Hydrogeochemical Characteristics of Water Quality in Miocene Aquifer (South-Eastern Tunisia)

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Abstract: Groundwater quality in South-East of Tunisia has special significance and needs great attention of all concerned since it is the major alternate source of domestic, industrial and drinking water supply. Miocene aquifer, located in south-eastern Tunisia, has been used intensively as a primary source to meet the growing needs of the various sectors. Sampling surveys were undertaken in July 2004 from 18 wells. 18 variables (temperature, pH, Total Dissolved Solids (TDS), Na^+, Cl^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, K^+, HCO_3^-, Fe^{3+}, Mn^{2+}, Zn^{2+}, Al^{3+}, Pb^{2+}, Cr^{3+}, Cu^{2+} and F^-) of water samples were measured and analyzed. We applied conventional classification techniques, like Piper diagram, to evaluate geochemical processes. Because of the limitations of these methods, statistical analyses together with refined mapping tools (kriging methods) were used to identify mineralization distribution. The TDS measurements show a strong mineralization of the water in the east of the study area, notably in Jerba, where the TDS is about 8000 mg/L. besides, Results reveal that salinity and the major elements concentrations, with the exception bicarbonates, increase towards groundwater flow. The saline load of these waters is in first place controlled by chloride and sodium. The concentrations of trace elements such as Mn^{2+}, Zn^{2+}, Al^{3+}, Pb^{2+}, Fe^{3+}, Cu^{2+}, Cr^{3+} and F^- were low, under the maximum recommended level. Water chemistry is mainly dominated by dissolution/precipitation of minerals (calcite, dolomite, aragonite, anhydrite, gypsum, halite and fluoride). The application of PCA and CA has achieved a meaningful classification of wells waters samples based on spatial criteria. Results obtained from principal component analyses (PCA) indicate that the variables responsible for water quality composition are mainly related to soluble salts species (Na^+ and Cl^-). The results of the HCA showed three groups of water types. Samples from group 1and group 2 are mostly located in Southeastern areas. Samples from group 3 characterize waters from the aquifer system under confined conditions.

Key words: Hydrogeochemical Characteristics • Water Quality • Miocene Aquifer

INTRODUCTION

Southern Tunisia is located in the arid zone of North Africa where the permanent fresh water surface (i.e. reservoirs) is limited or absent because the hard climatic conditions. The very low average annual precipitation and the high rate of evaporation are the main cause of the scarcity of the natural water resources.

Since the 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, tourism, *etc.*) during the last decades. Growing population, agriculture expansion and urbanization augment its utilization, diminish availability and enhance vulnerability to contaminate the quality. Thus groundwater quality assessment needs more attention to cope with the increasing water demand in this arid zones and limited water resources. Therefore, water quality and its management have received more attention in developing countries where water is commonly of critical economical and social significance.

Water quality analysis is one of the most important aspects in groundwater studies. As groundwater moves along its path from recharge to discharge areas, its chemical composition is controlled and modified by many hydrogeochemical processes such as dissolution,

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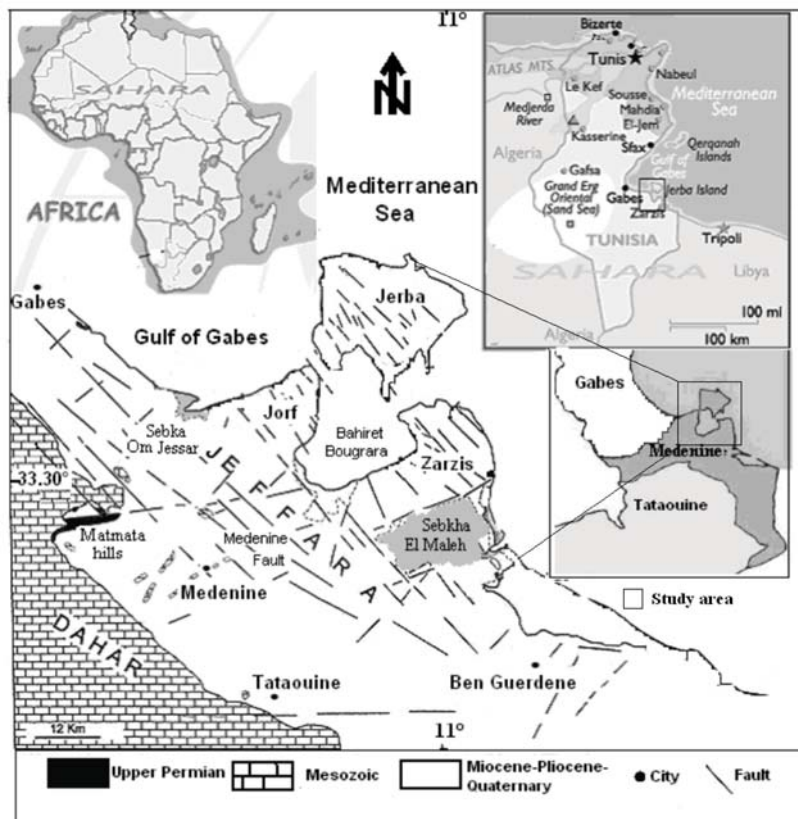National Engineers School of Tunis, Tel: +21670860396; Fax: +21670860396.

Fig. 1: Context of the study area: location and geology

leaching, precipitation, ion exchange, impact of agriculture and urbanization. The interaction of all factors leads to various water types and play a significant role in classifying and assessing water quality depending on the geology and chemical characteristics of the aquifer. Knowledge of geochemical evolution of groundwater in these arid regions could lead to improved understanding of hydrogechemical systems in such areas, leading to sustainable development of water resources and effective management of groundwater resource.

On the other hand, the study area is relatively vulnerable to the contamination by seawater intrusion since the Miocene aquifer was located close the sea shore (*i.e.* coastal aquifer). In fact, heavy pumping and excessive use of groundwater can cause artificial seawater intrusion which becomes unsuitable for drinking and agricultural activities. Therefore, to prevent seawater intrusion and to cope with its consequent problems, it is necessary to examine closely the hydrogeochemical characteristics of groundwater in the Miocene aquifer. The problem of seawater intrusion is very common in many parts of the world in which many of the ground waters in the coastal aquifer are suffering from seawater

intrusion by over-abstraction. This problem has been described in many Mediterranean coastal aquifers: such as in Spain [1, 2], in Morocco [3], in Algeria [4] in Tunisia [5, 6], in Libya [7], in Greece [8, 9], in Italy [10, 11] and in France [12].

