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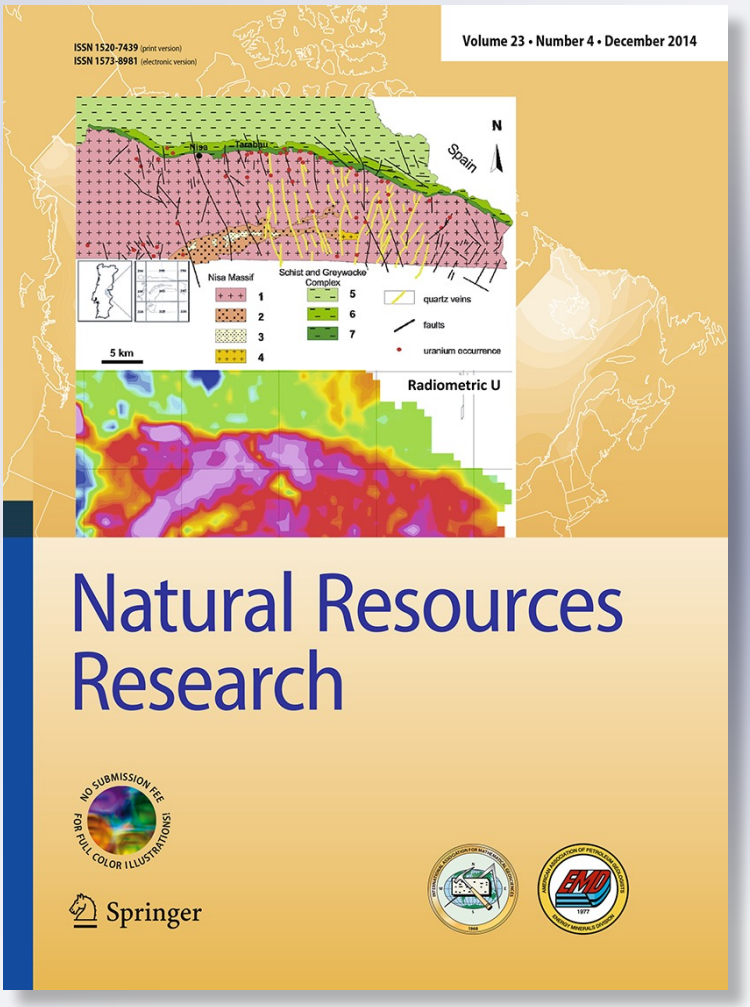

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Geochemical Characterization of Surface Water and Groundwater in Soummam Basin, Algeria

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Multivariate statistical methods and geochemical modeling were used to assess spatial variation of water quality of the Soummam basin, Algeria. The application of hierarchical cluster analysis (HCA) showed three main groups of samples. Group 1 samples are exclusively composed of surface water. Groups 2 and 3 samples consist of groundwater. Discriminant analysis assigned about 98.6% of the cases grouped by HCA. All groups are super-saturated with Ca-montmorillonite, dolomite, gibbsite, K-mica, kaolinite, and quartz, and all these groups are under-saturated with albite, anhydrite, anorthite, $CO_{2(g)}$, gypsum, halite, melanterite, and smithsonite. The results of analysis of variance indicate that the saturation indices of each of the mineral phases are significant except for chalcedony and quartz ($p > 0.05$). The results obtained by inverse geochemical modeling show the dissolution of albite, which justifies Na enrichment during the chemical evolution of groundwater. Calcite, dolomite, Ca-montmorillonite, kaolinite, illite, gibbsite, and K-mica are shown to have always precipitated.

KEY WORDS: Multivariate statistical methods, Saturation indices, Inverse geochemical modeling, Surface water and groundwater, Soummam basin, Algeria.

INTRODUCTION

Water quality gets modified in the course of its movement through the hydrological cycle and through the processes: evaporation, transpiration, selective uptake by vegetation, oxidation/reduction, cation exchange, dissociation of minerals, precipitation of secondary minerals, mixing of waters, leaching of fertilizers and manure, pollution of lake/sea, and biological process (Appelo and Postma 1993). Because of the various factors or variables that control water attributes, multivariate statistical techniques are appropriate tools for a meaningful data reduction and interpretation of multi-constituent chemical and physical measurements obtained from water (Massart et al. 1988). Multivariate statistical techniques such as hierarchical cluster analysis (HCA), discriminant analysis (DA), and analysis of variance (ANOVA) have been used widely for unbiased analysis of water quality data for drawing meaningful conclusions (Vega et al. 1998; Helena et al. 2000; Voncina et al. 2002; Raghunath et al. 2002; Simeonov et al. 2003a, b; Simeonov et al. 2004; Singh et al. 2004). Multivariate analysis is widely used to characterize and evaluate groundwater quality and is useful for evidencing spatial variation caused by natural and anthropogenic processes (Jayakumar and Siraz 1997; Vega et al. 1998; Reisenhofer et al. 1998; Helena et al. 2000; Singh et al. 2004; Belkhiri et al. 2010; Belkhiri and Mouni 2013).

Rock weathering is generally an incongruent process because the composition of groundwaters

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does not iso-chemically reproduce that of the host rock and because it is often the result of a series of constraining mechanisms. In fact, besides the composition of rock-forming minerals and their reaction to weathering, the concentration of chemicals in groundwater depends on the extent of leaching of host rock and the formation of secondary minerals, which in turn depend on water temperature and flow rate, the presence of a gas phase, and redox conditions. Frequently, water composition does not represent a state of equilibrium but a step along a succession of reactions leading to a state of overall equilibrium (Helgeson 1968). Different waters collected in a given aquifer may represent different steps of water–rock interaction along the same evolutionary process. The inverse modeling approach allows computing the mass balance of each chemical element in two water samples, provided that they are evolutionary (Glynn and Brown 1996; Plummer et al. 1991). However, the correctness of the assumptions made about dissolving and precipitating minerals, and about the eventual gas phase composition. Moreover, inverse modeling only takes into account the initial and the final stages of the water–rock interaction process, where the compositional changes are rather, path dependent (Helgeson 1968).

The objective of this study is to analyze 15 physico-chemical parameters in surface water and groundwater samples from the Soummam basin. The large data set obtained was subjected to HCA, DA, and ANOVA, and geochemical modeling to evaluate information about the similarities and dissimilarities present among different sampling sites, to identify water quality variables for spatial dissimilarity, and to ascertain the influence of pollution sources on the water quality parameters.

GEOLOGICAL SETTING

The Soummam basin is situated in northeastern Algeria and occupies 36°–36°45′N latitudes and 3°40′–5°45′E longitudes (Fig. 1). The Soummam basin area is bounded by the Djurdjura mounts to the west, by the Babor mounts to the east and southeast, and by the Mediterranean Sea to the north. The climate of the Soummam basin defined by series of transitions between humid climate in mountains near the Mediterranean and semi-arid climate in high plains. The mean annual rainfall of the basin is about 700 mm, and the mean minimum and maximum temperatures are 11.8 and 24.8 °C, respectively (Mouni 2004).

