Organization (WHO) guideline values set for potable water (WHO 2004).

Little is known about the natural phenomena that govern the chemical composition of groundwater or anthropogenic factors that presently affect them. Generally, the quality of groundwater is controlled by many factors that include composition of recharge water, geological structure and mineralogy of the watersheds and aquifers as well as the residence time and reactions that take place within the aquifer (Fetter 1994; Appelo and Postma 2005). The interaction of all factors leads to various water types. Increased knowledge of geochemical evolution of groundwater quality could lead to improved understanding of hydrochemical systems in such areas, leading to sustainable development of water resources and effective management of groundwater resource.

Therefore, our objective in this study was to identify the processes controlling the geochemical evolution of groundwater quality and to characterize water–rock interaction and its effects on the chemistry of the water. Finally, to aid the management and future development of groundwater resources in the region, the hydrochemical approach and statistical methods were also applied to divide the territory into areas with distinct groundwater quality. This may help in the long run to support new and more efficient remedial measures to combat the deterioration of water quality.

Study area

The study area is situated in the Mediterranean Sea region of the southeastern part of Tunisia and lies between longitudes 10° 16′ and 10° 61′E and latitudes 33° 39′ and 33° 75′N.

The aquifer of Zeuss–Koutine is situated in the north of the city of Medenine (Fig. 1). It stretches out from the southwest, in the Matmata mountains near Béni Khdache and Toujane, going through the Jeffara plain, into the Gulf of Gabès, actually ending in the saline depression (Sebkhat)

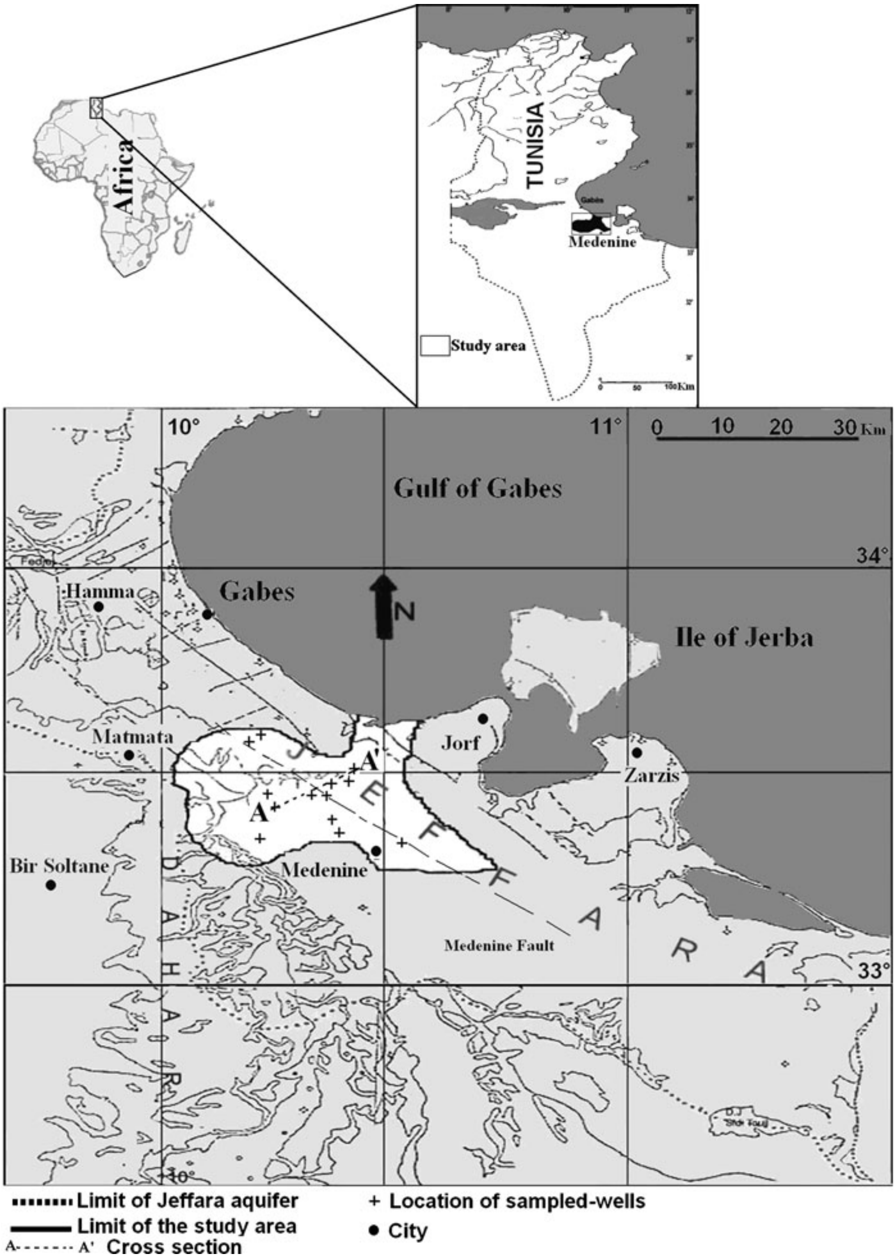
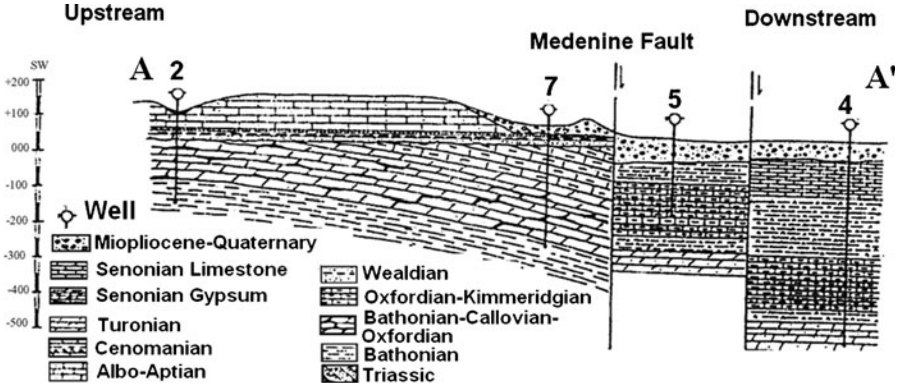


Fig. 1 Locality map of the study area showing location of wells sampled for groundwater analysis

of Om Zessar. The geological formations consist of alternating continental and marine origin. The oldest submerging layers are represented by a marine, superior Permian, and the most recent ones are of the recent Quaternary (Morhange and Pirazzoli 2005). Between the Permian and Quaternary formations is a confined strata of different age, which is generally declining in northward direction (Gaubbi 1988). Zeuss–Koutine region is bordered by three main structures that define southeastern Tunisia: the Dahar monocline, west and northwest; the Medenine Tebaga monocline, south; and the plain of the Djeffara, east and north.