Miocene aquifer is one of the most important aquifer in southern Tunisia. Therefore the objective of this study was to better identify the processes controlling the geochemical evolution of groundwater of this aquifer by using two well-proven multivariate methods to analyze the geochemical data, hierarchical cluster analysis (HCA) and principal components analysis (PCA). Finally, as an aid to management and future development of groundwater resources in the region, these approaches were also applied to divide the territory in areas with distinct groundwater quality.

Study Area: The investigation area of the present work is located mainly in the Southeast part of the Jeffara plain that corresponds to one of the most important aquifers of southern Tunisia. It is limited to the southwest by Matmata hills and Dahar plateau (Fig. 1). The Mediterranean Sea forms the eastern limit. The southern limit is constituted by Tataouine city.
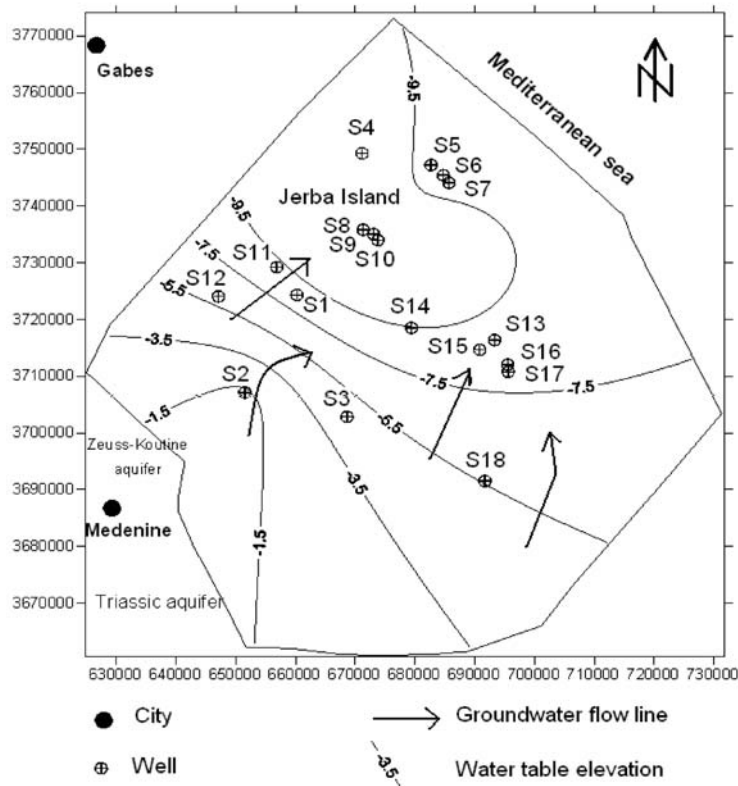
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Fig. 2: Piezometric head (in meters above mean sea level) contour maps in the Miocene aquifer and the sample locations

Following the topography, two different climate environments are found: a coastal portion, with marine influence and the mountain part, which is semi-continental.

The rainfall is characterized by high irregularity (both in time and space) and torrentially. The average annual precipitation is around 200 mm. The mean annual temperature is 20°C with a minimum of 10°C and a maximum of 40°C. Active dominant winds are those from the coast (NE), but sirocco is also reported. The potential evapotranspiration (ETP) is very high. For example, in Medenine, it reaches 1321 mm [13].

The climatic water balance in this region is almost negative around the year [14]. The simplified geological map of southern Tunisia shows two principal geological provinces [15-17].

- The "Jeffara Basin" was filled up by a thick Neogene sequence. It represents a collapsed block that extends eastward into Libya and the Pelagian Basin and was formed during the late Cretaceous and Cenozoic by extensional faulting, along NW-SE to NNW-SSE direction of the 'South Tunisia Fault' or "Medenine Fault'.

- The Dahar Plateau, which separates the Jeffara lowland in the East from the Sahara Platform in the West. This mountain range consists of N-S oriented escarpments where lower Jurassic to Middle Cretaceous strata is exposed.

The geological formations consist 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. In between, appear strata of different ages, which are generally declining northward [18].

In the region of Jorf-Jerba-Zarzis, the upper of 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 aquifer is overlain by an impermeable layer of a thickness of several hundred meters.

The general flow runs from the South-West to the North-East, converges to Mediterranean Sea (Fig.2). The average annual volume of groundwater pumped from the aquifer has been 502 l/s [19]. This aquifer is recharged by water flowing from the Triassic aquifer, the Jurassic aquifer and the south of Gabes aquifer [20].

The water of this aquifer is used unevenly by different economic sectors. Anthropogenic activities in this region rely mainly on agricultural and tourism.

Potential resources are estimated to 720 l/s. The withdrawal rate increased from 330 l/s in 1994 to 500 l/s in 2005 [19]. The piezometric data over the period of 1989-2005, show an average decline of 1.10 m/year [19]. This decrease is due to the decline of rainfall and is linked to the intensive demand for water supply for domestic, touristic and agriculture activities.

MATERIALS AND METHODS

Sample Collection and Analytical Techniques: A total of 18 groundwater samples were collected from boreholes ranging in depth from X to Y m in summer 2004 for the purpose of this investigation. The geographical location of the sampling sites is shown in Fig. 1.

Field measurements of Temperature (T) and pH were determined at all sampling sites in order to acquire representative values of ambient aquifer conditions. These variables were measured using a digital meters. The pH-meter was calibrated against a standard solution of 3 mol KCl before use.

The sample preservation and analyzing techniques were in accordance with the Groundwater samples in the deep aquifer were collected from wells with depths of 50-240 m.

Protocol for samples collection and preservation was taken using the 19ᵗʰ edition of the Standard Methods of APHA [21]. The chemical analyses were performed in certified laboratories (ISO 17025) of SONEDE of Ministry of agriculture and hydraulic resources, using standard methods.