The Soummam area is distinguished by these formations: Triassic, Jurassic, Cretaceous, Eocene–Oligocene, Miocene, and Quaternary. Triassic formation consisting of two sub-formations: the Tellian sub-formation formed by gypsum and clay, and the Alpin sub-formation formed by sandstone and dolomite. Jurassic formation contains various rocks with differing compositions including dolomite, calcareous, and marl. Cretaceous formation includes two sub-formations: the Tellian sub-formation formed by conglomerate, calcareous, and marl and the flysch sub-formation formed by sandstone, calcareous, and marl. Eocene–Oligocene formation divides in two facies:the Oligo-Miocene Kabyle facies (Chellata and Bouhattem Mountains) includes conglomerate, calcareous, and marl and the Numedian flysch facies (Soummam valley and Amizour) formed by clay, quartzite, schistose marl, and sandstone. Miocene formation divides in two sub-formations: the sedimentary sub-formation generally characterized by two facies— marine facies (conglomerate and marl) and continental facies (sandstone)— and magmatic sub-formation characterized by two facies— plutonic facies (quartz-monzonite and granodiorite) and volcanic facies (andesite and rhyolite). Quaternary formation is an alluvial formation (Fig. 2) (Perrier 1964).

The structure of the aquifer was highlighted by geophysical prospection carried out by the General Company of Geophysics in 1970 that was supplemented by the surveys carried out in the alluvial plain. The prospection and the surveys showed the presence, under the alluvia, of a coarse formation made up of rollers, gravels (generally sandy), and of sand, corresponding to Miocene (Clinckx 1973).

MATERIALS AND METHODS

Chemical Data

Surface water ($n = 4$) and groundwater samples ($n = 20$) from the Soummam basin were collected in April 2007 (Fig. 1). Four surface water samples were selected in the studied area along the flow path from upstream to downstream of the watershed (Akbou, Sidi Aich, El-Kseur and Bejaia). Twenty wells currently in use were selected based on the preliminary field survey carried out to understand the overall distribution of the various types of wells in the

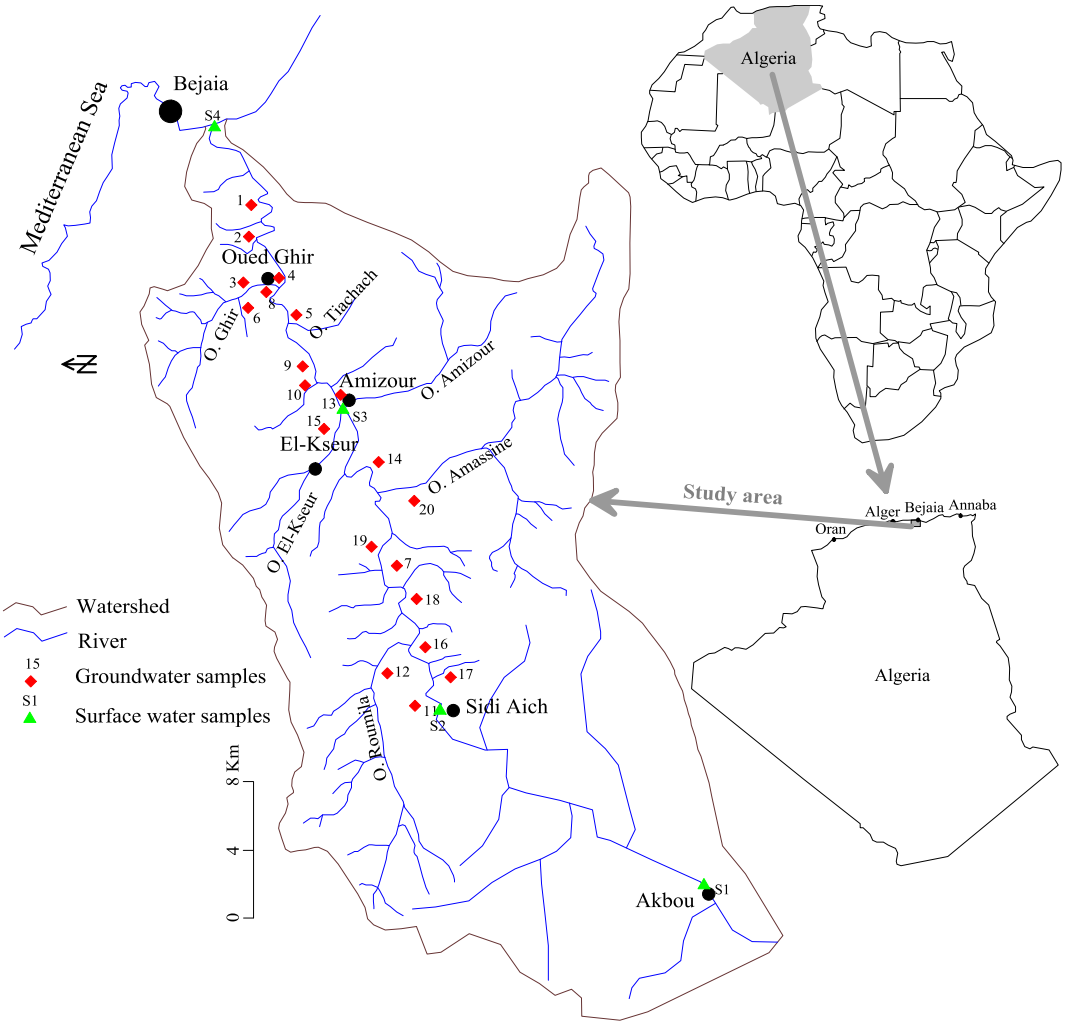

Figure 1. Water sampling locations in the study area.

studied area. The selected wells are used for domestic, agricultural, and domestic/agricultural purposes and were found to be uniformly distributed over the area of concern.

The samples were analyzed following the methods outlined in the American Public Health Association manual (APHA 1989, 1995a, b). Water samples were collected in stopper-fitted polyethylene bottles and refrigerated at 4 °C in order to be analyzed as soon as possible. Conductivity, temperature, and pH were measured in situ using a portable water tester.

The water samples were analyzed for major and trace elements. Anions analyzed include sulfate, chloride, bicarbonate, and nitrate. Cations analyzed include calcium, magnesium, sodium, and potassium. Trace elements analyzed include Fe, Zn, SiO_2, and Al. Calcium, Mg, HCO_3, and Cl were analyzed by volumetric titrations. Concentrations of Ca and Mg were estimated titrimetrically using 0.05 N and 0.01 N EDTA and those of HCO_3 and Cl by H_2SO_4 and $AgNO_3$ titration, respectively. Concentrations of Na and K were measured using a flame photometer (Model: Systronics Flame Photometer 128) and that of sulfate (SO_4) by turbidimetric method (Clesceri et al. 1998). Nitrate (NO_3) was analyzed by colorimetry with a UV–visible spectrophotometer (Rowell 1994). Standard solutions for the above analysis were prepared from the respective salts of analytical reagents grades. Trace elements were determined by graphite furnace atomic absorption spectrophotometer (Perkin–Elmer AAnalyst 700) using multi-element Perkin–Elmer standard solutions. The accuracy of the chemical analysis was

