









Analysis of groundwater quality in the lower Soummam Valley, North-East of Algeria

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Abstract: Analysis of groundwater quality in the alluvial aquifer of the lower Soummam Valley, North-East of Algeria, was realised through the application of multivariate statistical methods: hierarchical cluster analysis (HCA) in Q and R modes, factorial correspondence analysis (FCA), and principal component analysis (PCA), to hydrochemical data from 51 groundwater samples, collected from 17 boreholes during periods of June, September 2016 and March 2017. The objectives of this approach are to characterise the water quality and to know the factors which govern its evolution by processes controlling its chemical composition. The Piper diagram shows two hydrochemical facies: calcium chloride and sodium bicarbonate. Statistical techniques HCA, PCA, and FCA reveal two groups of waters: the first (EC , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and NO_3^-) of evaporitic origin linked to the dissolution processes of limestone rocks, leaching of saliferous soils and anthropogenic processes, namely contamination wastewater and agricultural activity, as well marine intrusion; and the second group (Na^+ , K^+ , and HCO_3^-) of carbonated origin influenced by the dissolution of carbonate formations and the exchange of bases. The thermodynamic study has shown that all groundwater is undersaturated with respect to evaporitic minerals. On the other hand, it is supersaturated with respect to carbonate minerals, except for water from boreholes F9, F14, and F16, which possibly comes down to the lack of dissolution and arrival of these minerals. The results of this study clearly demonstrate the utility of multivariate statistical methods in the analysis of groundwater quality.

Keywords: Algeria, analysis of groundwater quality, hydrochemical data, multivariate statistical analysis, Soummam Valley

INTRODUCTION

Water is the life and survival of humanity. In addition to satisfying the basic needs of life to the human being, it provides luxury and comfort. Groundwater is a very important and main source of water supply for most parts of the world, especially where there is low rainfall such as in Algeria. This approach aims to characterise the groundwater quality and to find out the factors which govern its evolution by processes

controlling its chemical composition, thus, perceive the state of the alluvial water table of the lower valley of the Soummam.

Water quality depends on physical, chemical and biological parameters, and their variations depend on natural and anthropogenic effects.

Natural factors such as the local climate by seasonal variation in temperature and precipitation, geology, the lithology of which corresponds to the nature of rocks in a geological formation [FOUCAULT *et al.* 2010], the hydraulic properties of

the medium (transmissivity, hydraulic conductivity, and storage coefficient), the residence time of groundwater will also have an influence on its geochemistry given the chemical kinetics that governs the reactions [FRAPE *et al.* 1984; SILVA *et al.* 2009] and the water flow paths through the geological medium. Anthropogenic factors depend mainly on irrigation practices (use of fertilisers) and wastewater discharges. The factors mentioned above govern the evolution of water through processes controlling its chemical composition.

The dissolution of minerals due to chemical weathering of the surrounding rock is the dominant process in the region, this process is known as dolomitisation where calcite dissolves and dolomite precipitates. Dolomitisation increases the concentration of calcium in saline water and can cause precipitation of calcium sulphate [ROUAHNA 2007].

Some minerals such as carbonates and evaporates are rapidly dissolved and significantly alter the chemical composition of water, while other minerals, such as silicates, dissolve more slowly and therefore have less effect on the chemical composition of water [SEMAR *et al.* 2013]. This hydrogeochemical process occurs along with the flow of groundwater as a function of the residence time which controls the evolution of its chemical composition [APODACA *et al.* 2002].

The increase in chloride ions in the lower part of the aquifer of the lower Soummam Valley near the sea during the low-water period is due to the reverse flow and marine intrusion. The basic exchange process is present in the chemism of the waters of the region, reflected by the release of the Na⁺ ions contained in the clays, and their combination with the bicarbonate waters characterises the waters with a sodium bicarbonate facies.

Knowing these hydrogeochemical processes is fundamental to determining the origin of groundwater chemical composition. In eastern Algeria several studies have been carried out using statistical analysis to determine the groundwater quality focusing on understanding the mechanisms responsible for geochemical typology [BELKHIRI *et al.* 2011; BOUDIAF *et al.* 2017; GAAGAI 2017; GHODBANE 2018; MOUNI *et al.* 2009].

Multivariate statistical techniques, the principal component analysis (PCA), hierarchical cluster analysis (HCA), and factorial correspondence analysis (FCA) help us explain the correlation between a large number of variables and reduce their number in a limited number of factors without loss of critical information [MOMEN *et al.* [1996] in the USA, MONJEREZI *et al.* [2008] in Malawi, BELKHIRI [2011] in Algeria, GRZYWNA and MIELNICZUK [2020] in Poland). These methods are a useful tool for the characterisation of groundwater quality and the investigation of groundwater contamination by trace elements [FARNHAM *et al.* 2003; RAZACK *et al.* 1990]. In Iran, the HCA has been applied to the evolution of brines to highlight the correlation between ions and suggest a non-marine type of saline system [ASHLEY, LIYOD 1978; TORSHIZIAN *et al.* 2009]. The PCA and FCA were used to discuss the geochemical evolution, groundwater contamination, and mineralisation and to interpret hydrochemical data based on factor scores [BOUDOUKHA, GHODBANE 2014; GAAGAI *et al.* 2017; KIM *et al.* 2005; MAHLKNECHT *et al.* 2003; OLMEZ *et al.* 1994; REGHUNATH *et al.* 2002].

HCA and PCA have shown that groundwater salinisation is controlled by cationic exchange related to seawater intrusion, but also by cationic exchange and pollution resulting from anthropogenic activities [ZGHIBI *et al.* 2014]. The use of FCA has shown that seawater intrusion, rock weathering, and salt leaching are the main processes controlling groundwater geochemistry [SINGARAJA *et al.* 2013].

The PCA has also been applied to distinguish several groundwater signatures, including uncontaminated groundwater, agricultural activities, mining, and wastewater pollution [GHODBANE *et al.* 2016; LOVE *et al.* 2017].

The usefulness of statistical methods such as principal component analysis (PCA), hierarchical cluster analysis (HCA) and factorial correspondence analysis (FCA), appear formally in the analysis and characterisation of groundwater quality of the alluvial water table of the lower Soummam Valley, as well as in the knowledge of the factors which manage their evolution by processes controlling its chemical composition.