All of the water samples were pumped from wells continuously used. Water was only taken from boreholes that were pumping for a significant amount of time (more than 10 min) to get a representative sample. All water samples were filtered through a 0.45-ìm membrane filter immediately after sampling. The samples were collected in two new 500 ml polyethylene bottles. 35% nitric acid

(HNO_3) was added to one of these polyethylene bottles until pH of samples reached 2. This bottle was dedicated to analysis of major cation and trace element, whereas the other is used for the determination of dissolved anions (Cl^-, SO_4^-, HCO_3^- and F^-). All bottles had been rinsed three or four times with deionised water and again with filtered sample water before filling it to capacity and then labelled accordingly. Prior to analysis in the laboratory, the samples were stored at a temperature below 4°C.

Analyses of groundwater samples were carried out using the standard methods for water analyses as suggested by [22] (Table 1).

The accuracy of the chemical analyses was carefully inspected by repeated analyses of samples and standards and then calculating their percent charge balance errors (% CBE). The latter was calculated according to the following equation [23]. Percent (%) Charge Balance Error= [(• z m_c - • m_a)/(• z m_c + • m_a)]x100. 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. Generally, the ion-balance error does not exceed ± 6%.

Statistical Treatment of the Data: The first step consists of standardization (mean, $Xm = 0$ and standard deviation $\sigma = 1$) of the raw data. The standardized data are obtained by subtracting the mean of the distribution from each data and dividing by the standard deviation of the distribution. This standardization is given by the formula: $Zi = (Xi-Xm)/\sigma$, where Zi is the i th value of the standardized variable Z, Xi is the concentration value of variable i. 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 [24, 25].

Multivariate Statistical Analysis: The multivariate statistical analysis is a quantitative and independent approach of groundwater classification allowing the grouping of groundwater samples and the making of correlations between chemical parameters and

Table 1: Methods used for major ion analysis of groundwater samples

Parameters	Methods
TDS	Evaporating a prefiltered sample to dryness
Cl	Mohr method using $AgNO_3$
Ca and Mg	Titration using EDTA
Na and K	Atomic emission spectrophotometry.
HCO_3	Potentiometric titration method
F	Colorometric
Metal Elements	Atomic absorption spectrometry

ground-water samples. In this study, two multivariate methods were applied using the computer program ANDAD 6.00 (Geo-Systems Center of Institute Superior Tecnico, Portugal; [26] and Statistica®, version 5.1 (Statsoft Tulsa, Oklahoma, USA): the hierarchical cluster analysis (HCA) and the principal components analysis (PCA). The description of HCA and PCA techniques and the methodology used for their application, in hydrogeochemistry, are detailed in [27]. However, these techniques will be briefly described in this paper.

Hierarchical Cluster Analysis (HCA): HCA is used to classify groundwaters into specific groups based on the Euclidean distance between the different hydrochemical variables. This classification may be interpreted Such that each cluster represents a specific process in the system which led to understand geochemical evolution for a given aquifer(s) system. Thus, this method groups samples into distinct populations (clusters) that may be significant in the geologic/hydrologic context, as well as from a statistical point of view. Data was analyzed in Q-mode in order to get similarity information between cases. The similarity coefficient used was the simple distance defined in Euclidean distance for similarity measurement [28] and the clustering was performed by the Ward's method for linkage [29]. This mode produces the most distinctive groups where each member within the group is more similar to its fellow members than to any member outside the group [30].

The Principal Components Analysis (PCA): As a multivariate data analytic technique, PCA reduces a large number of variables (measured physical parameters, major anions and cations in water samples) to a small number of variables which are the principal components [30]. In fact, PCA reduces a large number of variables (measured physical parameters, major and minor elements in water samples) to a small number of variables [31]. Besides, PCA combines two or more correlated variables into one variable. This approach has been used to extract related variables and infer the processes that control water chemistry [32,33]. Principal components analysis (PCA) allows defining eigen vectors of a variance-covariance or a correlation matrix from a data set corresponding to a raw matrix of N rows of observations by P columns of variables [27]. In our study, PCA was applied to chemical data to extract the principal factors corresponding to the different processes that control water chemistry and sources of variation in the data.

Geochemical Modelling: Geochemical modeling is a powerful technique for characterising geochemical phenomena and predicting their evolution in time as well as in space when coupled with flow modeling. The geochemical modeling software PHREEQC [34] was used to calculate aqueous speciation and the thermodynamic equilibrium conditions of waters with respect to the main mineral phases present in the aquifer. The mineral reaction mode (dissolution or precipitation) is constrained by the saturation indices for each mineral [35]. The saturation indices (SI) describe quantitatively the deviation of water from equilibrium with respect to dissolved minerals and are expressed as S.I. = Log (IAP/Kt), where IAP is the ion activity product and Kt is the equilibrium solubility constant. If the solution is in equilibrium with a mineral, the S.I. = 0. Saturation indices greater than zero indicate supersaturation and the mineral would tend to precipitate; less than zero, they indicate undersaturation and the mineral would tend to dissolve [36, 37].

RESULTS AND DISCUSSION

Groundwater Chemistry: Understanding the quality of groundwater is as important as its quality because it is the main factor determining its suitability for drinking, domestic, agricultural, industrial and touristic purposes. The analytical results of physical and chemical parameters of groundwater were compared with the standard guideline values as recommended by the World Health Organisation [38] for drinking and public health purposes.