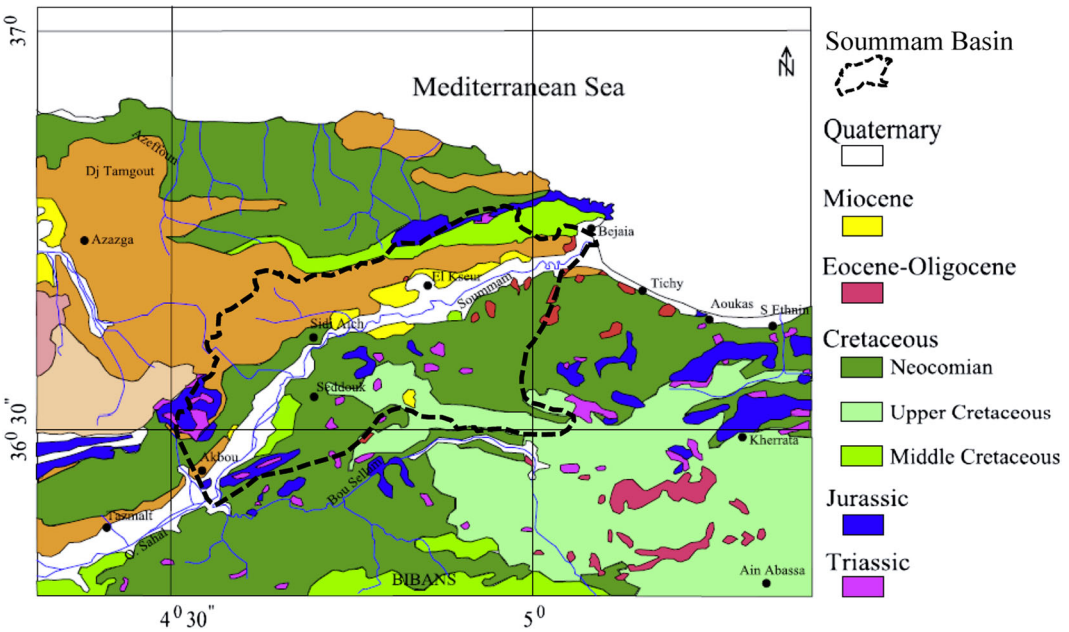

Figure 2. Geological map of the study area.

verified by calculating ion-balance errors where the errors were generally within 10%.

Multivariate Statistical Methods

The water quality data sets were subjected to cluster analysis (CA), discriminant analysis (DA), and analysis of variance (ANOVA). These techniques were applied to experimental data, standardized through z-scale transformation to avoid misclassifications arising from the different orders of magnitude of both numerical values and variance of the parameters analyzed (Liu et al. 2003; Simeonov et al. 2003). All mathematical and statistical computations were made using Microsoft Office Excel 2008 and STATISTICA 8.

Cluster Analysis

Cluster analysis is the name given to an assortment of techniques designed to perform classification by assigning observations to groups such as each group is more-or-less homogeneous and distinct from other groups (Davis 1986). As an exploratory technique with graphic output, CA does not require many of the assumptions that other statistical methods do, except that the data are heterogeneous. It provides an easily understood graphic display (dendrogram), and is a method used frequently in the geological sciences to help classify or group samples/variables of a data set. It helps to identify natural groupings for samples (Q-mode), and in turn, reduces the size of the samples/variables into smaller numbers of groups.

Discriminant Analysis

Discriminant analysis is a multi-component statistical technique that has been used in many geochemical studies (Suk and Lee 1999; Ashley and Lloyd 1978; Kim et al. 2005; Güler and Thyne 2004; Vaseli et al. 1997) to classify water sampling into mutually exclusive and exhaustive groups on the basis of a set of independent variables. The linear combinations of the independent variables found by DA will discriminate the groups in such a way that the misclassification error rates are minimized. This objective is achieved by maximizing the between-group variance to the within-group variance (Swanson et al. 2001).

To perform the DA, we need a qualitative dependent variable and a set of independent variables. The categorical-dependent variable is a grouping factor that allows each object to be placed in only one of the defined groups. In the linear discriminant equation:

$$D = B_0 + B_1X_1 + B_2X_2 + \cdots + B_pX_p \quad (1)$$

X_1, X_2, …, X_P are the values of the independent variables, and B_0, B_1, B_2,…, B_P are the coefficients estimated from the data. The obtained function allows discriminating in the best way among the objects belonging to different groups; it, therefore, constitutes itself as a quality index, which integrates all the available information into a single variable (Taboada et al. 1997).

Analysis of Variance

Analysis of variance is a statistical technique to test for significant differences between means with respect to their variances (Snedecor and Cochran 1989). It tests whether the variation from the mean value of hydrochemical element concentration for a categorical variable class is significantly less than the variation from the mean values of the different categorical variable classes.

RESULTS AND DISCUSSION

Cluster Analysis

The hydrochemical data with complete analysis of the variables were classified by hierarchical cluster analysis (HCA) in 12-dimensional space (Ca, Mg, Na, K, Cl, HCO_3, SO_4, NO_3, Fe, Zn, SiO_2, and Al); and the result is presented as a dendrogram (Fig. 3). Three preliminary groups are selected based on visual examination of the dendrogram. Each representing a hydrochemical facies. The choice of the number of clusters is subjective and the optimal number of groups depends on the researcher, since there is no test to determine the optimum number of groups in the data set (Güler et al. 2002). However, the large linkage distances between groups 1, 2, and 3 suggest that three groups exist in the data set (Fig. 3). Detailed evaluation of the data (comparing Fig. 3 and Table 1) revealed that group 1 samples are exclusively surface water and groups 2 and 3 samples are groundwater.

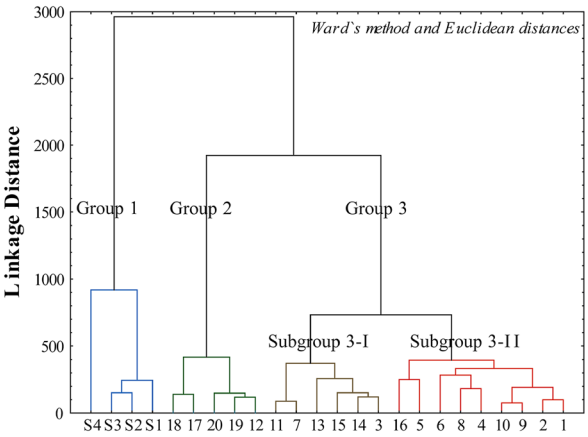

Figure 3. Dendrogram of Q-mode cluster analysis.

Group 1

The EC in this cluster (surface water) ranges from 2,950 to 5,480 μS/cm with a mean value of 3,610 μS/cm. The EC shows strong positive correlation with Ca, Mg, Na, Cl, SO_4, SiO_2, and Al, and the mean value of pH is 8.03 indicating that the surface water of the study area is mainly alkaline in nature. The abundance of the major cations and anions in surface water (group 1) is in the following order: $Mg > Na > Ca > K$ and $SO_4 > HCO_3 > Cl > NO_3$, respectively (Fig. 4). The desirable limit of Mg for drinking water is specified as 50 mg/l and that of SO_4 as 200 mg/l (WHO 2006). Based on the data, all the surface water samples from the study area are within the permissible limit for Mg but exceed that for SO_4. Higher sulfate concentrations in the water indicate breaking of organic substances from topsoil/water, leachable sulfate present in fertilizer and other human influences (Miller 1979; Craig and Anderson 1979). Most of the surface water samples from the study area exceed the desirable limit of 0.3 mg/l for Fe (WHO 2006).