MATERIALS AND METHODS

NATURAL CONDITIONS OF THE STUDY AREA

The lower Soummam Valley is located in the Béjaia Wilaya in Northeastern Algeria, between Sidi Aich and Béjaia. This coastal plain of lower Soummam covers an area of 709 km² and is characterised by a humid Mediterranean climate with an average yearly temperature of 18°C and an average yearly rainfall of 750 mm [SAOU *et al.* 2012]. The topography of this region is characterised by a predominance of Atlas Mountains with altitudes varying between sea level and 1000 m with steep slopes often exceeding 25% [DAHMANA 2016]. In terms of tectonics, the Soummam is made up of several structures, namely – the Kabyle Massif in the north, the limestone chain, and the south and north flysch Kabyles. To the south, the southern Tell, which includes the chains of the Bibans and the Babors [HASSISSENE 1989]. Along this valley and its tributaries lies an alluvial plain oriented from the southwest to the northeast. It contains an aquifer of the Mio-Plio-Quaternary consisting mainly of coarse alluvial: sands, pebbles, Miocene gravel, overlying the Miocene marl substrate, Oligocene clay, and sometimes, even more or less deep, Cretaceous, and because of its porosity of interstice, it contains a considerable reservoir for the storage of water [DUPLAN 1960].

Previous hydrogeological studies [DAHMANA 2016; DUPLAN 1960; HASSISSENE 1989] highlighted the existence of a shallow aquifer located in the alluvial Mio-Plio-Quaternary formation, corresponding to a large alluvial depression, deposited in the form of terraces and composed of marls and clays with very low permeability in the Sidi Aich area and a wide silt cover overlying the aquifer to the south of the Ghir stream. The area presents two recharge zones, the first zone from El Kseur to Béjaia with a recharge of $6 \cdot 10^{-9} \text{ m} \cdot \text{s}^{-1}$ and the second zone that extends from Sidi Aich to the upstream of El Kseur – $1.89 \cdot 10^{-9} \text{ m} \cdot \text{s}^{-1}$ [KESSASRA *et al.* 2012]. This aquifer is one of Algeria's main coastal aquifers and the only water resource available locally from shallow groundwater. This pro-pumping provision has been one of the major assets of the socio-economic development of the region. However, the

increase in pumping has led to a significant decrease in the aquifer reserves.

Furthermore, waters of the lower Soummam Valley aquifer are subjected to urban (wastewater discharge) and agricultural (use of manure and fertilisers) polluting pressures, which influence and degrade water quality, hence threatening the sustainability of the water resource [BENNABI 1985]. The piezometric survey carried out on the groundwater of the alluvial filling during the high water period (March 2017) showed a slight rise in groundwater of about 0.2 and 0.37 m, respectively, compared with two measurements

carried out on the same water points during the low water periods (June and September 2016), this is due to the drought season and the lack of rainfall. However, the water table has generally retained the same typology with the flow mainly from the southwest to the northeast. Except that we can report a reverse flow from the Mediterranean Sea to the water table in the lower part of the valley close to the Mediterranean Sea during periods of low water (marine intrusion), this was confirmed in the hydrochemical study by the increase in chloride concentrations during these periods (Fig. 1).