Groundwater temperatures vary from 15.3°C to 34.6°C with median, mean and standard deviation values of 29.8°C, 27.69°C and 5.01°C, respectively. The small range of values shows the uniformity of groundwater temperatures within the Miocene aquifer. The pH values of groundwater range from 6.50 to 7.94 which show that the groundwater samples of Miocene aquifer are neutral. Their pH values are very homogeneous and present a narrow range of variation (between 6.5 and 7.94). According to the WHO, the range of desirable pH values of water prescribed for drinking purposes is 6.5 - 9.2 [38]. There are no water samples with pH values outside of the desirable ranges. Physical and chemical parameters including statistical measures, such as minimum, maximum, median, the 25th and 75th percentiles, are reported in Figure 3 for July 2004. The abundance of the major ions in groundwater is in the following order: $Na^+ > Ca^{2+} > Mg^{2+} > K^+ = Cl > SO_4^{2-} > HCO_3^-$
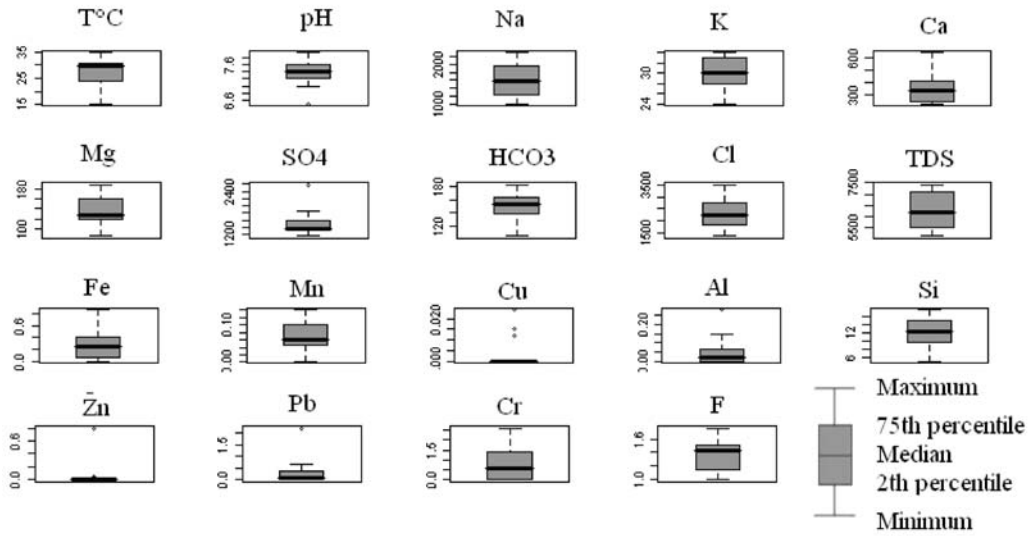
Fig. 3: Boxplots of temperature, pH and concentrations (mg/l) of major and minor elements in groundwater samples from Miocene aquifer

In all the samples, the mean concentrations of cations, such as Na^+, Ca^{2+}, SO_4^{2-}, Mg^{2+}, are above the maximum acceptable level (1538, 349, 1492 and 133 mg/l, respectively) for dinking waters [38]. Hardness of water depends mainly upon the amounts of divalent metallic cations, of which Ca^{2+} and Mg^{2+} are the more abundant in groundwater. The hardness values in water samples range from 328 to 828.

Potassium concentration in groundwater ranges from 24 to 34 mg l/1. All groundwater samples have lower K^+ content than the acceptable limits (200 mg/1) for drinking water [38]. The contribution of K^+ to the groundwater in these samples is modest (see Table 1). The low levels of K^+ in natural waters are a consequence of its tendency to be fixed by clay minerals and to participate in the formation of secondary minerals [39].

To ascertain the suitability of groundwater for any purposes, it is essential to classify the groundwater depending upon their hydrochemical properties based on their salinity [40] Groundwater salinity, represented by the TDS values, shows a range of variation from 5136 mg/l to almost 7418 mg/l. These values are above the maximum permissible limit (1000 mg/l) of the WHO's drinking water guideline [38]. Thus the groundwater of the Miocene aquifer is brackish-salt water category, as all TDS concentrations are greater than 1000 mg/l [40].

Figure 4 illustrates the spatial distribution of TDS in the groundwater of the Miocene aquifer for July 2004. The TDS zonation map shows that 2/3 of the basin is above 6000 mg/l of TDS, indicating high content of soluble salts in groundwater.

The trace elements concentrations have a few extreme values. The concentrations of Fe^{3+}, Mn^{2+}, Zn^{2+}, Al^{3+}, Pb^{2+}, Cu^{2+} and Cr^{3+} were lower than the maximum permissible level prescribed by the World Health Organization (WHO) standards set for drinking water. The observed variations are not explained by concurrent variations in TDS.

Fluoride is one of the main trace elements in groundwater, which generally occurs as a natural constituent. The concentration of fluoride in groundwater of the Miocene aquifer varies between 1.01 mg/l and 1.74 mg/l during July 2004 with an average value of 1.38 mg/l and median of 1.48. ¾ of the groundwater samples have lower fluoride content than the acceptable limits (1.5 mg l/1) for drinking water [38].

The formation of Na-Ca-Cl, Na-Ca-SO4-Cl and Na-Cl-SO4 waters is a result of progressive salinisation of the waters. Salinisation, because of long residence times causes the formation of Na-Ca-Cl, Na-Ca-SO4-Cl and Na-Cl-SO4 waters types of the aquifer and is an area of preferential recharge.

In the Miocene aquifer, is highly saline (7418 mg/l). The causes of this salinization are linked to geological, hydrogeological and geochemical contexts of the aquifer and other phenomena, such as ionic exchange and dissolution of gypsum indicated by high sulfate concentrations and the origin of water recharge.