Group 2

The second group represents groundwater in the southwestern part of the study area (Fig. 1). The EC varies from 540 to 2,380 μS/cm with a mean value of 1,395 μS/cm. The general dominance of anions was in the following order: $Cl > SO_4 > HCO_3 > NO_3$ (Fig. 4). The concentration of Cl was higher than those in the other groups and ranges from 35.5 to 319.5 mg/l with a mean of 142.53 mg/l. The order of the general dominance of cations is: $Mg > Ca > Na > K$ (Fig. 4). Magnesium is the most abundant cation, with concentrations ranging from

Table 1. Parameter Values of the Three Principal Water Groups

	Cluster 1				Cluster 2			
	Min	Max	Mean	SD	Min	Max	Mean	SD
T	21	26	24	2	18	20	19	1
pH	7.74	8.20	8.03	0.21	7.46	8.02	7.76	0.20
EC	2,950	5,480	3,610	1,247	540	2,380	1,395	771
Ca	399	506	428.75	51.64	96	172	124.20	32.78
Mg	322	602	468.75	126.10	66.20	120	79.72	22.68
Na	416	627	517.50	86.27	17.80	49.36	33.83	11.80
K	2.33	3.34	2.78	0.46	0.84	10.81	3.39	4.28
Cl	339.40	887.50	483.68	269.30	35.50	319.50	142.53	123.52
SO_4	248	620	393	160.28	101	255	160.20	61.02
HCO_3	275.70	346	308.18	32.58	235.90	343	275.05	44.54
NO_3	25.82	70.55	44.67	22.02	20.31	94.50	47.59	33.20
Fe	0.090	5.750	2.798	2.559	0.001	0.045	0.015	0.020
Zn	0.030	0.390	0.165	0.158	0.090	0.428	0.174	0.143
SiO_2	11.40	15.80	13.28	1.89	10.30	17.30	12.04	2.97
Al	0.010	0.040	0.020	0.014	0.010	0.040	0.020	0.014
	Cluster 3-I				Cluster 3-II			
	Min	Max	Mean	SD	Min	Max	Mean	SD
T	16	21	19	2	18	21	20	1
pH	7.06	8.03	7.45	0.33	6.81	8.11	7.16	0.41
EC	1,047	2,120	1,595	427	806	3,440	2,183	733
Ca	70	201	123.50	57.44	100	292	166.22	72.67
Mg	176	300	251	46.57	148	340	262.22	64.19
Na	61.40	139.64	92.73	29.56	42.68	282.95	157.24	71.42
K	1.25	22.73	7.02	8.09	3.14	24.92	6.49	6.95
Cl	34.08	63.90	48.99	10.43	30.10	61.18	43.58	10.64
SO_4	290	455	387.83	55.98	430	730	575.78	99.36
HCO_3	158.60	475.80	319.64	111.67	261.08	402.60	347.29	40.81
NO_3	14.28	49.07	25.23	13.75	12.65	170.52	65.24	49.38
Fe	0.003	0.024	0.013	0.008	0.003	0.048	0.024	0.015
Zn	0.560	1.766	1.144	0.509	0.411	1.880	0.914	0.465
SiO_2	10.20	14.50	11.62	1.81	11.40	16.70	13.48	1.74
Al	0.010	0.030	0.017	0.008	0.010	0.070	0.038	0.018

All values are in mg/l except pH, T (°C) and EC (μSiemens/cm).
Min Minimum, *Max* maximum, *SD* standard deviation.

66.20 to 120 mg/l and a mean value of 79.72 mg/l, and calcium ion concentrations range from 96 to 172 mg/l with a mean of 124.2 mg/l. Both Ca and Mg concentrations in the groundwater are quite consistent and account for creating major water types in this group.

Group 3

The last group (groundwater) is further classified into two subgroups representing different residence times, recharge, circulation, water–rock interactions, and anthropogenic influences.

Group 3-I: This group is located at the center of the area (Fig. 1). The concentrations of HCO_3, Mg, and Ca in waters in this group were higher than those in group 2 and lower than those from group 3-II (Fig. 4).

Group 3-II: This subgroup of waters is found in the northeast part of the study area, which is the discharge area of the regional groundwater system (Figs. 1 and 4). These waters have Mg–Ca–HCO_3–Cl-type water with high EC values indicating pollution ($806 < EC < 3{,}440$ μS/cm; Table 1).

Table 2. Wilks' Lambda and Chi Square Test of DA of Water Quality

Functions	*R*	Wilks' Lambda	Chi Square	*p* Level
1	0.98	0.0015	109.989	0.000000
2	0.96	0.0510	50.596	0.000005
3	0.62	0.6134	8.307	0.216441

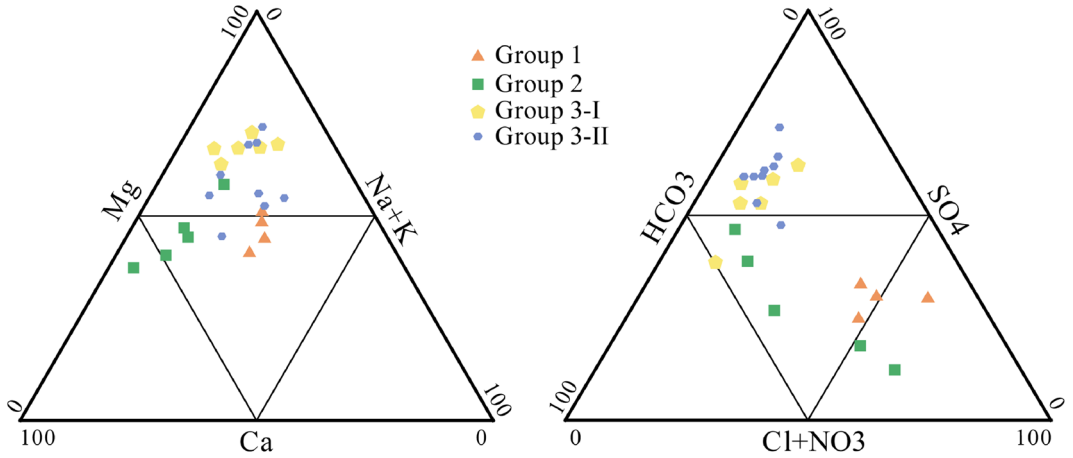

Figure 4. Ca–Mg–(Na + K) and HCO_3–SO_4–Cl–NO_3 trilinear diagrams for group samples.

Discriminant Analysis

Discriminant Analysis was performed on the raw data set comprised of 15 parameters. The objectives of DA in this study were (1) to test the significance of discriminant functions and (2) to determine the most significant variable associated with the differences between the groups. As shown in Table 2, the values of Wilks' lambda were small and those of Chi square were rather high for each discriminant function. These indicate that the DA in this study was valid and effective.

Discriminant functions (DFs) and classification matrices (CMs) were obtained from the forward stepwise mode of DA (Tables 3 and 4, respectively). In forward stepwise mode, variables were included step-by-step, beginning with the most significant, until no significant changes were obtained. Only 8 out of the 15 parameters analyzed were proven important in discriminating the location of the groups. The seven parameters which were of no importance in differentiating the water groups were T, pH, Ca, K, HCO_3, Zn, and Al. The first two DF accounted 98.6% of the variation in group separation. The scatter plot of DFs 1 and 2 is shown in Figure 5. Among the three groups, group 1 is clearly separated from groups 2 and 3, whereas little overlap is seen between subgroups 3-I and 3-II.

Hydrogeochemical Processes

Saturation State

In order to investigate thermodynamic controls on the water composition, equilibrium speciation calculation was performed using PHREEQC (Parkhurst and Appelo 1999). These calculations provided saturation indices (SI) of minerals that might be reacting in the system. The SI of a particular mineral can be defined as

$$\mathrm{SI} = \log(\mathrm{IAP} / K_T), \qquad (2)$$

where IAP is the ion activity product of the mineral–water reaction and K_T is the thermodynamic equilibrium constant adjusted to the temperature of the given sample. The SI values of the three groups are listed in Table 5. All groups are super-saturated with Ca-montmorillonite, dolomite, gibbsite, K-mica, kaolinite, and quartz, and all these groups are undersaturated with albite, anhydrite, anorthite, $CO_{2(g)}$, gypsum, halite, melanterite, and smithsonite.