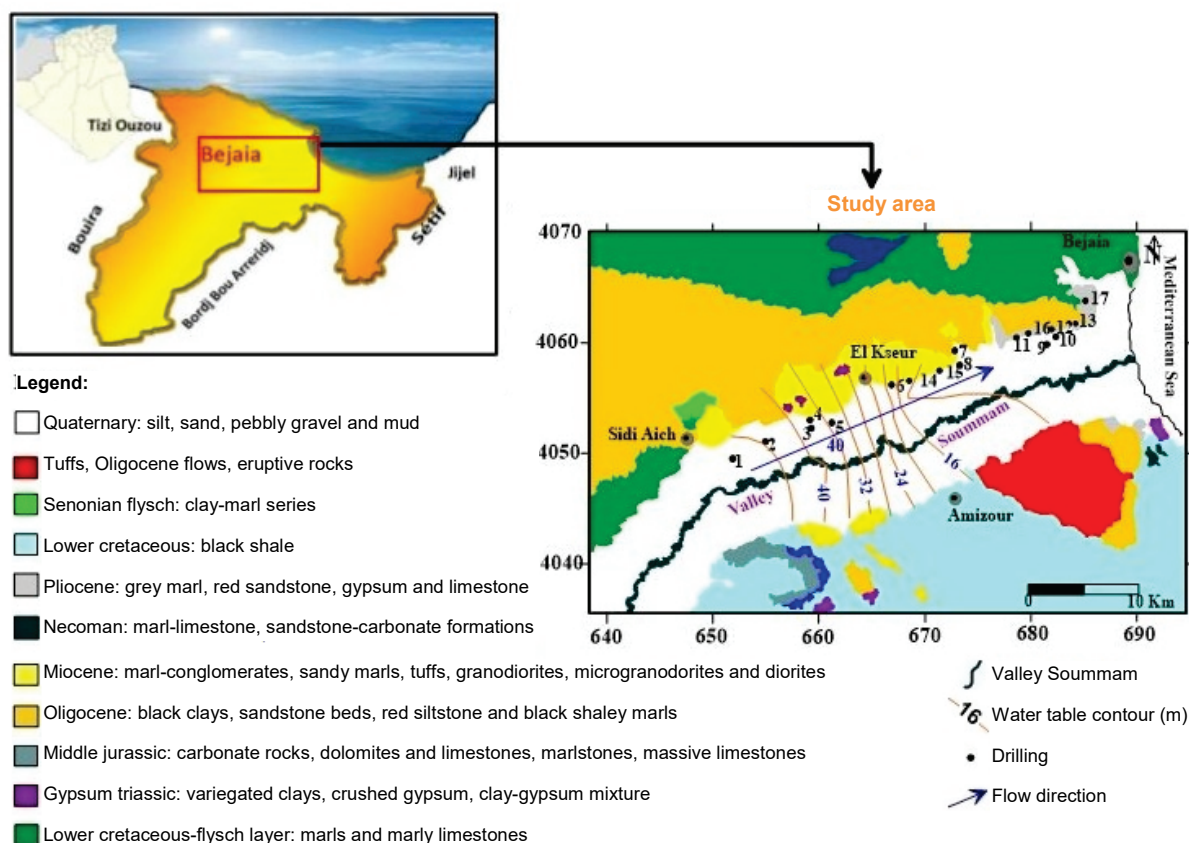


Fig. 1. Hydrogeological map of study area; source: own elaboration

SAMPLING AND ANALYSIS TECHNIQUES

The physicochemical analysis was carried out on 51 groundwater samples from the alluvial plain of the lower Soummam Valley, collected from 17 boreholes during the low water periods (June and September 2016) and the high water period (March 2017) to examine the evolution of physical and chemical parameters. These samples were taken from boreholes of a single aquifer level for representative sampling, according to the directives of the Geological Bureau and Mining Research (Fr. Bureau de recherches géologiques et minières) [LOUVRIER 1976], and after 15 min of pumping during the stabilisation of the water temperature in order to eliminate the water stored in the hydraulic structure. The sample was taken using two polypropylene bottles washed with acid. Each sample was immediately filtered *in situ* through 0.45 m filters on cellulose acetate. Filtered water for

cation analysis was transferred into 100 cm³ polyethylene bottles and immediately acidified to pH < 2 by the addition of Merck ultra-pure nitric acid (5 cm³ 6 N HNO₃). Concerning anion analyses, samples were collected in 250 cm³ polyethylene bottles without acidification. All samples were stored in a cooler at a temperature <4°C, later transferred to the laboratory of the National Water Resources Agency (Fr. Agence nationale des ressources hydrauliques) in Constantine, and stored in the refrigerator at a temperature <4°C until analysis (under 1 week). Immediately after sampling, pH, *T*, and electrical conductivity (*EC*) were measured *in situ* using a multiparameter WTW (P3 Multiline pH/LF-SET).

The chemical elements analysed are Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, HCO₃⁻, SO₄²⁻, and NO₃⁻ (Tab. 1). They were analysed using the standard processes suggested by the American Public Health Association (APHA) [APHA 1989; 1995a, b]. Ca²⁺, Mg²⁺, HCO₃⁻, and Cl⁻ were analysed by volumetric titrations.

Table 1. The statistical summary of the groundwater hydrochemical parameters in the alluvial aquifer of the lower Soummam Valley

Parameter	T (°C)	pH	EC ($\mu\text{S}\cdot\text{cm}^{-1}$)	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻
				mg·dm ⁻³							
June 2016 (n = 17)											
Min.	17.00	6.94	821.00	186.40	52.40	132.70	0.20	107.50	166.10	507.60	0.00
Max.	21.10	7.81	3125.00	658.80	237.00	2967.20	64.10	4752.20	825.70	1449.60	53.00
Mean	19.31	7.49	1409.88	312.55	102.91	1015.13	15.19	1578.98	449.66	986.09	15.63
SD	1.27	0.26	742.02	104.61	44.92	997.94	16.51	1507.35	171.02	237.24	18.93
CV	0.07	0.04	0.53	0.33	0.44	0.98	1.09	0.95	0.38	0.24	1.21
September 2016 (n = 17)											
Min.	20.10	7.88	4062.00	724.70	260.70	3263.90	70.50	5227.40	908.30	1594.60	58.30
Max.	16.20	7.00	871.00	205.00	60.00	146.00	0.20	118.30	260.20	558.40	0.00
Mean	18.40	7.49	1643.65	355.59	121.03	1106.64	17.36	1862.17	499.93	1065.88	16.88
SD	1.19	0.34	1009.65	131.03	46.91	1106.21	18.55	1626.69	180.82	293.86	20.99
CV	0.06	0.05	0.61	0.37	0.39	1.00	1.07	0.87	0.36	0.28	1.24
March 2017 (n = 17)											
Min.	15.50	6.87	681.00	155.30	45.40	110.60	0.20	89.60	138.40	423.00	0.00
Max.	17.72	7.44	880.65	260.46	87.24	845.96	12.18	1306.02	369.83	811.94	11.42
Mean	19.80	7.73	1284.00	549.00	197.50	2472.70	53.40	3960.20	688.10	1208.00	40.80
SD	1.20	0.25	268.24	87.19	36.15	831.63	13.84	1262.07	149.37	206.84	14.84
CV	0.07	0.03	0.30	0.33	0.41	0.98	1.14	0.97	0.40	0.25	1.30
Total (n = 51)											
Min.	15.50	6.87	681.00	155.30	45.40	110.60	0.20	89.60	138.40	423.00	0.00
Max.	21.10	7.88	4062.00	724.70	260.70	3263.90	70.50	5227.40	908.30	1594.60	58.30
Mean	18.80	7.49	2009.00	476.33	167.87	1949.07	41.37	3092.40	578.27	1075.20	33.03
SD	1.89	0.38	1173.10	213.05	82.01	1246.54	28.64	2036.27	279.11	417.12	23.08
CV	0.10	0.05	0.58	0.45	0.49	0.64	0.69	0.66	0.48	0.39	0.70

Explanations: T = temperature, EC = electrical conductivity, n = number of water samples, SD = standard deviation, CV = coefficient of variation.
Source: own study.

Concentrations of Ca²⁺ and Mg²⁺ were estimated titrimetrically using 0.05 N EDTA and 0.01 N and those of HCO₃⁻ and Cl⁻ by H₂SO₄ and AgNO₃ titration, respectively. Concentrations of Na⁺ and K⁺ were measured using a flame photometer (Model: Flame Photometer 128) and that of sulphate by turbidimetric method [CLESCERI *et al.* 1998]. Standard solutions for the above analysis were prepared from the respective salts of analytical reagents grades. The value of the percentage ionic balance obtained is considered acceptable with a deviation of $\pm 10\%$ error. Conversely, if the evaluated error is greater than $\pm 10\%$, the analysis is rejected [SUBRAMANI *et al.* 2010]. With the exception of nine samples, 82% of the total did not exceed this limit. Calculation of the ionic balance is done using hydrochemistry software Diagrams 6.76 – Water Software Quality Hydrochemistry [LHA 2021].