The climate is of the Mediterranean type and is characterized by hot and dry periods in summer and by cold and rainfall periods in winter, which is typical for the arid and semi-arid zones. The coldest

Fig. 2 Hydrogeological cross-section along transect AA′, as indicated in Fig. 1



months are those of December, January, and February, with occasional freezing (up to −3°C). June, July, and August are the warmest period of the year during which the temperature could reach as high as 48°C (in the shade). The rainfall is characterized by low averages, high irregularity (both in time and space), and torrentially. Surface water hydrology in the study area is represented by the following Rivers: Zeuss, Koutine-Om Ezzassar, and Zigzaou. There is no perennial river in the study area.

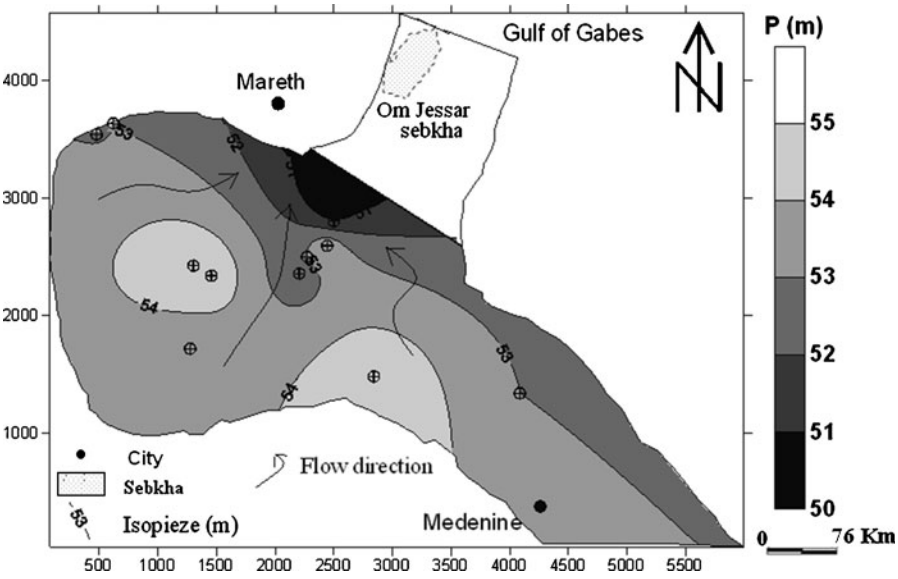
The Zeuss–Koutine aquifer constitutes an important water resource used for various purposes; potential resources are estimated to 350 l s^{-1}. The exploitation of this reservoir started in 1962 (Gaubbi 1988). The continuous monitoring of the exploitation of this aquifer has shown that the withdrawal rate increased from 102 l s^{-1} in 1974 to 440 l s^{-1} in 2005, which resulted in a decline of the mean piezometric level of 0.33 m in 1982 and 1.02 m in 2005 (DGRE 2005).

Results of aquifer tests indicate that transmissivity of the aquifer varies between 0.055 and 0.2 m^2 s^{-1} (OSS 2005).

The aquifer geometry is controlled by Medenine fault (Fig. 2) and differs from one locality to another. The Zeuss–Koutine aquifer is constituted by the following litho-stratigraphic units (Yahyaoui 2004):

Upper Jurassic limestone and dolomite (Callovian Oxfordian);

Fig. 3 Piezometric map of Zeuss–Koutine aquifer



Albo–Aptian calcitic dolomites;
Turonian dolomites and dolomitic limestone;
Lower Senonian limestone which is divided into two distinct entities:

1. The marly-gypsitic Senonian intermediate limestone
2. The Summit limestone of the top.

Leakage between different layers of the Zeuss–Koutine aquifer is made through intermediary faults, with Medenine fault being the most important. These aquifers are intercepted by several wells at various depths. However, in Medenine region, Jurassic constitutes the main layer because of its considerable thickness reaching up to 120 m. This layer is dolomitic and karstified, while the Upper Jurassic layer (Oxfordian–Kimmeridgian), which is marlacious and dolomitic, forms the top of this aquifer.

This aquifer is recharged by water flowing from Matmata Mountains, where important outcrops are made up of Jurassic limestone, as well as by local infiltration from the several rivers. Groundwater flow in the study area is towards the Sebkhat Om Jessar and the Mediterranean Sea (Fig. 3). The highest contour lines are at the west of study area and the lowest contour lines are close to the Om Jessar Sebkha.

Water of the Zeuss–Koutine aquifer is used unevenly by different economic sectors. However, drinking water supply remains the primary use. Anthropogenic activities in the study area rely mainly on agricultural and industrial activities such as construction (brick production, ceramics, etc.) and agro-food industry.

Methodology

Sample collection and analytical techniques

Between 1995 and 2005, groundwater quality monitoring in Zeuss–Koutine aquifer was carried out by collecting water samples from 13 wells capturing the different Zeuss–Koutine layers and representing a homogeneous spatial distribution on the whole aquifer. Figure 1 shows the locations of the selected wells. These wells are numbered from 1 to 13 and specific names are provided in Table 3. Water samples were obtained from one sampling campaign which corresponds to the summer season. This period was chosen because it coincides with the maximum water abstraction from the Zeuss–Koutine aquifer and minimum precipitation and recharge in the area.

General procedures for groundwater sampling, preservation, and chemical analyses were carried out according to the standard procedures described by Eaton et al. (1995). All of the water samples were pumped from wells continuously used. Water was only taken from boreholes that were pumped for a significant amount of time to get a representative sample. For deeper wells, a larger volume of stagnant groundwater existed and consequently needed to be drained away from the well area. This was done in order to avoid the sampling of stagnant annulus water that would be in the region of pump and pump systems. During removal of the casing volumes, water stabilization parameters (temperature and pH) are monitored during purging to determine when the stagnant water was replaced by formation water. When sampling, all water samples were filtered through a 0.45-μm Millipore cellulose type membrane. Each sample was collected in two new 500-ml polyethylene bottles. All sampling bottles were washed with de-ionized water and again with filtered sample water before filling it to capacity and then labeled accordingly. For each sample and to prevent precipitation, one bottle is acidified (until pH of samples reached 1) with 35% nitric acid for cation analysis (Na^+, K^+, Ca^{2+}, and Mg^{2+}), whereas the other is used for the determination of dissolved anions (Cl^-, SO_4^{2-}, and HCO_3^-). Prior to analysis in the laboratory, the samples were stored at a temperature below 4°C.