Inferring the sources of solutes in groundwater using simple mass-balance approaches does not provide unequivocal results, but does provide, in the absence of detailed mineralogical analyses, a reasonable way of constraining the processes that might

Table 3. Classification Functions Coefficients for DA of Water Quality

Discriminant Function	1	2	3
Percent separation	73.2	25.3	1.4
Cumulative separation	73.2	98.6	100.0
Parameter	Factor structure coefficients (correlations between parameters in the model and the discriminant functions)		
Na	0.48	−0.40	−0.09
SO_4	−0.07	−0.50	−0.33
NO_3	−0.01	−0.05	−0.55
Cl	0.26	0.03	−0.05
Mg	0.23	−0.40	0.48
Fe	0.20	−0.06	0.06
EC	0.15	−0.17	−0.20
SiO_2	0.02	−0.09	−0.38

Table 4. Classification Matrix for DA of Water Quality

Prior Classification	% Correct	Assigned by DA			
		Cluster 1	Cluster 2	Cluster 3-I	Cluster 3-II
Cluster 1	100	4	0	0	0
Cluster 2	100	0	5	0	0
Cluster 3-I	100	0	0	6	0
Cluster 3-II	100	0	0	0	9
Total	100	4	5	6	9

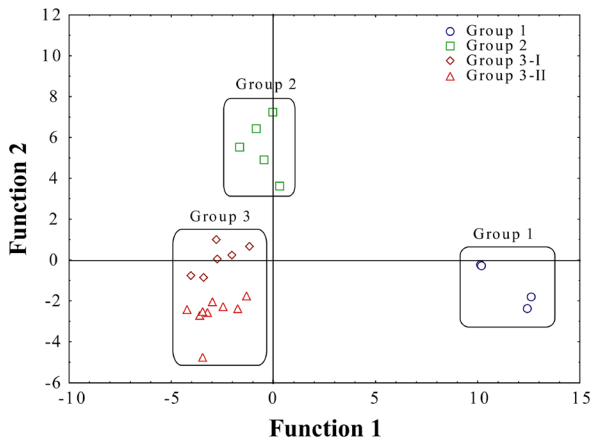

Figure 5. Bivariate plot of discriminant functions 1 and 2.

influence the major-ion chemistry. The controls on the hydrochemical evolution of groundwater largely depend on the chemistry of the recharging water, water-aquifer matrix interaction (e.g., cation exchange), or both, as well as groundwater residence time within the aquifer. Three general processes contribute solutes to groundwater: evaporite dissolution, carbonate dissolution, and silicate weathering (Garrels and MacKenzie 1971). The chemistry of the evolving water depends not only on the bulk chemistry of the matrix but also on the rate of weathering. Meybeck (1987) commented that weathering rates of evaporites and carbonates are up to 80 times and ~12 times, respectively, faster than silicate weathering rates. Hence, even relatively minor proportions of carbonates and evaporites can significantly influence water chemistry.

In natural systems, carbonate mineral dissolution can be written as (Garrels and Mackenzie 1971):

$$CaCO_3(\text{calcite}) + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \quad (3a)$$

$$CaMg(CO_3)_2(\text{dolomite}) + 2\,H_2CO_3 \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \quad (3b)$$

$$CaCO_3 + H_2SO_4 \rightarrow Ca^{2+} + SO_4^- + H_2CO_3 \quad (4a)$$

$$CaMg(CO_3)_2 + 2H_2SO_4 \rightarrow Ca^{2+} + Mg^{2+} + 2SO_4^- + 2H_2CO_3 \quad (4b)$$

Table 5. Statistical Summary of Thermodynamic Speciation Calculation of Saturation Indices Using PHREEQC

Phase	Group 1					Group 2				
	Min	Max	Mean	SD	CV	Min	Max	Mean	SD	CV
Albite	−1.19	−0.41	−0.93	0.35	−37.89	−2.51	−1.09	−1.94	0.58	−29.83
Anhydrite	−1.36	−0.94	−1.15	0.18	−15.45	−1.82	−1.52	−1.62	0.12	−7.32
Anorthite	−3.06	−1.70	−2.56	0.61	−23.75	−3.52	−1.73	−2.88	0.78	−27.20
Aragonite	0.88	1.25	1.12	0.17	15.62	0.23	0.60	0.45	0.15	32.70
Ca-montmorillonite	0.20	1.17	0.68	0.40	58.66	0.44	3.12	1.66	1.08	65.01
Calcite	1.03	1.40	1.27	0.17	13.61	0.38	0.75	0.60	0.15	24.52
Chalcedony	−0.16	−0.04	−0.09	0.06	−62.86	−0.15	0.07	−0.09	0.09	−101.77
Chlorite	4.18	9.69	6.70	2.57	38.34	−2.90	1.73	0.56	1.95	350.13
$CO_{2(g)}$	−2.95	−2.37	−2.73	0.27	−10.03	−2.73	−2.18	−2.41	0.21	−8.63
Dolomite	2.51	3.24	2.90	0.35	11.97	0.62	1.54	1.28	0.39	30.32
Gibbsite	0.18	0.39	0.30	0.11	35.93	0.34	1.18	0.80	0.37	45.78
Gypsum	−1.14	−0.73	−0.92	0.18	−18.97	−1.58	−1.28	−1.38	0.12	−8.59
Halite	−5.50	−4.97	−5.34	0.25	−4.65	−7.50	−6.50	−7.09	0.39	−5.44
Illite	0.07	1.08	0.45	0.44	98.65	−0.15	2.55	1.02	1.00	98.06
K-feldspar	−1.08	−0.42	−0.85	0.30	−35.14	−1.43	0.31	−0.74	0.73	−97.59
K-mica	4.88	5.98	5.34	0.47	8.75	4.84	8.25	6.44	1.24	19.24
Kaolinite	1.72	2.38	2.10	0.28	13.56	2.09	4.19	3.12	0.86	27.56
Melanterite	−7.24	−5.43	−6.04	0.83	−13.66	−9.12	−7.42	−8.41	0.85	−10.14
Quartz	0.27	0.39	0.35	0.06	16.65	0.30	0.51	0.36	0.09	24.06
Siderite	−0.11	1.40	0.91	0.70	77.41	−2.68	−0.68	−1.72	0.91	−52.63
Smithsonite	−2.18	−1.02	−1.56	0.48	−31.02	−1.74	−0.96	−1.48	0.30	−20.52
Phase	Group 3-I					Group 3-II				
	Min	Max	Mean	SD	CV	Min	Max	Mean	SD	CV
Albite	−1.85	−1.42	−1.59	0.14	−8.88	−1.33	−0.32	−0.92	0.36	−39.02
Anhydrite	−1.63	−1.23	−1.44	0.14	−9.60	−1.43	−0.95	−1.19	0.16	−13.14
Anorthite	−3.83	−2.65	−3.11	0.44	−14.11	−3.00	−1.75	−2.28	0.42	−18.32
Aragonite	−0.40	0.60	0.06	0.40	678.51	−0.48	0.59	−0.07	0.35	−496.91
Ca-montmorillonite	1.19	3.37	2.10	0.82	38.85	2.04	4.81	3.59	0.94	26.20
Calcite	−0.25	0.75	0.21	0.40	190.10	−0.33	0.74	0.08	0.35	447.92
Chalcedony	−0.17	−0.02	−0.10	0.06	−62.72	−0.12	0.06	−0.03	0.06	−171.03
Chlorite	−3.38	4.78	0.09	2.77	3131.19	−4.91	4.76	−1.45	2.71	−187.01
$CO_{2(g)}$	−2.95	−1.61	−2.08	0.45	−21.68	−2.81	−1.34	−1.73	0.46	−26.62
Dolomite	0.16	1.94	1.03	0.69	67.05	0.15	1.86	0.66	0.58	88.67
Gibbsite	0.62	1.73	1.05	0.41	39.12	0.89	2.09	1.63	0.43	26.20
Gypsum	−1.39	−0.99	−1.20	0.14	−11.51	−1.19	−0.71	−0.95	0.16	−16.43
Halite	−7.28	−6.78	−7.00	0.20	−2.86	−7.24	−6.60	−6.86	0.20	−2.88
Illite	0.86	2.32	1.55	0.60	38.90	1.70	3.74	2.80	0.68	24.43
K-feldspar	−1.06	0.24	−0.48	0.52	−106.61	−0.47	0.86	0.04	0.42	1176.73
K-mica	6.23	8.29	7.20	0.88	12.18	7.44	10.12	8.88	0.93	10.46
Kaolinite	2.71	4.88	3.61	0.79	21.77	3.36	5.93	4.89	0.88	17.98
Melanterite	−8.29	−7.34	−7.78	0.33	−4.21	−8.17	−6.94	−7.43	0.45	−6.02
Quartz	0.27	0.43	0.35	0.06	17.78	0.32	0.50	0.41	0.06	13.84
Siderite	−2.19	−1.04	−1.66	0.45	−27.29	−2.53	−0.62	−1.68	0.59	−34.80
Smithsonite	−1.10	−0.61	−0.82	0.20	−24.74	−1.69	−0.82	−1.14	0.30	−26.33