CHEMICAL EQUILIBRIUM

Saturation indices (SI) and chemical equilibrium have been calculated to track the mechanisms of mineralisation

acquisition resulting from the water–rock interaction (dissolution and/or precipitation process) on the basis of thermodynamic code (PHREEQC) [PARKHURST 1999]. The SI was calculated by the following equation:

$$SI = \log (K_{IAP}/K_{sp}) \quad (1)$$

where: SI = saturation indices, K_{IAP} = the product of ion activity, K_{sp} = the product of mineral solubility.

The waters can therefore be in a state of equilibrium, oversaturated or undersaturated depending on the value of their saturation indices, these indices are defined as follows:

- SI = 0, the water–rock balance is reached;
- SI > 0, water is assumed to be oversaturated, and mineral precipitation is necessary to achieve equilibrium;
- SI < 0, the water is undersaturated, and the dissolution of the minerals is necessary to achieve balance [YIDANA *et al.* 2008].

Mathematical and statistical calculations were made using Excel 2010 and STATISTICA 6. A multivariate analysis of the

groundwater quality dataset was conducted using techniques: HCA, PCA and FCA.

The HCA technique is used to group objects or data into classes based on their similarities or dissimilarities [DANIELSSON *et al.* 1999]. Numerous studies have applied this technique to successfully classify water samples [FARNHAM *et al.* 2000; GAAGAI *et al.* 2020; MENG, MAYNARD 2001; WILLIAMS 1982; WUNDERLIN *et al.* 2001]. The purpose of this method is to classify samples according to their different parameters compared to each other, in order to gather them into statistically distinct hydrochemical groups that can be significant in the geological context.

The classification can be carried out with two methods (*Q*-mode and *R*-mode), applied to identify the dendrogram beams. *R*-mode is usually applied to water quality variables to indicate their mutual interactions, while *Q*-mode indicates the interactions between the studied samples. In this study, HCA was used to classify samples into distinct hydrochemical groups using Ward's aggregation method [WARD 1963].

Ward's method of grouping produces the most distinctive groups where each member of the group is more similar to its pairs than any other member of the group. Subsequently, they were standardised according to their standard scores (*Z* scores) as described by GÜLER *et al.* [2001]. The Ward grouping procedure is used in this study and the classification of hydrogeochemical data was carried out using the Euclidean square distance, which is one of the most commonly, adopted measures [FOVELL, FOVELL 1993]. The HCA was applied using Euclidean distance as a measure of distance between samples, and Ward's method as a binding rule for the classification of hydrogeochemical data from the Soummam area.

The PCA is a descriptive statistical method of determining the correlation of variables and their grouping into groups in families of the same origin. These sets of new variables, namely the main components, identify the main factors that control groundwater chemistry [DAGNELIE 1993]. The PCA has many variations depending on transformations in the data table. Of these variants, the standardised one (centered-reduced cloud) is certainly the most used and it is this one that we choose to present the principles of analysis. The sets of initial variables are represented graphically on factor planes.

The interpretation of the results is generally limited to factorial planes accounting for the most part of the initial variables cloud variance. The FCA is a statistical method of data analysis developed by BENZACRI *et al.* [1976], this method aims to gather in a small number of dimensions most of the initial information by focusing not on absolute values but on the correspondences between variables, i.e. relative values. The FCA offers the distinction of providing a common space for graphic representation of variables and individuals [DOMINIQUE 2009].

The FCA investigates links between two nominal variables, as opposed to the correlation evoking links between numerical variables. The objective of the FCA is to detect proximity, and on the other hand to reveal some abstract synthetic variables debauched (reduction of dimensionality) [BAUDOT 2019]. The FCA is used to describe and prioritise statistical relationships that may exist between individuals placed in lines and variables placed in columns in a data table.

Both the FCA and the PCA take the data table as a cloud of dots in a mathematical space with as many dimensions as there are columns in the data table. These two methods project the dots on axes or planes (namely factorials) so that we can visualise and study the form as best as possible, and thus look for correlations globally [BRIGITTE, JEROME 2008].

RESULTS AND DISCUSSION

GENERAL HYDROCHEMISTRY

Chemical parameters measured in groundwater samples (Tab. 1) highlight that the pH varies between 6.87 and 7.88, indicating that the water is slightly alkaline. Knowing that the calcite and dolomite buffering process is dominant in the 6.5–7.5 pH range [BLOWES *et al.* 2003]. The average water temperature was 18.8°C. The electrical conductivity (*EC*) of groundwater samples ranges from 681 to 4062 $\mu\text{S}\cdot\text{cm}^{-1}$, with values exceeding 3000 $\mu\text{S}\cdot\text{cm}^{-1}$ observed at the water points (F13, F17) located in the lower part of the valley characterizing the waters of the sea. The ranking of the abundance of the main cations is $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and all samples exceeded the maximum acceptable concentration of Na and Ca^{2+} for drinking water (50 and 75 $\text{mg}\cdot\text{dm}^{-3}$ respectively). For Mg, almost all samples exceeded the maximum acceptable concentration for drinking water (50 $\text{mg}\cdot\text{dm}^{-3}$) with the exception of samples 43, 48, and 50 of the March 2017 campaign, taken from water points F9, F14, and F16, which was possibly due to dilution during the high water period. The ranking of the abundance of major anions is $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$ and all samples exceeded the maximum acceptable concentration for drinking water (200 $\text{mg}\cdot\text{dm}^{-3}$) of Cl. For sulphates, almost all samples exceeded the maximum acceptable concentration for drinking water (200 $\text{mg}\cdot\text{dm}^{-3}$) except samples 46, 48, and 50 [WHO 2004], also due to dilution. We stated that 83% of the standard deviation values are lower than the average, which means the existence of some homogeneity in the type of water.

Plotting water analyses issued from the Mio-Plio-Quaternary aquifer on the Piper triangular diagram [PIPER 1994], illustrates two chemical facies: the first calcium chloride with 59% of the samples representing the boreholes (2, 4, 5, 6, 8, 9, 11, 12, 14, and 16) which are related to the marl and clay formations, followed by sodium bicarbonate facies with 41% of the samples representing the boreholes (1, 3, 7, 10, 13, 15, and 17) related to the carbonate formations forming the edges of the aquifer which correspond to the recharge limits (Fig. 2, 3).