The salinity of the aquifer increases in the direction of groundwater movement toward the north-northeast. Generally, salinity varies with specific surface area of the aquifer materials, solubility of minerals and contact time [40]. Values tend to be highest where movement of
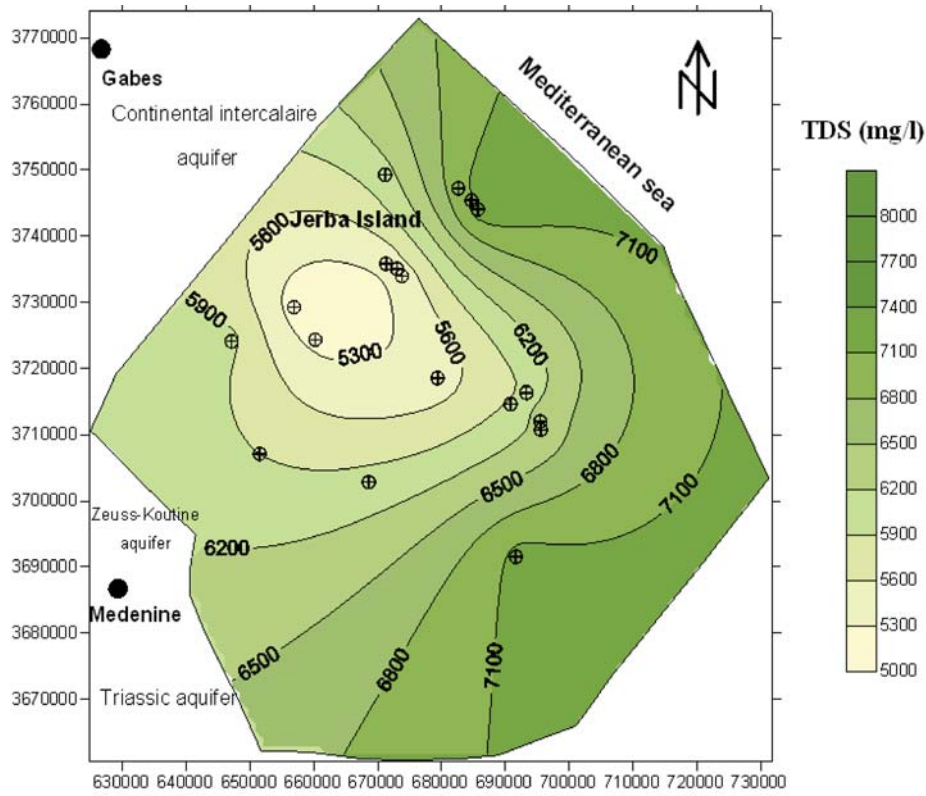
Fig. 4: Areal distribution of the TDS of the study area (mg/l)

groundwater is at its least, hence salinity usually increases with depth/time and recharge/discharge area relationships. Water from recharge areas (S13) is usually relatively fresh while in discharge areas (Jerba Island) it is often saline.

Correlation coefficient is a commonly used as measure to establish the relationship between two variables. It is simply a measure to exhibit how well one variable predicts the other [39]. Since the concentrations of the trace elements are extremely low compared to those of the major ions, they were not included in the correlation coefficient. The correlation matrix of the 12 variables analyzed (Table 1) allows us to distinguish several relevant hydrochemical relationships (indicated by underlined values):

TDS show good positive correlation with Na^+ and Cl^-. Mg^{2+} also exhibit high positive correlation with SO_4^{2-} and Ca ions. Furthermore, SO_4^{2-}, Ca^{2+} and HCO_3^- ions also show negative correlation. pH exhibit with most of the variables no significant correlation with any one of the variables in the matrixes.

Temperature has a weak correlation with all variables, but a negative correlation with SO_4 and K occurs as the lowest values of pH are related to groundwater samples.

The Na^+-Cl^- relationship has often been used to identify the mechanisms for acquiring salinity and saline intrusions in semi-arid regions [39]. The high Na^+ and Cl^- contents detected in almost all samples may suggest the dissolution of chloride salts. The dissolution of halite in water release equal concentrations of sodium and chloride into the solution.

Figure 5A shows the value of Cl^- as a function of Na^+ in the groundwater samples and there is a strong correlation (r = 0.95) between them. Since the correlation coefficient between Na^+ and Cl^- is positively high, it can be deduced that for most of the groundwater samples Na^+ and Cl^- originate from a common source. The plot of sodium against chloride concentration (Fig.6A) shows that some of the points fall close to the 1:1 line suggesting that these wells derive their salinity mainly from the dissolution of halite, since groundwater derived from halite dissolution would have Na^+/Cl^- ratio of approximately equal to 1 [40]. However some others points in Fig. 6A deviate from the expected 1:1 trend line, indicating that some of the Na^+ to be derived from other processes.

A Na^+/Cl^- molar ratio greater than 1 is typically interpreted as reflecting Na^+ released from silicate
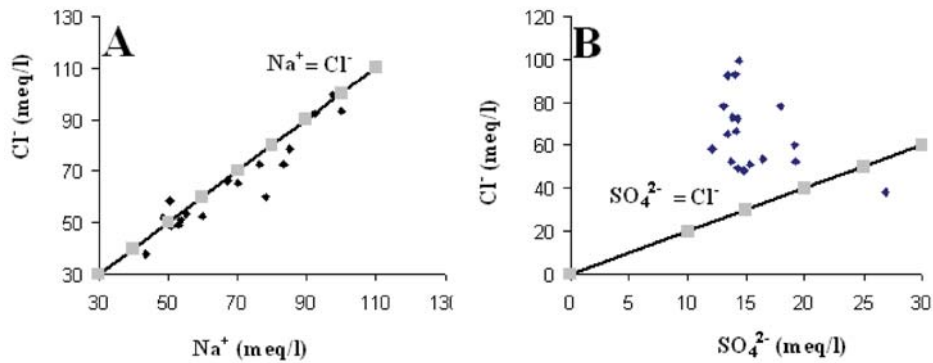
Fig. 5: Scatter diagrams of Cl⁻ *vs* Na⁺ (A) and Cl⁻ *vs* SO₄⁻ (B) for groundwater from the Miocene aquifer
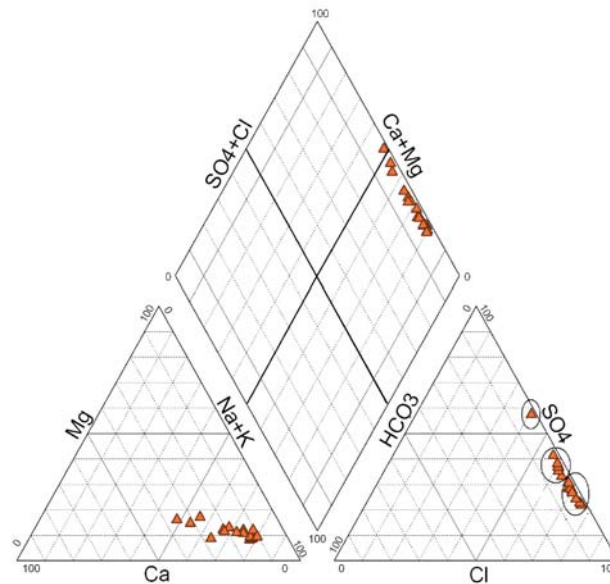

Fig. 6: Piper diagram of groundwater samples from the Miocene aquifer

weathering reactions [40]. The Na⁺/Cl⁻ molar ratio in most groundwaters samples of the study area (83%) is more than 1 (average value = 1.1), indicating that Silicate dissolution can be a probable source for Na⁺ in groundwater of the Miocene aquifer and thus Na⁺ release from silicate weathering is important in this aquifer.