SD Standard deviation, *CV* coefficient of variation.

Hence, in a closed system with predominant carbonate weathering, Ca and Mg concentrations should be proportional to HCO_3 and SO_4 at Ca + Mg concentrations <∼2000 meq/l (Stallard and Edmond 1987). Inputs of Ca, Mg, and HCO_3 from carbonate weathering are mostly limited by $SI_{calcite}$ and somewhat by $SI_{dolomite}$ (Langmuir 1971). In systems dominated by

carbonate weathering, values of P_{CO_2} (CO_2 pressure) are generally up to a few orders of magnitude higher than that of the atmosphere ($10^{-3.5}$ atm).

Clay minerals as insoluble remnants can be formed during an incongruent dissolution of aluminosilicates. The stability diagrams of anorthite, albite, potassium feldspar, and biotite provide for better understanding of stability relations between minerals and groundwater in a complicated thermodynamic system. In this instance, the stock of silica is important to measure, because the effect of silicate weathering on water chemistry is primarily expressed as addition of cations (Na, Ca, Mg, and K) and silica.

Using albite as an example, the transformation into different weathering products can be described by the following equations (Appelo and Postma 1993):

$$3NaAlSi_3O_8(\text{albite}) + Mg^{2+} + 4H_2O \rightarrow 2Na_{0.5}Al_{1.5}Mg_{0.5}Si_4O_{10}(OH)_2(Na-\text{Mont}) + 2Na^+ + H_4SiO_4 \quad (5)$$

$$2NaAlSi_3O_8(\text{albite}) + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4(\text{kaolinite}) + 2Na^+ + 4H_4SiO_4 \quad (6)$$

The change of albite into kaolinite and montmorillonite clay minerals represents an increasing removal intensity of silica and sodium cations from the weathering product. When albite transforms into montmorillonite, groundwater leaches 89% and if into kaolinite ~33% of silica (Appelo and Postma 1993). Which clay mineral will form depends also on groundwater exchange intension.

Thermodynamic analysis demonstrates that when albite, anorthite, and biotite are hydrolyzed, all data points locate in the stability plot of kaolinite (Fig. 6). The main reactions of aluminosilicate transformation into kaolinite are (Appelo and Postma 1993):

$$2KAlSi_3O_8(K-\text{feldspar}) + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4(\text{kaolinite}) + 2K^+ + 4H_4SiO_4 \quad (7)$$

$$CaAl_2Si_2O_8(\text{anorthite}) + 2H^+ + H_2O \rightarrow Al_2Si_2O_5(OH)_4(\text{kaolinite}) + Ca^{2+} \quad (8)$$

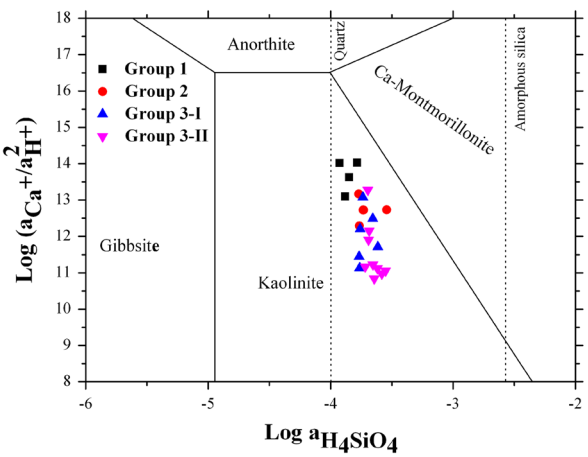

Figure 6. Stability field of Ca–Al silicate phases relative to water samples.

Variation of Saturation Indices Between the Three Groups

Analysis of variance was used to classify and test the significance ($p < 0.05$, least-significance difference, LSD) of saturation indices and groups found by CA. Relationships among the considered variables were tested using Pearson's coefficient with statistical significance set priori at $p < 0.05$ (Li et al. 2008; Alkarkhi et al. 2008). The ANOVA results (Table 6) indicate that the saturation indices of each of the mineral phases are significant except for chalcedony and quartz ($p > 0.05$).

The saturation indices of Ca-montmorillonite, illite, gibbsite, K-mica, and kaolinite increase from group 1 to subgroup 3-II, and these mineral phases represent super-saturated in all groups (Fig. 7a, b). The SI values of albite, anhydrite, anorthite, gypsum, and chalcedony increase in the groundwater from the group 2 to subgroup 3-II, and the SI values of these minerals are under-saturation (Fig. 7d). The variation of SI for aragonite, calcite, chlorite, and dolomite between the three groups is significant and the values of SI of these minerals decrease from group 1 to subgroup 3-II (Fig. 7c). The SI values of anorthite, halite, melanterite, and siderite are under-saturation in the three groups, and their variations are significant (Fig. 7e). Most silicate and carbonate minerals are super-saturated in the three groups, but all evaporite minerals are under-saturated in these groups.

Table 6. Analysis of Variance for SI in the Soummam Basin

Phase	Sum of Squares	df	Mean Square	F	*p* Level
Albite	4.42	23	1.47	10.39	0.000248
Anhydrite	0.81	23	0.27	12.17	0.000094
Anorthite	2.85	23	0.95	3.21	0.045232
Aragonite	4.37	23	1.46	14.85	0.000026
Ca-montmorillonite	27.89	23	9.30	11.97	0.000104
Calcite	4.35	23	1.45	14.81	0.000026
Chalcedony	0.02	23	0.01	1.47	0.253728
Chlorite	187.71	23	62.57	9.47	0.000423
$CO_{2(g)}$	3.27	23	1.09	7.00	0.002100
Dolomite	14.35	23	4.78	15.77	0.000017
Gibbsite	5.58	23	1.86	12.92	0.000064
Gypsum	0.78	23	0.26	11.85	0.000111
Halite	8.95	23	2.98	46.12	0.000000
Illite	19.64	23	6.55	12.87	0.000066
K-feldspar	3.15	23	1.05	4.11	0.019976
K-mica	41.50	23	13.83	15.77	0.000017
Kaolinite	24.65	23	8.22	13.17	0.000057
Melanterite	13.14	23	4.38	12.37	0.000085
Quartz	0.02	23	0.01	1.53	0.236753
Siderite	22.45	23	7.48	17.52	0.000008
Smithsonite	1.80	23	0.60	5.98	0.004405

df Degrees of freedom.