Temperature (T°) and hydrogen ion activity (pH) of groundwater were measured in the field in order to acquire representative values of ambient aquifer conditions. For the pH measurements, the electrode was calibrated with a reference buffer solution of pH 4 at each location.

Chemical analyses were performed in certified laboratories (ISO 17025) of the National Society of Drinking Water of the Ministry of Agriculture and Hydraulic Resources, using standard methods. Chloride was determined by standard $AgNO_3$

titration (Rodier 1996). Bicarbonates were determined by titration with H_2SO_4 (Rodier 1996). Sulfate (SO_4^{2-}) concentration was measured by the gravimeter method using $BaCl_2$, sodium (Na^+) and potassium (K^+) were measured by flame photometry, and calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions were determined titrimetrically using standard ethylenediaminetetraacetic acid (Rodier 1996). Total dissolved solids (TDS) were measured by evaporating a pre-filtered sample to dryness.

The accuracy of the chemical analyses was carefully inspected by repeated analyses (i.e., two analyses) of samples and standards and then calculating their percent charge balance errors (% CBE). The latter was calculated according to the following equation (Freeze and Cherry 1979):

$$\text{Percent (\%) charge balance error} = \left[\left(\sum zm_c - \sum m_a\right) / \left(\sum zm_c + \sum m_a\right)\right] \times 100$$

Where z is the absolute value of the ionic valence, m_c is the molality of cationic species, and m_a is the molality of the anionic species.

No samples in the database have a CBE greater than ±5% (which is an acceptable error for the purpose of this study).

The physico-chemical parameters (T°, pH, and salinity) and the concentrations of major ions were analyzed, and average concentrations during the period 1995–2005 are used for their interpretation. Spatial variation of groundwater salinity data was analyzed using a geographic information system.

Geochemical modeling

The geochemical modeling program PHREEQC (Parkhurst and Appelo 1999) was used to calculate aqueous speciation and the thermodynamic equilibrium conditions (mineral saturation indices) of waters with respect to the main mineral phases present in the aquifer which are indicators of the saturation state of a mineral with respect to a given water composition. The mineral reaction mode (dissolution or precipitation) is constrained by the saturation indices for each mineral (Deutsch 1997). The saturation indices (SI) describe quantitatively the deviation of water from equilibrium with respect to dissolved minerals and are expressed as SI = log (IAP/Kt), where IAP is the ion activity product and Kt is the equilibrium solubility constant. If the water is exactly saturated with the dissolved mineral, SI equals to zero. Positive values of SI indicate supersaturation and the mineral would tend to precipitate, and negative one indicates undersaturation and the mineral would tend to dissolve (Cidu et al. 2009; Subyani 2005).

Multivariate statistical analysis

Multivariate statistical analysis is widely used to identify the sources of solutes in a groundwater system (Zhang et al. 2009).

The application of various multivariate approaches such as cluster analysis (CA) and principal component analysis (PCA) offers a better understanding of water quality and allows comparison of different samples of waters (Yidana et al. 2008). The groundwater quality data (TDS, pH, temperature, Na^+, Cl^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, K^+, and HCO_3^-) were analyzed with a multivariate statistical method in order to test the reliability of the different processes that affect the mineralization of the groundwater aquifer system.

The combined use of PCA and CA enabled the classification of water samples into distinct groups based on their hydrochemical characteristics. These techniques will find groups and sets of variables with similar properties.

The parameters used in these multivariate statistical methods (PCA and CA) referred to different units of measurement. Therefore, their values should be standardized with the transformation function (Medina-Gomez and Herrera-Silveira 2003), $Z = (x - \mu)/\sigma$ (where Z is the standardized value, x indicates the original value of the measured parameter, μ is the mean of the variable, and σ is the standard deviation). Standardization tends to minimize the effect of the difference of variance in variables, eliminates the influence of different units of measurement, and renders the data dimensionless (El Yaouti et al. 2009).

Principal components analysis

In order to investigate the role of each variable and, at the same time, to simplify the original data structure, the first step of our analysis was the extraction of principal components from the original dataset. PCA allows defining eigenvectors of a variance–covariance or a correlation matrix from a dataset corresponding to a raw matrix of N rows of observations by P columns of variables (Davis 1986). In our study, PCA was applied to chemical data from the Zeuss–Koutine aquifer to extract the principal factors corresponding to the different processes that control water chemistry and sources of variation in the data. In fact, PCA reduces a large number of variables (measured physical parameters and major elements in water samples) to a small number of variables (Cloutier et al. 2008).

Cluster analysis

Cluster analysis is a data classification technique and one of the most powerful tools for analyzing water hydrogeochemical data (De Andrade et al. 2008). CA techniques allow the relationship investigation between the observations or the variables of a dataset, in order to recognize the existence of groups. The approach used in our study is based on hierarchical clustering. Besides, CA was used to split the standardized physico-chemical data into groups (clusters) based on similarities (or dissimilarities) so that each cluster represents a specific process in the aquifer system (Templ et al. 2008). There are two types of cluster analysis: R and Q modes. In the present study, Q-mode cluster analysis was performed on the water chemistry data to group the samples in terms of water quality.

The results of hierarchical clustering methods depend on the specific measure of similarity and the linking method (De Andrade et al. 2008). In our study, and in order to perform CA, an agglomerative hierarchical clustering was developed using a combination of Ward's linkage method as a clustering algorithm and Euclidean distances as a measure of similarity. The result of such analyses is a graph called dendrogram.

Software

The computer program ANDAD 6.00, developed by the Geo-Systems Center of Instituto Superior Tecnico, Portugal (CVRM 2000), and STATISTICA (StatSoft) software, were used to conduct several multivariate statistical analyses including CA and PCA.

Results and discussion

Chemical characteristics

A statistical summary of the physico-chemical and chemical data of all the investigated groundwater during the period 1995–2005 is presented in Table 1.