The relationship between sulphate and chloride concentrations is given in Fig. 5B. It is observed that there is an excess of Cl⁻ over SO_4^{2-}. [38] reported that, the loss of SO_4^{2-} might be related to precipitation of gypsum, but the water samples are highly under saturated with respect to gypsum. This suggests that contribution of ions is proportionally higher from halite than the anhydrite. [39] relate this anomaly to the wetting and drying mechanism in arid climate.

The cation exchange between Ca^{2+} or Mg^{2+} and Na⁺ may also explain the excess Na⁺ concentration

(Stimson *et al*. 2001). The samples which have values of Na⁺/Cl⁻ ratio above 1 also show a deficit in Ca^{2+} + Mg^{2+} and this is consistent with a Ca^{2+}-Na⁺ cation exchange process which leads to a softening of the water [40]. Calcium and Mg^{2+} can exchange Na⁺ sorbed on the exchangeable sites of the clay minerals, resulting in the decrease of Ca^{2+} and Mg^{2+} and the increase of Na⁺ in groundwaters.

Hydrochemical Facies: Figure 6 represents a Piper diagram representation of the chemical analysis for the 18 groundwater samples conducted in 2004. The results show that the water facies are dominantly Na-Cl-SO4, Na-Ca-Cl-SO4 with one water sample exhibiting Na-Ca-SO4-Cl facies. In the Miocene aquifer, the water type gradually changes from Na-Cl-SO4 to the Na-Ca-SO_4-Cl along the flow lines *i.e.* from west to east of the study area. The Na-Cl-SO4 in type is more influenced
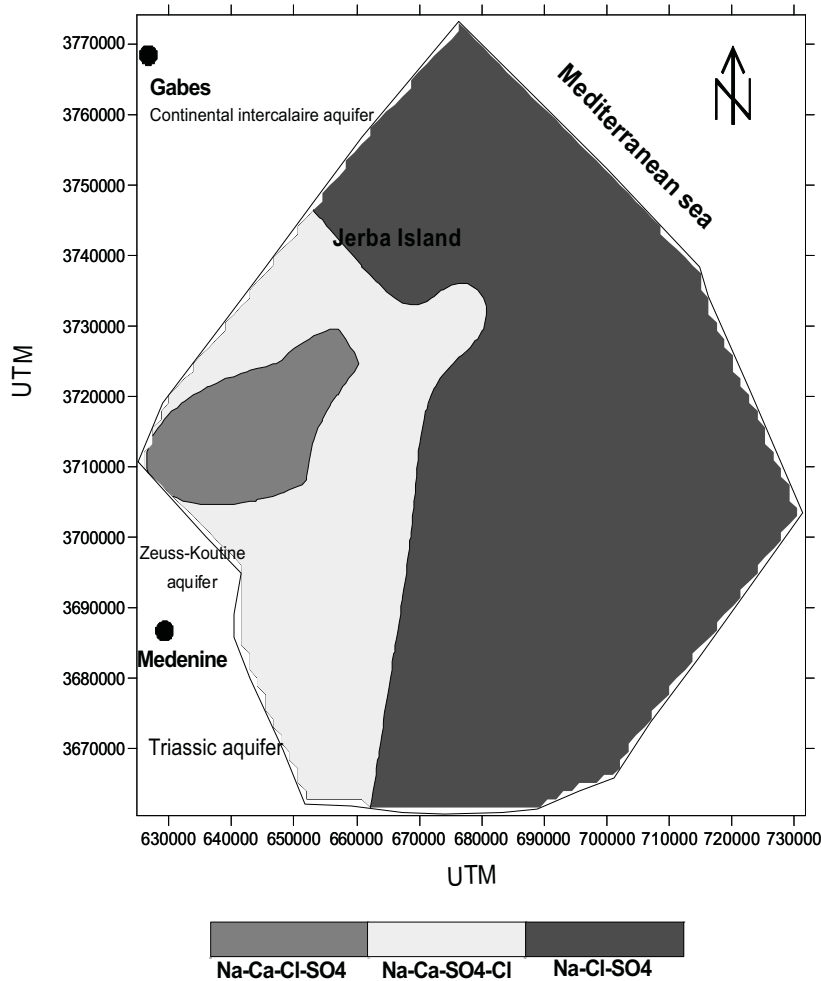
Fig. 7: Spatial distribution of the types of waters

by the chemistry of the rocks with which the waters come into contact. The Na-Ca-SO$_4$-Cl in type which corresponds to the wells S3 occurs mainly in the centre of the study area (Fig. 7). The composition of this type probably evolved from the interaction of recharging more fresh waters (average TDS =3000 mg/l) from Trias and Zeus Koutine aquifers as demonstrated in an earlier study [27]. The Miocene aquifer was fed by Trias aquifer and Zeuss Koutine aquifer and thus increases the mixture of fresh and salt water which lead to reduce salinization.

Furthermore, the observed heterogeneity in Ca^{2+} and Na$^+$ concentrations for these groundwater samples may reflect local mineralogical changes in the groundwater reservoir and/or variations in the weathering rate.

Geochemical Modeling: Interactions between groundwater and surrounding host rocks are considered to be the main processes which control the observed

chemical characteristics of groundwater in the Miocene aquifer. Evaluation of such processes requires the characterisation of the rocks mineral's in which water is found and the identification of chemical reactions responsible for the geochemical evolution of groundwater. Saturation index (SI) describes quantitatively the deviation of water from equilibrium with respect to dissolved minerals. Calculated saturation indices of Halite, gypsum and anhydrite, calcite, aragonite and dolomite are presented in figure 8.