The molar ratio $\text{Ca}^{2+}/\text{Mg}^{2+}$ of the samples is < 2 , indicating the dissolution of carbonates [MAYO, LOUCKS 1995]. The groundwater flowing through the alluvial water table of the lower Soummam Valley is issued from the carbonate formations which border the plain, and also from the infiltration of rainwater passed through a very heterogeneous environment made up of forests, agricultural land and then collected in talwegs and wadis of alluvial formations (sands, gravels, evaporite deposits, etc.). The flow path and crossed layers influence the acquisition of chemical elements. An analysis of the characteristic reports was carried out to distinguish more

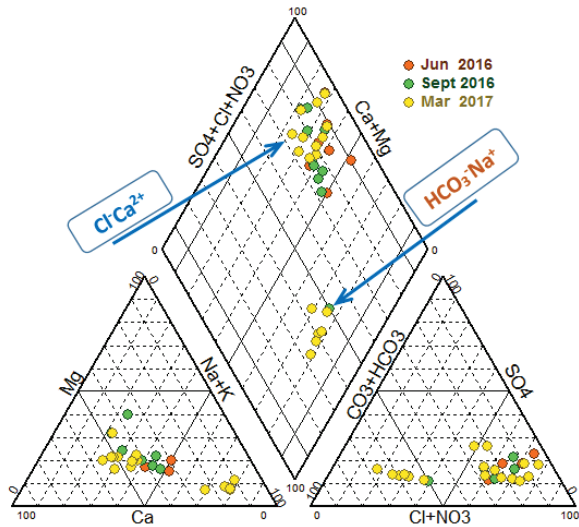


Fig. 2. Piper diagram applied to the groundwater of the lower Soummam Valley; source: own study

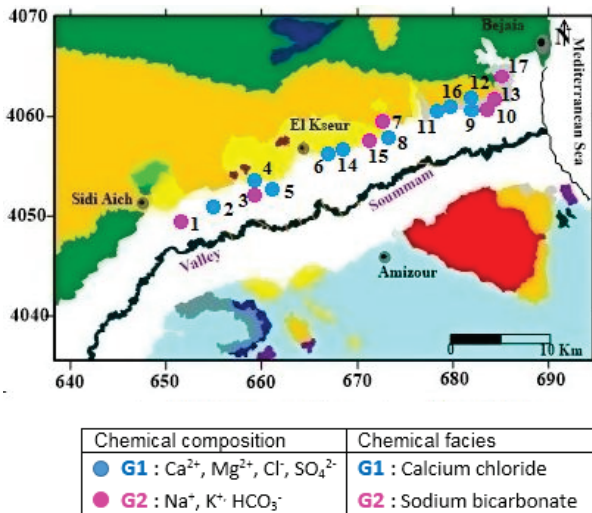


Fig. 3. The spatial variability of the chemical composition; source: own study

the facies of the groundwater (Fig. 4). This analysis demonstrates a dominance of chlorinated facies in the majority of water samples. The $(Na^+/Ca^{2+})/(SO_4^{2-}/Cl^-)$ report shows an abundance of sodium due to the phenomenon of bases exchange of Na⁺ ions contained in clays, and calcium ions related to dissolution, with a chlorinated tendency due to leaching of saliferous soils, also to the intrusion of seawater. There is a very strong relationship between chloride and calcium ions in the $(Ca^{2+}/Mg^{2+})/(SO_4^{2-}/Cl^-)$ report. This is due to the dissolution of carbonate rocks, linked to the chemical attack of the calcareo-dolomitic formations (calcite (CaCO₃) and CaMg dolomite CO₃²⁻) by water in the presence of carbon dioxide, in the sedimentary formations located on the left bank of Soummam Valley between Sidi Aich and El-Kseur.

The dissolution of dolomite CaMg(CO₃)₂ is done according to the following chemical reaction:

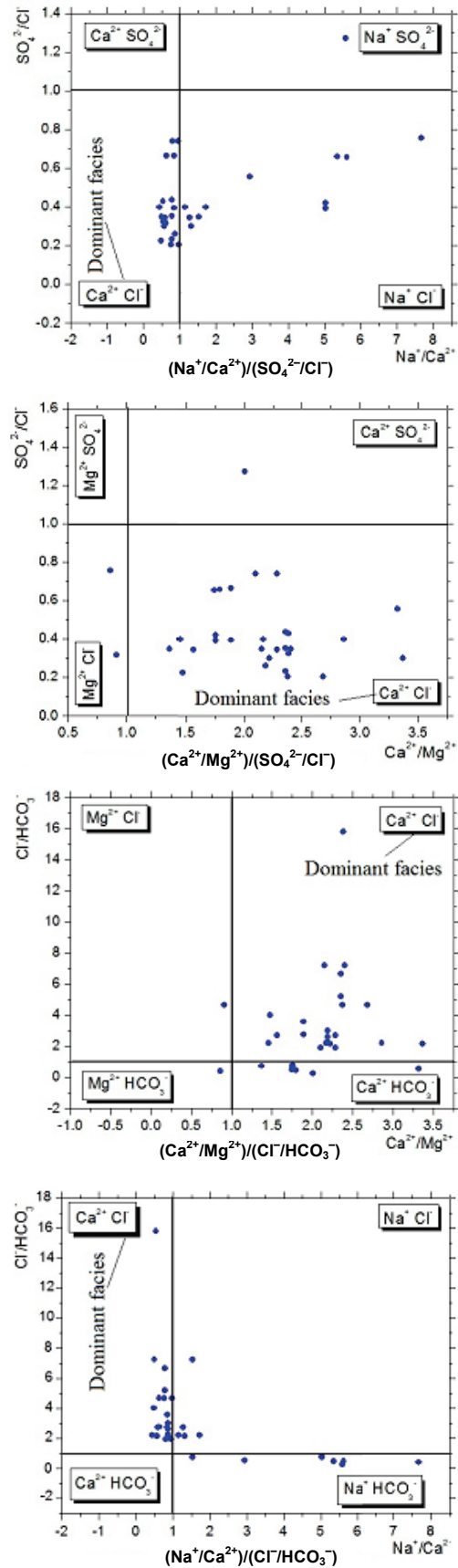
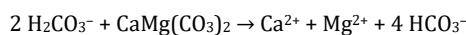


Fig. 4. The characteristic reports of chemical elements; source: own study

Thus, the solubility of CaCO_3 is highly increased by the presence of NaCl [FRIARS, JOHNSTON 1929].