Table 1 Summary statistics of the hydrochemical variables for the entire dataset considered in the study

Parameters	Min	Max	Mean	Stand. dev	Guideline values WHO (2004)
pH	7.10	8.50	7.66	1.43	6.5–9.2
T (°C)	12.7	29.00	20.52	2.87	–
Ca^{2+} (mg l^{-1})	117.67	374.67	241.56	75.33	200
Mg^{2+} (mg l^{-1})	62.00	148.75	108.12	21.69	150
Na^{+} (mg l^{-1})	144.50	867.00	438.99	182.65	200
K^{+} (mg l^{-1})	8.00	29.00	15.09	5.19	200
HCO_3^- (mg l^{-1})	93.00	243.00	173.55	32.19	240
Cl^- (mg l^{-1})	209.25	1,653.00	744.03	381.17	250
SO_4^{2-} (mg l^{-1})	400.00	1,120.00	818.69	177.50	250
TDS (mg l^{-1})	1,235.00	4,368.00	2,709.13	854.30	1,000

TDS, total dissolved solids; WHO, World Health Organization

Groundwater temperatures vary from 12.70 to 29.0°C with mean and standard deviation values of 20.52 and 2.87°C, respectively. This parameter varied with sampling location and year of collection. The pH values are in the range 7.10–8.50 with a mean value of 7.66 and standard deviation of 1.43, indicating that the waters are generally neutral to slightly alkaline. These values were found to be in the permissible range of 6.5 to 8.5, and trend evolution shows minor variations during the period evaluated (1995–2005).

The chemical compositions of the groundwater samples were statistically analyzed and the results are given in Table 1. Among the cations, only the mean concentrations of Na^+ exceed guideline values set by the WHO. The sodium ion concentration (Na^+) in the groundwater samples range from 144.5 to 867.00 mg l^{-1} with a mean value of 438.99 mg l^{-1} and a standard deviation of 182.65 mg l^{-1} (Table 1). The recommended limit for sodium in natural water is 200 mg l^{-1} (WHO 2004). Five percent (5%) of the groundwater samples fall above this limit. Regarding the analyzed anions, only the bicarbonate concentrations (HCO_3^-) in all samples are lower than the WHO allowable bicarbonate concentration of 348 mg l^{-1}.

Figure 4 shows that Na^+ and SO_4^{2-} are the dominant cation and anion, respectively. Among the cations, the concentrations of Ca^{2+}, Mg^{2+}, Na^+, and K^+ ions ranged from 117 to 374, 62 to 148, 144 to 867, and 8 to 29 mg l^{-1} with a mean of 241, 108, 439, and 15 mg l^{-1}, respectively. Their concentrations represent on average 30%, 13%, 55%, and 2% of all the cations, respectively. The order of relative abundance of major cations in the groundwater of the Zeuss–Koutine aquifer is $Na^+ > Ca^{+2} > Mg^{2+} > K^+$. Among the anions, the concentrations of HCO_3^-, Cl^-, and SO_4^{2-} ions lie in between 93 and 243, 209 and 1,653, and 400 and 1,120 mg l^{-1} with a mean of 173, 744, and 818 mg l^{-1}, respectively. The order of their abundance is $SO_4^{2-} > Cl^- > HCO_3^-$, contributing on average, respectively, 47%, 44%, and 9% of the total anions.

Hydrochemical facies

The criteria for delineating the hydrochemical processes and defining groundwater types of hydrochemical facies used in this study are simple and straightforward. These criteria were derived by constructing Piper and Durov diagrams for major dissolved constituents.

Different water types can be defined depending on the composition of the water (i.e., the cation and anion concentrations). The Piper diagram in Fig. 5a constructed using AquaChem Scientific Software shows the relative concentrations of the different ions from individual water samples. Two main hydrochemical facies have been identified on the basis of major ion concentrations. The first is Ca–Na–SO_4–Cl in type (which corresponds to wells 1, 2, 8, 9, 10, 11, 12, and 13) and located in the southwest of the study area, which corresponds to the downstream part of the aquifer, whereas the second is Na–Ca–Cl–SO_4 in type (which corresponds to wells 3, 4, 5, 6, and 7). This water group dominated by anions Cl^- is often localized in the confined aquifers in the north and east central part of the Zeuss–Koutine aquifer. This is clearly demonstrated in the Durov diagrams (Fig. 5b) where SO_4^{2-}-type waters evolve into