Identification of Rock-Weathering Sources

The geochemical variations of the ionic concentrations of water can easily be understood when they are plotted along X–Y coordinates (Güler et al. 2002). The graph of Ca + Mg versus SO_4 + HCO_3 will feature above 1:1 line if dissolutions of calcite, dolomite, and gypsum are the dominant reactions in the system. The plot of Ca + Mg versus SO_4 + HCO_3 (Fig. 8) shows that all of the points are located in the left side due to an excess of (Ca + Mg). An excess of Ca and Mg in the surface water and groundwater of Soummam area may be due to the exchange of Na present in the water with Ca and Mg in clay materials.

To examine the effect of lithological weathering in the Soummam area, two mixing diagrams using Na-normalized molar cation ratios were plotted (Fig. 9a, b; Gaillardet et al. 1999). Mg/Na ratios vary from 0.73 to 1 in surface water (group 1) and from 0.96 to 4.62 in groundwater, while Ca/Na ratios vary from 0.45 to 0.55 in the first group and from 0.29 to 5.54 in the other groups (Fig. 9a, b). Groundwater samples plotted between silicate and carbonate end-members, and surface water samples near the evaporite end-member. However, these samples are probably related to evaporite dissolution.

The Na vs. Cl graph (Fig. 10) suggests that either sea aerosols or halite dissolution is partially responsible for Na in the groundwater. The Na/Cl ratios in the surface water (group 1) ranged between 3.41 and 6.04, and all samples of this water plot above from the 1:1 line. Excess Na can be derived from sources that include plagioclase (albite) dissolution as per Eq. (6) or cation exchange (natural water softening) as shown by Eq. (9)

$$0.5\ Ca^{2+} + Na - clay \rightarrow 0.5\ Ca - clay + Na^{+} \quad (9)$$

Most samples of groundwater (groups 2 and 3) plot below the 1:1 line, suggesting that reverse ion exchange also occurs, but is not a major process responsible for chemical evolution of groundwater in this area.

Inverse Geochemical Modeling

The inverse modeling approach in the study of groundwater systems is the easiest way to evaluate mass exchanges between waters related to some extent to the same flow path. The PRHEEQC code, version 2.18, operating with the LLNL database, was used to perform inverse modeling on a few

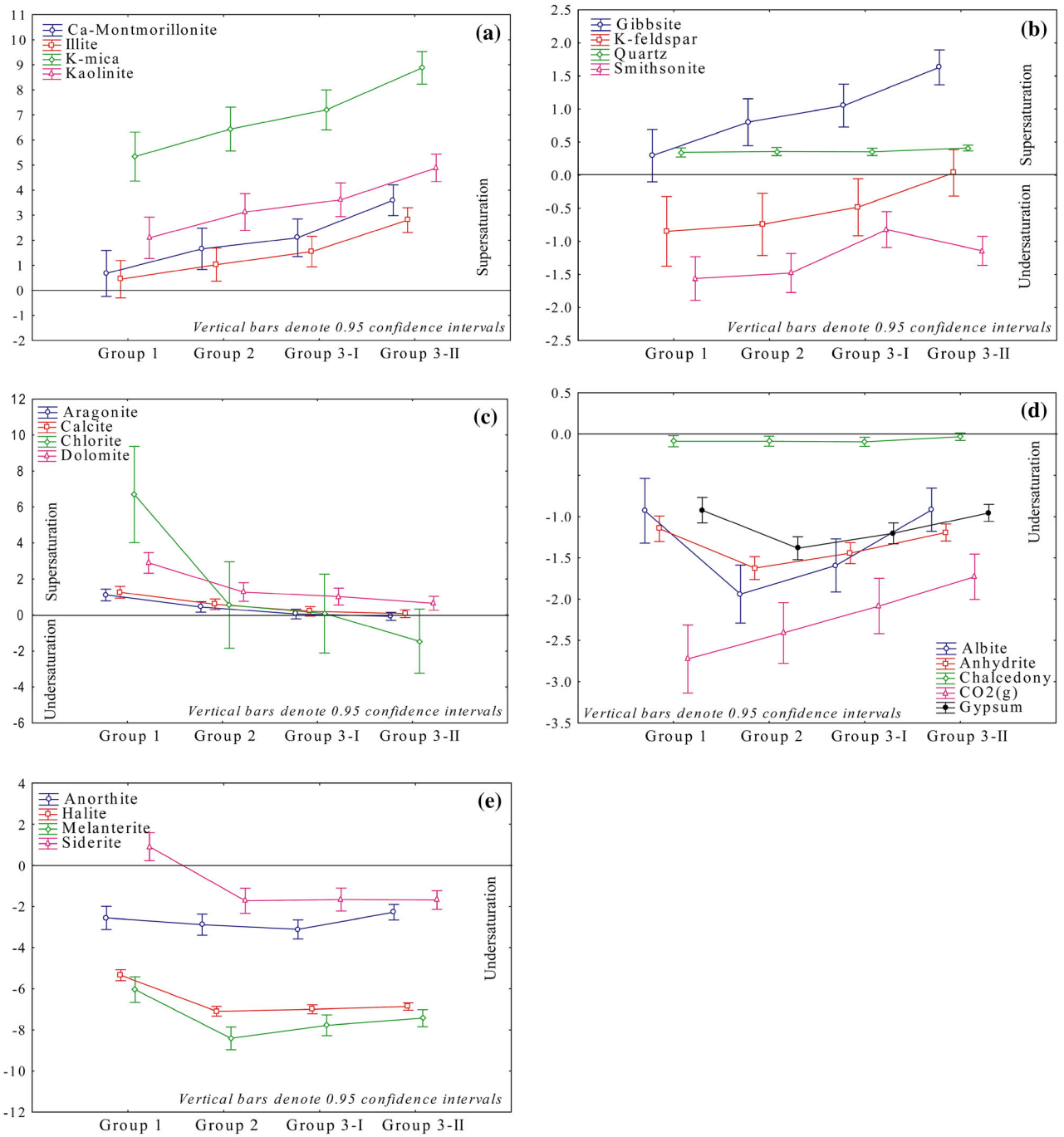

Figure 7. Variation of saturation indices in the principal water groups.

evolutionary samples, which were thought to be representative of different stages of water–rock interaction. This first modeling, together with information on local petrography, gave an idea of which solid phases were probably involved in the water–rock interaction process; these solid phases were then used as constraints for the reaction path modeling (Belkhiri et al. 2011). The following evolutionary waters were chosen for the simulation, based on the inferences described in Sect. 4.1: from group 1 (surface water) to group 2 (groundwater), from group 1 (surface water) to group 3-I

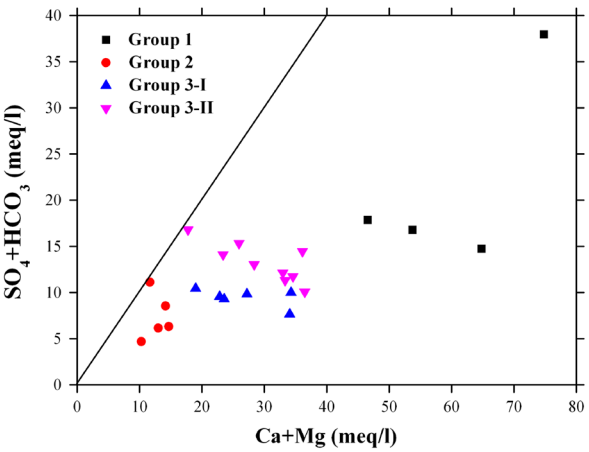

Figure 8. Relation between SO_4 + HCO_3 and Ca + Mg.