As shown in figure 8, all water samples were under saturated with respect to halite, gypsum and anhydrite suggesting that these gypsum mineral phases may have influenced the chemical composition of the study area. The calculated values of SI for the calcite, dolomite and aragonite of the groundwater samples range from - 0.67 to 0.76, -1.31 to 1.37 and -0.81 to 0.63, with average values of 0.19, 0.34 and 0.05, respectively.
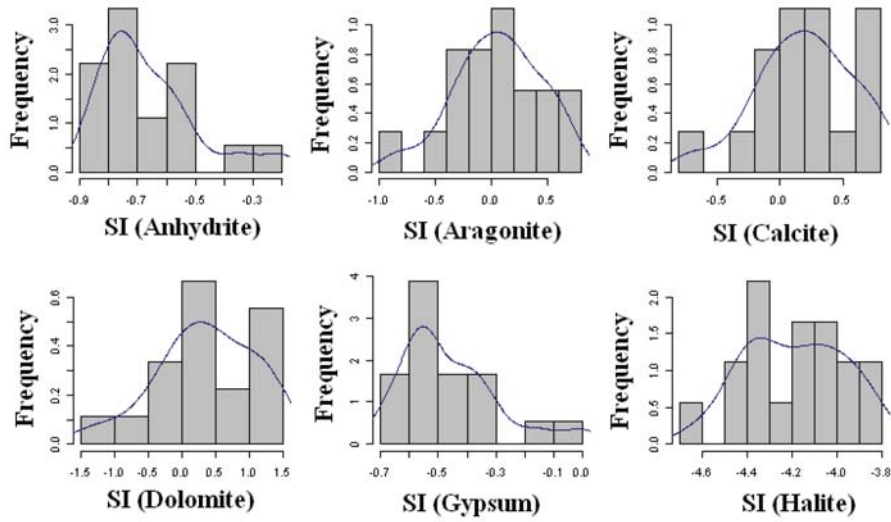
Fig. 8: Histograms showing saturations indices of several minerals

Table 2: Variance explained by the first seven principal components.

	T°	pH	Na	K	Ca	Mg	SO₄	HCO₃	Cl	TDS
T°	1									
pH	0.14	1.00								
Na	0.05	-0.07	1.00							
K	-0.10	-0.16	0.53	1.00						
Ca	0.14	0.27	-0.53	-0.24	1.00					
Mg	0.01	-0.07	-0.11	0.09	0.59	1.00				
SO₄	-0.18	0.19	-0.36	-0.15	0.62	0.35	1.00			
HCO₃	0.10	-0.15	0.36	0.26	-0.69	-0.22	-0.84	1.00		
Cl	0.14	-0.10	0.95	0.56	-0.40	-0.01	-0.46	0.37	1.00	
TDS	0.17	-0.08	0.86	0.54	-0.17	0.21	-0.15	0.14	0.86	1.00

Table 3: Presents the principal component loadings for these three components, as well as their respective explained variance.

Component	Eigen value	% total variance	%cumul. variance
1	4.03	40.27	40.27
2	2.09	20.90	61.17
3	1.25	12.52	73.69
4	1.00	10.04	83.73
5	0.70	6.97	90.70
6	0.51	5.14	95.85
7	0.25	2.51	98.36

Table 3: Principal Component loadings and explained variance for the seven components with Varimax normalized rotation

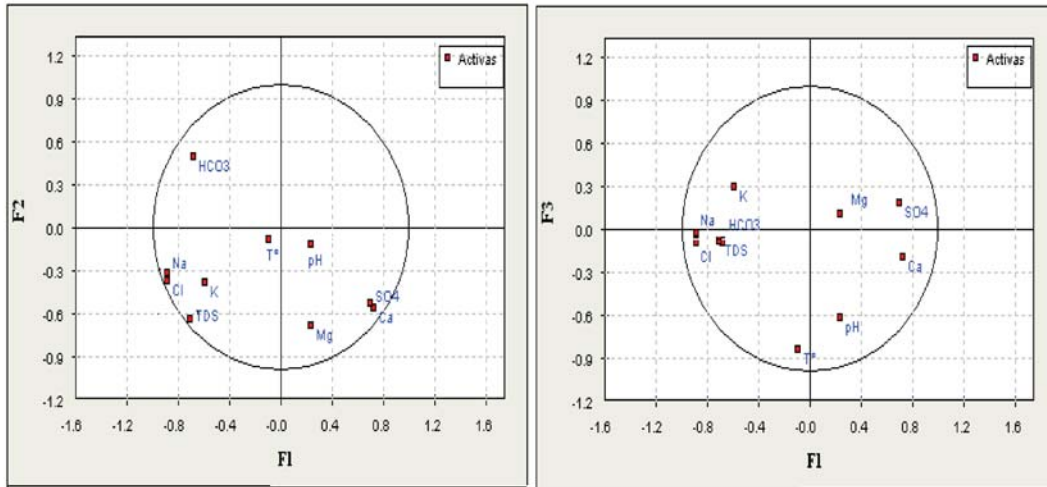|	1	2	3	4	5	6	7
T°	-0.10	-0.08	-0.83	0.38	0.26	-0.27	0.11
pH	0.23	-0.11	-0.61	-0.59	-0.46	0.05	0.04
Na	-0.89	-0.31	-0.03	-0.23	0.12	0.15	0.06
K	-0.60	-0.38	0.30	-0.04	-0.29	-0.57	-0.03
Ca	0.72	-0.55	-0.19	0.17	-0.10	-0.02	-0.28
Mg	0.23	-0.68	0.11	0.52	-0.34	0.23	0.14
SO₄	0.69	-0.53	0.19	-0.27	0.17	-0.10	0.30
HCO₃	-0.69	0.50	-0.08	0.28	-0.38	0.04	0.15
Cl	-0.89	-0.37	-0.09	-0.07	0.07	0.12	-0.15
TDS	-0.71	-0.63	-0.08	-0.04	0.13	0.11	0.03

Fig. 9: Plot of loadings for the first three components with Varimax normalized rotation

Figure 5 shows that a considerable number of samples are oversaturated in respect to minerals calcite, dolomite and aragonite. Approximately 77% of the SI values for calcite and 72% of the SI values for dolomite and 55% of the SI values for aragonite of the groundwater are greater than zero in the water samples. The groundwater is therefore evolving from a state close to saturation toward oversaturated with respect to these minerals and precipitation results. As saturation state indicates the direction of the process, thus, precipitation of calcite, dolomite and aragonite and dissolution of gypsum, halite and anhydrite are expected.