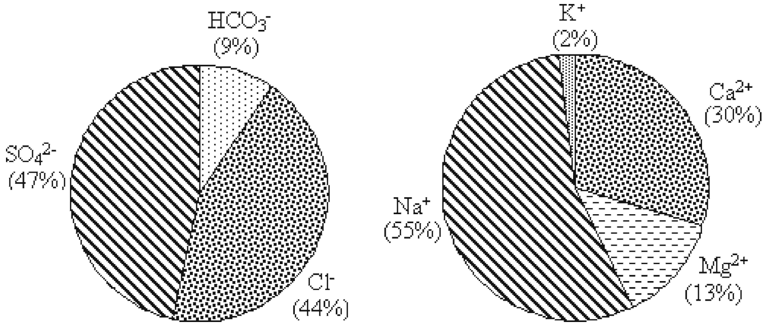


Fig. 4 Pie diagram of median values of major ions

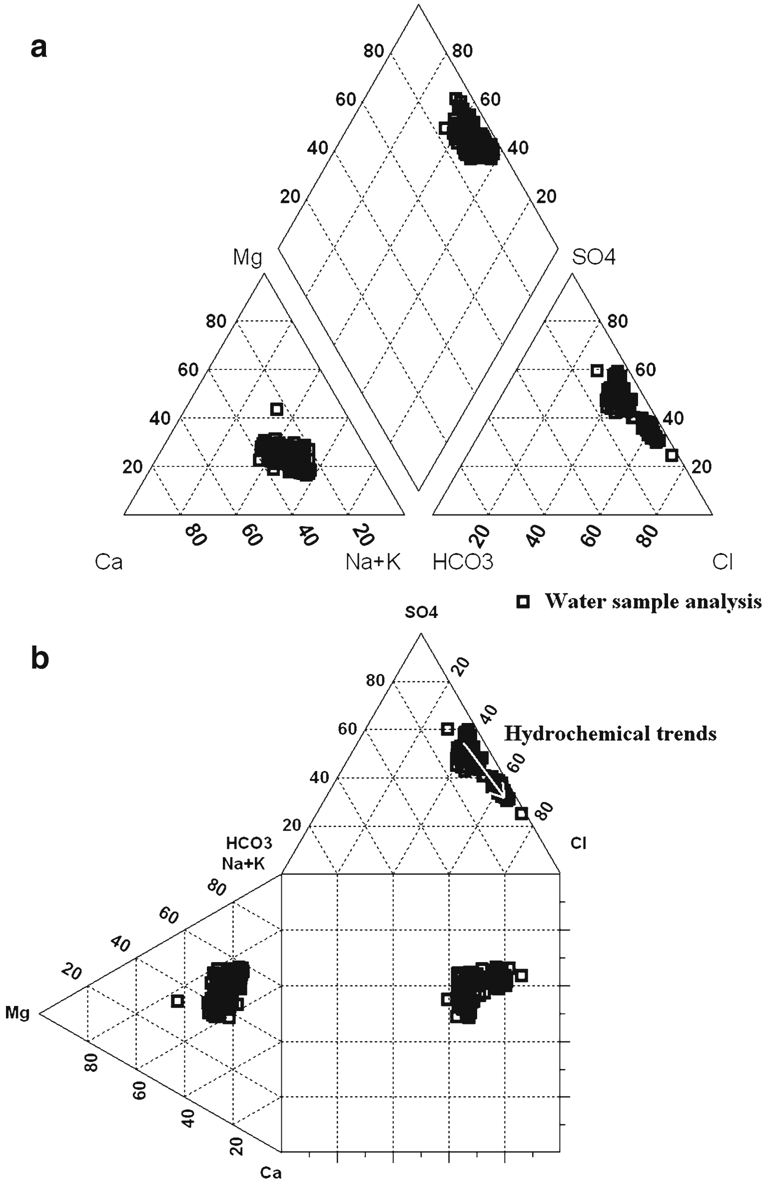


Fig. 5 **a** Piper plot of groundwater hydrochemical data (1995–2005) showing water facies. **b** Durov's diagrams demonstrating the evolution of a SO_4^{2-}-type water into Cl-type groundwater in the Zeuss–Koutine aquifer

Cl^- type. The ionic compositions of these groundwater samples show variable but very interesting systematic spatial variation of the chemical facies from southwest to northeast. The first type is characterized by low and moderate mineralization levels, while the second type groundwater shows relatively higher mineralization. In fact, the TDS contents of the two identified groups vary from 1,235 to 2,700 and 3,200 to 4,368 mg l^{-1} (Table 1) with a mean of 2,127 and 3,684 mg l^{-1}, respectively. These values are elevated compared to the guideline value of 1,000 mg l^{-1} set by the WHO (2004) which indicates that the groundwater is generally moderately saline or brackish. Brackish water has a TDS concentration in the range 1,000–10,000 mg l^{-1} (Freeze and Cherry 1979).

Spatial distribution maps of salinity from 1995 to 2005 show the same trend. A typical map is represented in Fig. 5. In general, a significant increase in the degree of water mineralization in the direction of flow is observed and the least mineralized water was found closest to the main

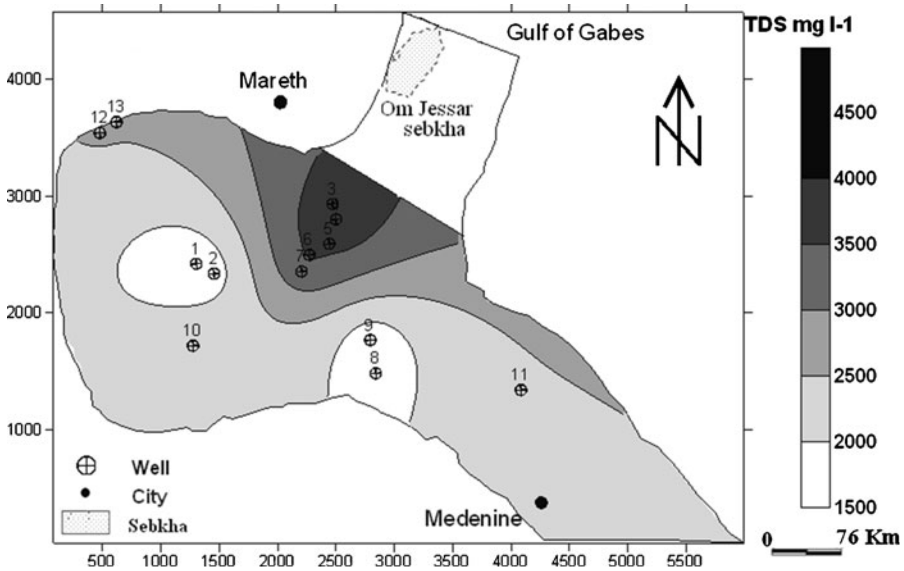


Fig. 6 Salinity iso-concentration map in Zeuss–Koutine aquifer (year 2005). Groundwater zones according to spatial distribution of TDS (mg l^{-1})

recharge area. In fact, the map (Fig. 6) shows that Ksar Chrarif region (wells 1 and 2) and Koutine region (wells 8 and 9) located in the upstream section of the aquifer (recharge zone) have the lowest salinity levels compared to downstream zones.

Correlation matrix

Compositional relations among dissolved species can reveal the origin of solutes and the process that generated the observed water compositions. The degree of a linear association between any two of the water quality parameters (Adhikary et al. 2009), as measured by the simple correlation coefficient (r), is presented in Fig. 7. The results show high correlations (>0.7) between some pairs of parameters.

Figure 7a shows the correlation matrix for the chemical variables of the groundwater samples. The concentration values of all elements correlate positively with higher similarity level, except HCO_3^-, which has a low correlation with all elements.

The Na^+–Cl^- relationship has often been used to identify the mechanisms for acquiring salinity in semi-arid regions (Magaritz et al. 1981; Dixon and Chiswell 1992; Sami 1992). As shown in Fig. 7, regarding to Na^+–Cl^- relationship, a high correlation ($r = 0.85$) was observed. The high Na^+ and Cl^- contents measured in the majority of samples may suggest the dissolution of chloride salts. Besides, high concentration of sodium may be attributed to base exchange and leaching of sodium salts such as halite during the movement of groundwater through sediments. A Na^+/Cl^- molar ratio greater than 1 is typically interpreted as reflecting Na^+ released from silicate weathering reactions (Meybeck 1987). Silicate dissolution can be a probable source for Na^+ in some groundwater samples (1, 9, 10, and 13). The Na^+/Cl^- ratio in most groundwater samples (70%) are less than 1 (average value = 0.96), indicating that Na^+ release from silicate weathering is not important in the studied area. On the other hand, the process of ion exchange is the predominant process for reduction of Na^+ in these groundwaters.