For the $(\text{Ca}^{2+}/\text{Mg}^{2+})/(\text{Cl}^-/\text{HCO}_3^-)$ report, there is a fairly important relationship between chloride ions and calcium ions, confirming the dominance of the calcium chloride facies. Also, the $(\text{Na}^+/\text{Ca}^{2+})/(\text{Cl}^-/\text{HCO}_3^-)$ report shows the dominance of chloride ions with calcium ions.

For a better understanding of the calcium and chlorides origin, the graphical representations of $\text{Ca}^{2+}/\text{HCO}_3^-$ and Na^+/Cl^- in relation to the slope line (1:1) were carried out (Fig. 5). The representation $(\text{Ca}^{2+}/\text{HCO}_3^-)$ makes it possible to show that the waters of the boreholes 1, 3, 7, 10, 13, 15, and 17 have a bicarbonate tendency linked to a carbonate origin. While those of the boreholes 2, 4, 5, 6, 8, 9, 11, 12, 14, and 16 have a calcium tendency linked to an evaporitic origin. The representation $(\text{Na}^+/\text{Cl}^-)$ shows that 65% of the water in the water table has a chlorinated dominance possibly due to the leaching of saline soils, contamination of wastewater, and marine intrusion, however, the rest of the water has a sodium dominance due to the basic exchange and also to the leaching of salty soils.

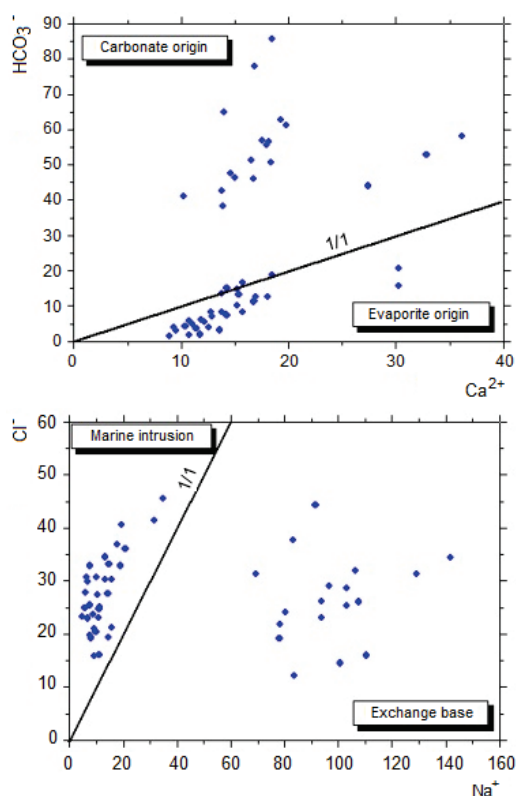


Fig. 5. Graphic representation of groundwater calcium and chlorides origin in the lower Soummam Valley; source: own study

MULTIVARIATE STATISTICAL ANALYSIS

The HCA technique was used to classify samples into separate hydrochemical groups. Nine measured hydrochemical variables (EC , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- , and NO_3^-) were used in this analysis. For statistical purposes, all variables have undergone a logarithmic transformation and,

more closely, correspond to the normally distributed data. Subsequently, they were unified to their standard scores (z -scores) as described by GÜLER *et al.* [2002]. The same results were obtained as the Piper diagram, where two groups of hydrochemical variables were selected from the dendrogram (Fig. 6) by visual examination based on the choice of the phenon line [SNEATH, SOKAL 1973], and at the bond distance of 550, where the groups can be distinguished in terms of hydrochemistry variables.

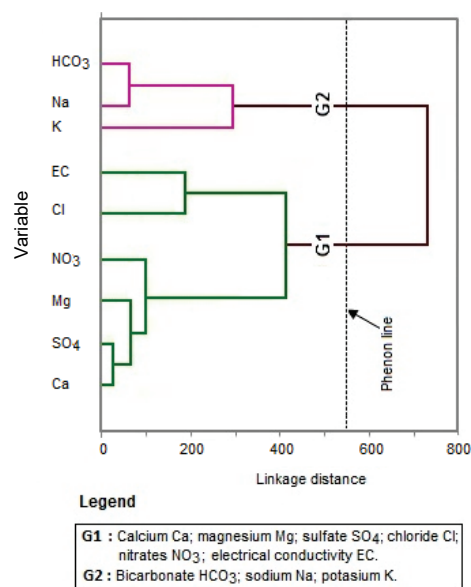


Fig. 6. Cluster dendrogram for variables; G1 = group 1, G2 = group 2; source: own study

The first group (G1) includes EC and ions: Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , and NO_3^- . This group represents the waters of boreholes 2, 4, 5, 6, 8, 9, 11, 12, 14, and 16 (Fig. 7), characterised by an EC varying from 681 to 2659 $\mu\text{S}\cdot\text{cm}^{-1}$ and marked as moderately mineralised group to mineralised, which is explained by the abundance of evaporite formations in the aquifer with a chloride-calcium tendency, due to the dissolution of limestone formations, leaching of salt-bearing soils, and marine intrusion. As one can mark, there is a sign of nitrate pollution in this group possibly caused by sewage and agricultural activity. The second group (G2) contains Na^+ , K^+ , and HCO_3^- , which characterises the waters of boreholes 1, 3, 7, 10, 13, 15, and 17, with an average EC of 1654 $\mu\text{S}\cdot\text{cm}^{-1}$, influenced by outcrops of the carbonate facies of nahcolite origin (NaHCO_3) and leaching of salty soils. As it was recorded during the low water period (June and September 2016), values above 3000 $\mu\text{S}\cdot\text{cm}^{-1}$ at the waters of boreholes (F13, F17) located in the lower part of the valley near the Mediterranean Sea, characterise saline waters due to reverse flow and marine intrusion.