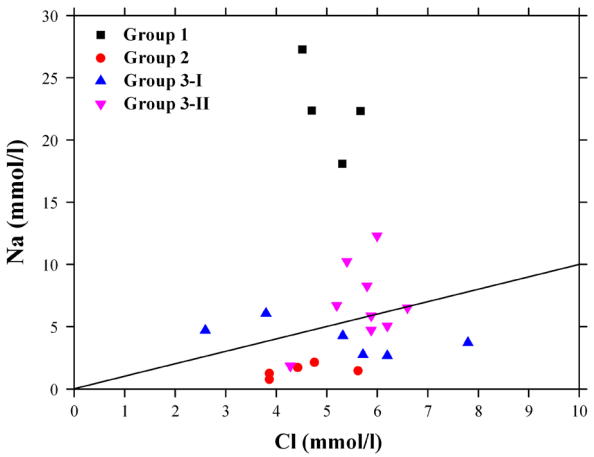

Figure 10. Relation between Na and Cl.

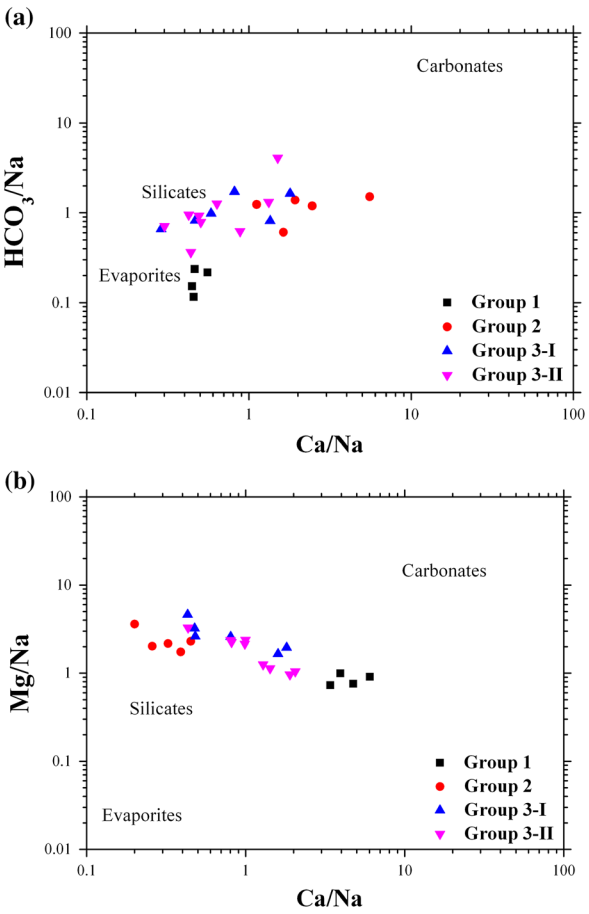

Figure 9. Molar ratio bivariate plots of **a** Na-normalized Ca and HCO_3 and **b** Na-normalized Ca and Mg.

(groundwater), and from group 1 (surface water) to group 3-II (groundwater). Input data were temperature, pH, major ion, Fe, Zn, Al, and SiO_2 contents.

Table 7. Results of Inverse Modeling

Simulation	1	2	3
Solution			
Initial	G1 (Surface water)	G1 (SW)	G1 (SW)
Final	G2 (groundwater)	G3-I (GW)	G3-II (GW)
Models obtained	9	12	18
Phases transferred	G1–G2	G1–G3-I	G1–G3-II
Albite	0.0491	0.1546	–
Anorthite	–	0.3602	0.2619
Ca-montmorillonite	−0.1212	−0.1193	–
Calcite	−0.3324	−1.119	−2.841
Chalcedony	–	0.3984	2.256
Chlorite	–	−0.0842	0.3121
$CO_{2(g)}$	0.2633	0.9009	4.346
Dolomite	−0.1662	−0.5593	−2.514
Gibbsite	−0.098	−0.2911	−5.025
Gypsum	–	–	2.27
Halite	–	–	−3.813
Illite	−0.0882	−0.1092	−1.06
K-feldspar	0.0491	0.1546	−1.06
K-mica	−0.049	−0.1492	−0.849
Kaolinite	−0.0882	−0.2686	−11.11
Melanterite	–	–	−8.826
Quartz	–	–	–
Siderite	–	–	8.161
Smithsonite	–	–	−0.0428

The amount of dissolving and precipitating minerals is expressed as mmol/kg water.

The results of all simulations are given in Table 7. Simulation 1 describes the evolution from group 1 to group 2. Albite, anorthite, $CO_{2(g)}$, gypsum, halite, K-feldspar, melanterite, siderite, and smithsonite were selected as dissolving phases, whereas Ca-montmorillonite, calcite, dolomite, gibbsite, illite, K-mica, kaolinite, and quartz as precipitating ones. In all the 9 obtained models, albite,

$CO_{2(g)}$ and K-feldspar were always dissolved, whereas Ca-montmorillonite, calcite, dolomite, gibbsite, illite, K-mica, and kaolinite always were precipitated.

The evolution from group 1 to group 3-I is represented by simulation 2. Dissolving and precipitating phases were chosen as in simulation 1. In the 12 resulting models, albite, anorthite, chalcedony, $CO_{2(g)}$, and K-feldspar were always dissolved and Ca-montmorillonite, calcite, chlorite, dolomite, gibbsite, illite, K-mica, and kaolinite were always precipitated.

Finally, simulation 3 represents the evolution from group 1 to group 3-II. In the 18 resulting models, anorthite, chalcedony, chlorite, $CO_{2(g)}$, gypsum, and siderite were always dissolved. Among the precipitating phases, calcite, dolomite, gibbsite, illite, K-feldspar, K-mica, kaolinite, melanterite, and smithsonite were always precipitated.

A general result of all the models was the dissolution of albite, which justifies Na enrichment during the chemical evolution of groundwater. Calcite, dolomite, Ca-montmorillonite, kaolinite, illite, gibbsite, and K-mica were always precipitated.

CONCLUSION

In this study, hierarchical cluster analysis (HCA), discriminant analysis (DA), analysis of variance (ANOVA), and geochemical modeling were used to determine the spatial variations of hydrochemical elements, and the control factors, and to identify the origin of these elements in surface and groundwater in the Soummam basin, Algeria. For this purpose, 20 well samples and 4 samples of surface waters were collected. The HCA grouped the 24 water samples into three groups based on the similarity of water quality characteristics. The first group is exclusively composed of surface water, but the second and the third groups consist of groundwater. This grouping was supported by the stepwise DA as 98.6% of the water samples were grouped. All groups are super-saturated with Ca-montmorillonite, dolomite, gibbsite, K-mica, kaolinite, and quartz, and under-saturated with albite, anhydrite, anorthite, $CO_{2(g)}$, gypsum, halite, melanterite, and smithsonite. ANOVA results indicate that the variation of the saturation indices of each mineral phase is significant except for chalcedony and quartz ($p > 0.05$). Therefore, the spatial similarities and differences may allow optimization of a monitoring program in the future by decreasing the number of sampling stations, the number of monitored parameters, and thus, the subsequent costs. The results obtained by inverse geochemical modeling indicate the dissolution of albite, which justifies Na enrichment during the chemical evolution of groundwater. Calcite, dolomite, Ca-montmorillonite, kaolinite, illite, gibbsite, and K-mica always precipitate.

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