The relationship between Ca^{2+} and SO_4^{2-} concentrations is characterized by a relatively high correlation coefficient (0.78) and a SO_4^{2-}/Ca^{2+} ratio, in moles per liter, superior to 1. This indicates that calcium and sulfate are not involved in the same geochemical processes (Hounslow 1995). Actually, sulfates are mostly found in a dissolved form, whereas calcium can undergo a precipitation of calcite and/or a Ca/Na base exchange between clay minerals and water (Desbarats 2009).

The sources of Ca^{2+} and Mg^{2+} on groundwater can be determined from the (Ca^{2+} +

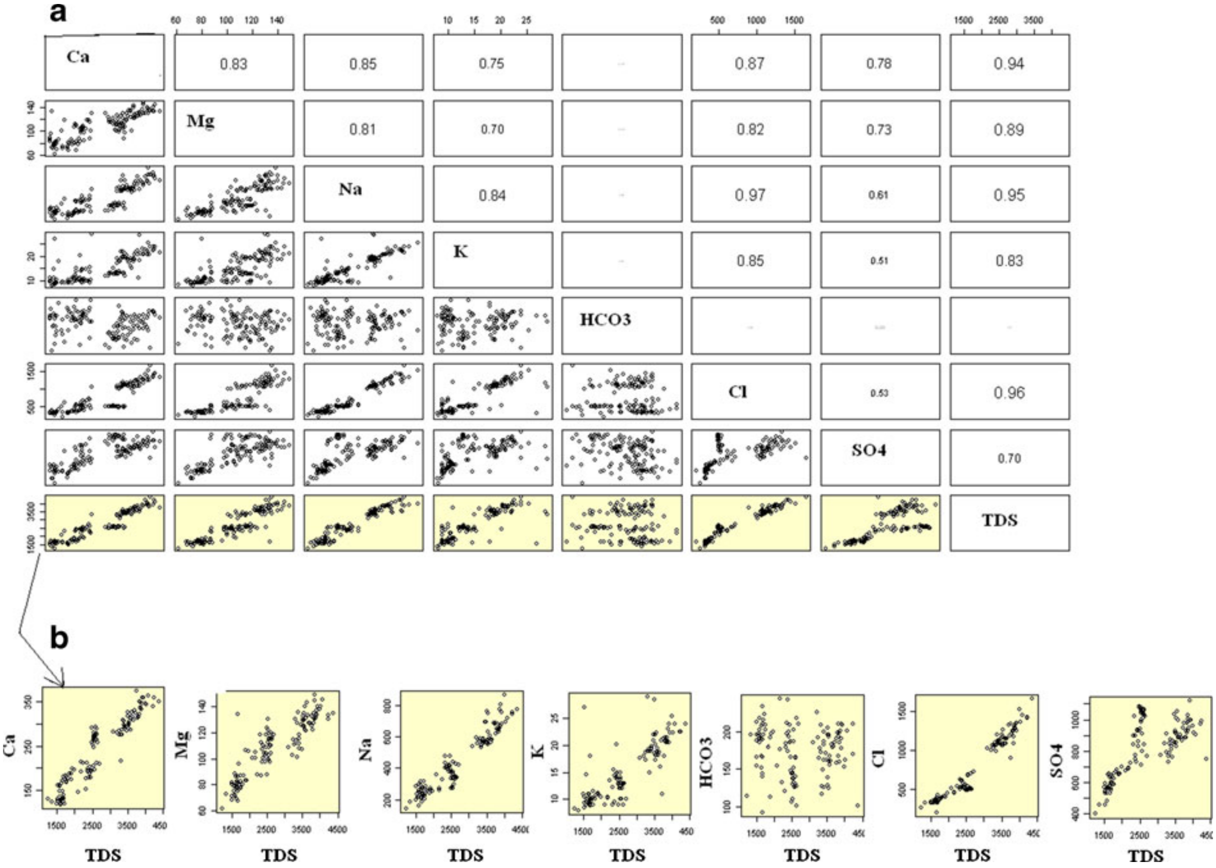


Fig. 7 Correlation matrix of the variable. *Yellow colors* indicate bivariate diagrams of major elements versus TDS values

Mg^{2+})/HCO_3^- ratio. If Mg^{2+} and Ca^{2+} only originate from the dissolution of carbonates in the aquifer materials, this ratio would be about 0.5 (Sami 1992). The low $Ca^{2+} + Mg^{2+}/HCO_3^-$ ratio (<0.5) could be the result of either $Ca^{2+} + Mg^{2+}$ depletion by cation exchange or HCO_3^- enrichment. However, high ratios cannot be attributed to HCO_3^- depletion; under the existing alkaline conditions, HCO_3^- does not form carbonic acid (H_2CO_3) (Spears 1986). In the present study, high ratios suggest that an excess of alkalinity in these waters is balanced by the alkalis Na^+ and K^+. The excess of $Ca^{2+} + Mg^{2+}$ over HCO_3^- reflects an extra source of Ca^{2+} and Mg^{2+} and is balanced by Cl^- and SO_4^{2-}.

The cation exchange between Ca^{2+} or Mg^{2+} and Na^+ may also explain the excess Na^+ concentration. Ca^{2+} and Mg^{2+} can exchange Na^+ sorbed on the exchangeable sites of the clay minerals, resulting in the decrease in Ca^{2+} and Mg^{2+} and the increase in Na^+ in groundwater.

The good correlation between SO_4^{2-} and Mg^{2+}($r = 0.73$) suggests that a part of the SO_4^{2-} and Mg^{2+} may also be derived by the weathering of an Mg^{2+} sulfate mineral. There is no relation between Ca^{2+} and HCO_3^- and correlation coefficient is not significant. This indicates that calcite may not be the source of Ca^{2+}.

Strong correlations exist among the major elements (Fig. 7b), Na^+, Ca^{2+}, Mg^{2+}, and Cl^-, and TDS ($r > 0.75$). These relationships clearly identify the main elements contributing to the groundwater salinity and their tendency to follow a similar trend. The salinization of the groundwater would be expected to result from the ionic concentrations increasing due to the effects of interactions between the groundwater and the geological formations.