According to [38-40] the oversaturation in calcite is related to incongruent dolomite dissolution and dedolomitization, both of which cause precipitation of calcite. Once the system is saturated in calcite, the hydrochemical evolution is affected by the dissolution of gypsum, which will be influencing factor in the process of dolomite dissolution. Interaction between groundwater, which contains saturated calcite and dolomite and sufficient amounts of Ca^{2+} and $CO_3{}^{2-}$ with the gypsum layer would lead to the dissolution of gypsum [39]. According to the common-ion effect, calcite would inevitably be deposited to keep the balance of calcite dissolution.

Multivariate Analysis: Principal component analysis (PCA): Table 2 presents the Eigen values, the percentage of variance, the cumulative eigen value and the cumulative percentage of variance associated with each other. It reveals that the first three factors explain approximately 74% of total variance.

Evidently, the first factor is generally more correlated with the variables than the second and third factor. This is to be expected because these factors are extracted successively, each one accounting for as much of the remaining variance as possible.

Loadings, that represent the importance of the variables for the components, are in bold for values greater than 0.6. The first two components explain 40.27% and 20.90% of the variance, respectively and thus, account for the majority of the variance in the original dataset. Components 3 are not as important and explain 12% of the greatest amount of the variance. Component 1 is characterized by highly positive loadings in Ca^{2+} and SO_4 and by highly negative loading in TDS, Cl and Na. Fig. 9 summarizes this information by showing the position of the loadings of chemical parameters in the plane defined by the axes of components 1 and 2 and components 1 and 3. Because of the association of Na+ and Cl, component 1 is defined as the ''salinity'' component in reference to the salt NaCl. Component 2 is defined as the ''hardness'' component because of it's highly loadings in Ca^{2+} and Mg^{2+}, the two ions generally used to calculate hardness. Finally, component 3 is characterized by highly negative loadings in T°C and pH.

Cluster Analysis: The result of the HCA is presented as a dendrogram in Fig. 10. Samples that compose the main groups obtained through the cluster analysis were mainly classified according to their quality. The spatial differentiation appears reflect the geology and general groundwater flow. The groups established from the Q-mode HCA appears to indicate different degrees of
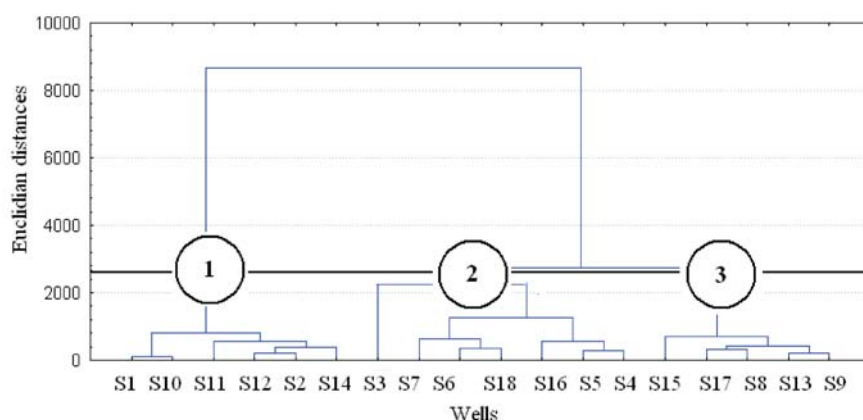
Fig. 10: Dendrogram of Q-mode HCA, including all water samples. The cluster analysis is based on parameters TDS, Na^+, Cl^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, K^+, HCO_3^-,. The water samples are linked into clusters on the x axis and the linkage distance is plotted on the y axis

weathering, which could further indicate varying aquifer hydraulic properties resulting from the various degrees of fracturing and weathering in the area. We note that most of the highest yielding wells in the area are classified within the group 1. The local structure and geology play important roles in the weathering of the aquifer units and the subsequent ionic enrichment of the ground waters. The sample points in group 2 are located within the fresh to slightly weathered aquifers. The samples that fall within group 3 are influence by water recharge from continental intercalaire aquifer (TDS > 10000 mg/l) [38].

CONCLUSION

The spatial variations of groundwater chemistry in the study area suggest that the hydrogeochemical compositions of groundwater have been mainly controlled by its interaction with hydrologic parameters such as the flow path, residence time,

Groundwater of the Miocene aquifer is generally unsuitable for drinking purposes. The various major ions are above the maximum permissible limit of the WHO's drinking water guideline [38]. The groundwater of Miocene aquifer is affected by significant salinity. Groundwater salinity, represented by the TDS values, shows a range of variation from 5136 mg/l to almost 7418 mg/l.The groundwater of this aquifer is brackish-salt water category, since all samples have TDS above 1000 mg/l.

The trace elements concentrations of all samples have lower content than the acceptable limits for drinking water [38].

Ionic ratio data suggests that rock weathering and evaporation are the dominant factor affecting the major

ion composition in the study area. The high ratio of Na^+/Cl^- indicates a significant contribution from silicate weathering.

All water samples were under saturated with respect to halite, gypsum and anhydrite. However, the SI of calcite, dolomite and aragonite is generally greater than zero in the area. Thus, precipitation of calcite, dolomite and aragonite and dissolution of gypsum, halite and anhydrite are the geochemical processes which characterize Miocene aquifer.

CA grouped the 18 sampling wells stations into three clusters of similar water quality characteristics. Groundwater in the study area can be classified into the Na-Ca-SO4-Cl, Na-Ca-Cl-SO4 and Na-Cl-SO4 types in an increasing degree of salinization.

The management and the future development of groundwater resources in the study area require multidisciplinary hydrological and geochemical approaches to assess the origins and the evolution of salinity in water. Gathering accurate and timely data will constitute first step toward a regional action plan for reducing salinity and improving water quality in the Miocene aquifer.

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