The application of the PCA to data of a table of 17 individuals and 9 variables (EC , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- , and NO_3^-), based on the correlation coefficient between two variables, allowed to visualise the degree of connection and to distinguish group sets of waters of the same origin. The results show that the first two factors (F1, F2) explain most of the information sought and allowed to significantly represent the grouping of water samples with 67.44% of the total

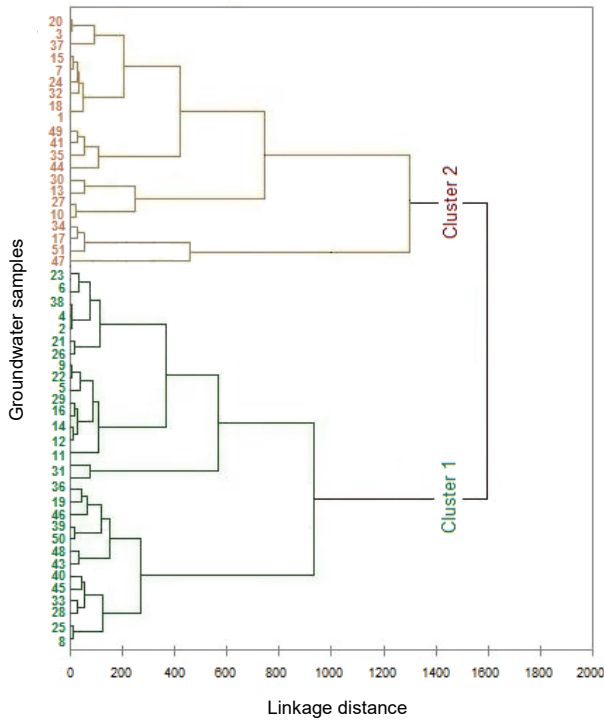


Fig. 7. Cluster dendrogram for water samples; source: own study

variance (Fig. 8), which can be considered sufficient for analysing the approach of variables and individuals in order to identify the main sources of hydrochemical variation. The first factor (F1) expresses 47.83% of the total variance and, this factor is considered as a mineralisation factor by its correlation with the majority of elements and its charged positively with EC , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and negatively with nitrates NO_3^- . The second factor (F2) corresponds to 19.62% of the total variance and is negatively charged by Na^+ , K^+ , HCO_3^- . The projection of individuals (observations) on the factor plane F1–F2 (Fig. 9), allows us to distinguish two groups of water:

- group 1: represents the groundwater samples of boreholes: F2, F4, F5, F6, F8, F9, F11, F12, F14, and F16 from moderately mineralised to mineralised, with a tendency to chlorination and affected by nitrate pollution from wastewater and agricultural activity;

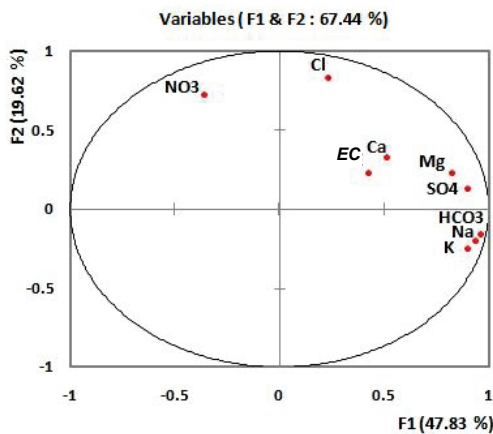


Fig. 8. F1–F2 factorial plan; source: own study

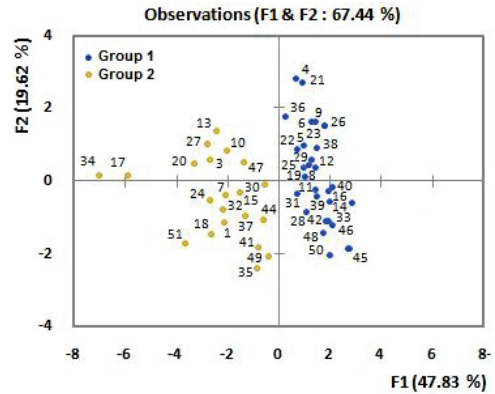


Fig. 9. Principal component analysis scores graphic on F1–F2 plan; source: own study

- group 2: represents the groundwater samples of boreholes: F1, F3, F7, F10, F15, and F17, carbonated of deep origin.

The FCA studied the links contained in a table of individuals (water boreholes) –variables (chemicals parameters). The objectives of the FCA are similar to those of the PCA – to obtain a typology of the lines and columns and to study the link between these two types. However, the concept of similarity between lines and columns is different. Here, the similarity between two lines or two columns is completely symmetrical. A symmetrical graph called barycentric representation mixes the dots–lines and dots–columns, a graph of the dots–lines, and the proximity between two modalities on the graph is representative of their association.

The FCA, applied to chemical data, has grouped water samples (lines) and chemical elements (columns) into two groups (Fig. 10) and gives the same results as the PCA and HCA. Group 01 – cluster boreholes F2, F4, F5, F6, F8, F9, F11, F12, F14, and F16, which are in conjunction with the elements (EC , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , and NO_3^-) characterising mineralised water due to the contact with marine layers, with a sign of nitrate pollution. Group 02 – contains the boreholes F1, F3, F7, F10, F13, F15, and F17, which are in conjunction with the elements (Na^+ , K^+ , and HCO_3^-) characterising carbonated waters linked to two origins: the dissolution of the evaporitic and carbonate rocks, and the salinity of the seawater during the low water period.