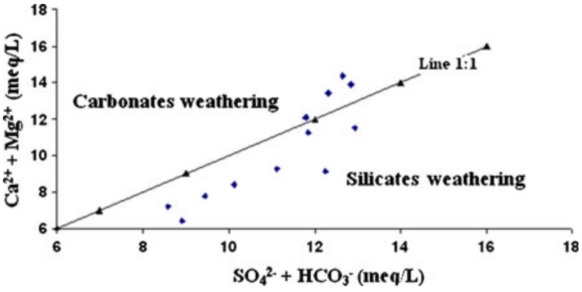


Fig. 8 Scatter plot of $Ca^{2+} + Mg^{2+}$ against $HCO_3^- + SO_4^{2-}$

To identify the processes of mineralization of groundwater, it is also interesting to make the (Ca^{2+} + Mg^{2+}) vs. (HCO_3^- + SO_4^{2-}) scatter diagram (Kumar et al. 2009). Data points all along or close to the 1:1 line are attributed to carbonate and sulfate mineral weathering. Those that fall above the 1:1 line resulted from the effects of the reverse ion exchange processes in the system. Data points that fall below the equiline are deemed to have also resulted from the dissolution of carbonates and sulfates. In Fig. 8, though, some of the points (four samples) fall above the 1:1 line, signifying the effects of cation exchange and silicate mineral weathering. About 0.69% of all the points fall around and below the equiline, indicating the contribution of carbonate and sulfate mineral dissolution, and cation exchange in the hydrochemistry.

Geochemical modeling

The processes of dissolution and precipitation are actively taking place within the groundwater system. SI describes quantitatively the deviation of water from equilibrium with respect to dissolved minerals. In Table 2, the SI for anhydrite, gypsum, halite, aragonite, calcite, and dolomite are shown.

Nearly all water samples were oversaturated with respect to aragonite, calcite, and dolomite, and undersaturated with respect to anhydrite, gypsum, and halite, suggesting that these carbonate mineral phases may have influenced the chemical composition of the groundwater of the study area. As saturation state indicates the direction of the process, thus, precipitation of aragonite, calcite, and dolomite and dissolution of anhydrite, gypsum, and halite are expected.

Table 2 Average saturation indices (S.I.) of anhydrite, gypsum, halite, aragonite, calcite and dolomite

Name	Number	Depth	SI (anhydrite)	SI (gypsum)	SI (halite)	SI (aragonite)	SI (calcite)	SI (dolomite)	Na/Cl
Ksar Cherif1	1	96.6	−1.08	−0.84	−5.80	0.12	0.27	0.53	1.20
Ksar Cherif 2	2	173.8	−1.00	−0.77	−5.68	0.17	0.32	0.58	0.99
Zeuss 1	3	344	−0.72	−0.49	−4.79	0.17	0.31	0.52	0.87
Zeuss 2	4	576.7	−0.73	−0.50	−4.68	0.21	0.35	0.59	0.81
Zeuss 3	5	207.3	−0.76	−0.52	−4.83	0.19	0.34	0.58	0.81
Zeuss 4	6	75	−0.78	−0.55	−4.83	0.22	0.36	0.63	0.85
Zeuss 5	7	318.5	−0.79	−0.56	−4.87	0.13	0.28	0.44	0.83
Koutine 2	8	219	−1.01	−0.77	−5.60	0.14	0.29	0.61	0.94
Koutine 3	9	148	−1.15	−0.92	−5.70	0.03	0.18	0.43	1.15
Henchir Titoun	10	200	−0.96	−0.73	−5.24	0.21	0.36	0.79	1.02
Hassi Malek	11	249	−0.89	−0.65	−5.32	0.14	0.29	0.58	0.99
Henchir Frej 1	12	300	−0.72	−0.48	−5.43	0.12	0.27	0.44	0.98
Henchir Frej 2	13	280	−0.71	−0.47	−5.43	0.04	0.19	0.26	1.03

Table 3 Loading for varimax rotated factor matrix of three factors explaining 80.42% of the total variance for groundwater system aquifer

Variable	Varifactors		
	1	2	3
T (°C)	−0.01	0.40	0.38
pH	−0.11	−0.04	**−0.90**
Ca^{2+}	**−0.95**	0.11	0.01
Mg^{2+}	**−0.91**	0.05	−0.04
Na^{+}	**−0.95**	−0.16	0.05
K^{+}	**−0.86**	−0.20	0.05
HCO$_3^-$	0.10	**−0.89**	0.18
Cl$^-$	**−0.95**	−0.17	0.03
SO$_4^{2-}$	**−0.76**	0.37	0.00
TDS	**−0.99**	−0.04	0.02
Eigenvalues	5.83	1.21	1.00
% total variance	58.31	12.11	10.00
% cumulative variance	58.31	70.42	80.42

All chemical parameters are in milligrams per liter. The bold values indicate absolute component loadings higher than 0.5, which are considered significant contributors to the variance in the hydrochemistry. Positive factor scores indicate waters most affected by the presence of the considered specific factor, and negative scores indicate those essentially unaffected

According to Hidalgo and Cruz-Sanjulian (2001), the oversaturation in calcite is related to incongruent dolomite dissolution which causes the precipitation of calcite. Once the system is saturated in calcite, the hydrochemical evolution is affected by the dissolution of gypsum, which will be the influencing factor in the process of dolomite dissolution (Jalali 2005). All of the groundwaters are oversaturated with respect to dolomite. Interaction between groundwater, which contains saturated calcite and dolomite and sufficient amounts of Ca^{2+}, with the gypsum layer would lead to the dissolution of gypsum (Feng and Han 2002).

Statistical analyses

Principal component analysis

To investigate the relationships between major elements in groundwaters, PCA was performed on a dataset of 13 samples and 10 chemico-physical elements (T°, pH, TDS, Na$^+$, Cl$^-$, Ca^{2+}, Mg^{2+}, SO$_4^{2-}$, K$^+$, and HCO$_3^-$). PCA was applied to the data to rank the main players in the hydrochemistry. Factor loadings were further calculated for each of the sample and used to determine the level of intensity of each of the factors controlling the hydrochemistry at each location. The PCA with varimax rotation resulted in three main components representing three sources of variation in the hydrochemistry of groundwater from the Zeuss–Koutine aquifer and explaining 70% of the variance in the hydrochemistry or information contained in the original dataset which is sufficient to give a good idea of the data structure. The eigenvalues and the percentage of the variance explained by each eigenvector are listed in Table 3.

The scores of variables onto the three principal component axes are plotted in Fig. 9, which enable the identification of several processes of water mineralization.

Factor 1 (F1) explains more than 58.31% of total variance and contains large loadings on temperature, Na$^+$, Cl$^-$, Ca^{2+}, Mg^{2+}, SO$_4^{2-}$, and

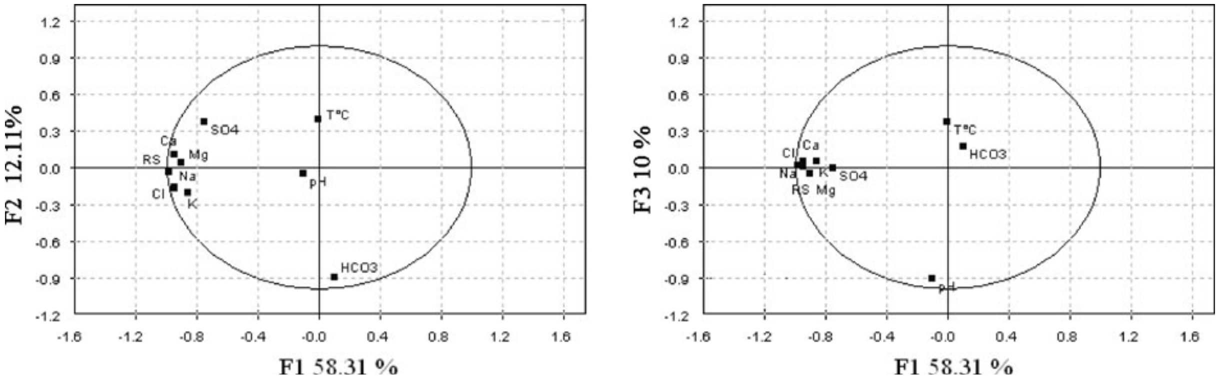


Fig. 9 Representation of the parameters in the first and second factorial plane

K^+. It represents the weathering of halite and evaporates minerals from the underlying geology. Factor 2 represents the weathering carbonate minerals and contributes to 12% of the total variance and is strongly associated with HCO_3^-, and to a lesser extent temperature. The pH is described by F3, accounting for a further 10% of the remaining variance.

Cluster analysis

The dendrogram of the *Q*-mode cluster analysis built on the wells shows three main groups of waters (Fig. 10).

The decision on the number of clusters to use in an hierarchical cluster analysis (HCA) is somewhat subjective and is based on the expert knowledge of the researcher on the subject matter being investigated. In this study, the differentiation was based on the knowledge of the geology and groundwater flow patterns in the area (Cloutier et al. 2008). These groups are:

Group 1: Made up of a total of eight water samples (wells 1, 2, 8, 9, 10, 11, 12, and 13), which have the lowest salinity levels. Based on the overall chemical composition, these waters are characterized by SO_4^{2-}–Cl^-–Ca^{2+}–Na^+ facies. This group is located in the upstream zone of the study area where the aquifer system seems to receive most of its meteoric recharge.

Group 2: It consists of eight water samples from Zeuss–Koutine aquifer. This group is characterized by Cl^-–Na^+ water types and by high salinity. This is located downstream of the study area. The most pronounced characteristic of this group is the increase in Na^+ and Cl^- contents.

Conclusion

Based on hydrochemical studies, the chemical composition of groundwater differs according to water types. Two types are identified. The hydrochemical types Ca–Na–SO_4–Cl and Na–Ca–Cl–SO_4 are characteristics of the studied area. The spatial variation of groundwater chemistry in the study site suggests that the hydrogeochemical compositions of groundwater have been mainly controlled by groundwater flow pattern that follows the topography of the study area. In general, a significant increase in the degree of water mineralization was observed in the direction of the water flow (southwest to northeast). The least mineralized water is found closest to the main recharge area. The water displays a chemical evolution from Ca–Na–SO_4–Cl in recharge area towards Na–Ca–Cl–SO_4 facies in the discharge area. The concentration of TDS in all groundwater samples is greater than 1,000 mg l^{-1}, indicating slightly saline or moderately saline water.

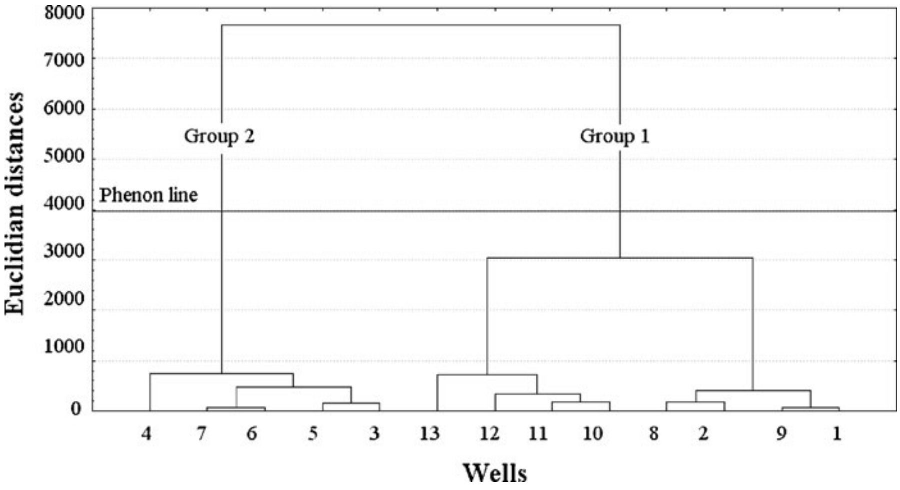


Fig. 10 Dendogram of *Q*-mode cluster analysis (Ward's linkage method and squared Euclidean distances)

The geochemical modeling study, established by calculation of the saturation indices of mineral phases, shows that all water samples were oversaturated with respect to aragonite, calcite, and dolomite, and undersaturated with respect to anhydrite, gypsum, and halite. Thus, dissolution of halite, gypsum, and anhydrite determines Cl^-, SO_4^{2-}, Na^+, Ca^{2+}, and Mg^{2+} contents in the groundwater. Other geochemical processes, such as cation exchange of Na^+ for Ca^{2+} and Mg^{2+} and leaching of sodium salts during the movement of groundwater through sediment, also contribute to the content of Na^+.

By comparing the analytical results with national and international (WHO) drinking water norms, we notice that water quality tends to deteriorate. In fact, water sampled in wells located in the northeast part of the aquifer corresponding to the discharge zone of the aquifer (wells 3, 4, 5 and 6) have concentrations exceeding the drinking water legislation norms and thus should be treated before human consumption. The conclusions from the current study as well as other available water quality data should be taken into account when developing strategies for safe drinking water supplies.

The results of the statistical analyses (PCA and CA) corroborate the geochemical methods and results and provide further information about the water quality of Zeuss–Koutine aquifer.

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