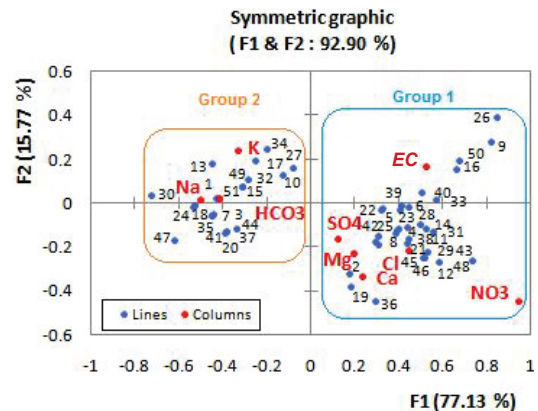


Fig. 10. Factorial correspondence analysis score graphic on F1–F2 plan; source: own study

SATURATION INDICES

In order to observe the process of mineral dissolution in groundwater in the lower Soummam Valley, a chemical equilibrium study using thermodynamics was conducted to describe the degree of the chemical equilibrium (saturation index – *SI*) of a mineral solution, which can be considered a quantification of the dissolution process and/or precipitation concerning water–rock interaction [APPELO, POSTMA

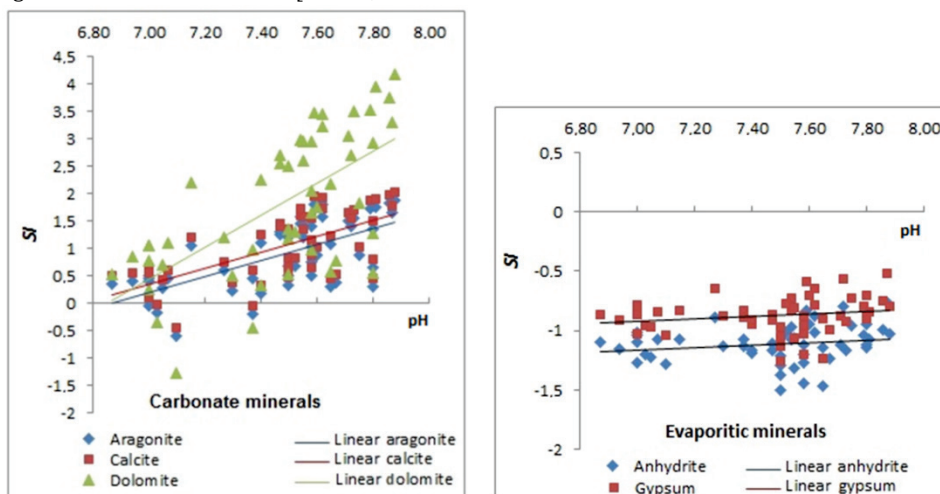


Fig. 11. Saturation indices of carbonate and evaporitic minerals, calculated with the PHREEQC software; *SI* = saturation index; source: own study

CONCLUSIONS

The groundwater quality of the lower Soummam Valley has been analysed by multivariate graphic and statistical methods. The obtained results revealed the main parameters contributing to geochemical processes that induce water chemical quality. The general analysis of the chemical data showed the abundance of mineral ions in the following order: cations – $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and anions – $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$. The values of the groundwater samples vary from 681 to 4062 $\mu\text{S}\cdot\text{cm}^{-1}$, the average values of which are recorded, except for boreholes 4, 5, 6, 15, 16, capturing water in contact with the formations of Miocene, Oligocene, and Pliocene with moderate mineralisation. High values ($>3000 \mu\text{S}\cdot\text{cm}^{-1}$) are marked, except for boreholes F13, F17, at the lower part of the valley and influenced by the marine intrusion. The decrease in *EC* at the rest of the boreholes is explained by the dilution of the mineral elements in the direction of the flow, as it is noted that the groundwater in the lower part of the plain is influenced by the marine intrusion. The Piper diagram shows that water quality is characterised by two chemical facies. The first one, dominant calcium chloride with 59% of all samples, collected from boreholes F2, F4, F5, F6, F8, F9, F11, F12, F14, F16, results from the leaching of marl-clay formations. The second one, sodium bicarbonate, represented by 41% of cases, collected from boreholes F1, F3, F7, F10, F13, F15, F17, is due to the dissolution of carbonate rocks (calcite – CaCO_3), dolomite – $\text{CaMg}(\text{CO}_3)_2$ and nahcolite – NaHCO_3) representing the recharge limits.

The results of the characteristic reports show the processes controlling and conditioning the chemical composition

1973]. The results of saturation calculations highlight that all groundwater is oversaturated regarding carbonate minerals (aragonite, calcite, and dolomite), except for the waters of the boreholes F9, F14, and F16, which is possibly due to the contact water–carbonate rocks during the low water period when there is a lack of dissolution and the arrival of these minerals. Conversely, groundwater is undersaturated with evaporitic minerals (anhydrite and gypsum) – Figure 11.

of the waters, namely the dissolution by the chemical attack of the calcareo-dolomitic formations due to the contact water–carbonate rocks bordering the plain and by the infiltration of rainwater in a very heterogeneous environment in the sedimentary formations, hence the abundance of calcium ions. As it was very clear, the existence of a base exchange process was observed in the abundance of sodium ions released from clays, as well as chloride ions due to the leaching of saliferous soils, contamination of wastewater, and also the intrusion of seawater. In the presence of natural and anthropogenic factors, these processes have made it possible to characterise the waters of the alluvial aquifer of the lower Soummam Valley by two main facies: calcium chloride and sodium bicarbonate.

Multivariate statistical techniques (PCA, HCA, and FCA) have specified two groups of chemical elements. The first group (*EC*, Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , and NO_3^-) characterises mineralised waters of an evaporative origin related to the dissolution process of limestone rocks, leaching of salt soils, and anthropogenic process represented by pollution of nitrates from wastewater and agricultural activity, as well as marine intrusion. The second group (Na^+ , K^+ , and HCO_3^-) is influenced by outcrops of the carbonate facies and base exchange by the release of sodium ions.

The study of chemical balance showed that all groundwater is undersaturated compared to the evaporitic minerals (anhydrite, gypsum). On the other hand, it is oversaturated compared to carbonate minerals (aragonite, calcite, and dolomite), except for the water from the boreholes F9, F14, and F16, which is undersaturated during the low water period, and this is possibly due to the lack of the contribution

arrival of these minerals resulting from the dissolution process by contact water-carbonate rocks.

In conclusion, in this study, the groundwater quality of the lower Soummam Valley has been analysed by multivariate graphic and statistical methods. The obtained results revealed the main geochemical processes that influence water chemical quality.

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