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Hydrochemical characterization of surface water in the Timgad watershed, East Algeria

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ABSTRACT

Multivariate statistical methods, i.e. cluster analysis (CA) and analysis of variance (ANOVA), were used to assess spatio-temporal variation of the surface water quality of the Timgad, East Algeria. Two major hydrochemical facies were identified using Piper diagram. $MgHCO_3$ for the first and the second station, and $MgSO_4$ for the last station. The ANOVA results indicate that all parameters are significant except for Na, K, and HCO_3 in the first station and EC in the second, also pH and NO_3 in the last station. Cluster analyses were applied to 42 data points from the three stations after the data had been log-transformed and standardized for homogeneity. The application of hierarchical CA, based on all possible combinations of classification method, showed two main groups at each station. The major ion chemistry (Mg, Ca, HCO_3, and SO_4) in the three stations are derived from the anthropogenic sources and the water–rock interaction.

Keywords: Hydrochemistry; Cluster analysis; Analysis of variance; Surface water; Timgad watershed; East Algeria

1. Introduction

The increased demand for water due to agriculture expansion, growing population, and urbanization, as well as the frequent and intense drought episodes due to anticipated climatic change will cause water shortages in many Mediterranean coastal areas. Furthermore, since water resources management has become increasingly important for sustainable development of these regions, it is necessary to assess the suitability of water for agricultural use and human consumption. The quality of water is controlled by natural and anthropogenic factors that include geological structure and mineralogy of the watersheds and aquifers, the residence time, the reactions that take place within the aquifer as well as the type of land uses [1–12]. The interaction of natural and anthropogenic factors leads to various water types. According to Hamzaoui-Azaza et al. [13], the increased knowledge of geochemical evolution of water quality could lead to effective management of water resources. Thus, the quality of water is as important as quantity. By “proper management of water resources” is meant how the quality and quantity of water can be maintained in a sustainable manner.

The multivariate statistical techniques are the appropriate tool for a meaningful data reduction and interpretation of multi-constituent chemical and

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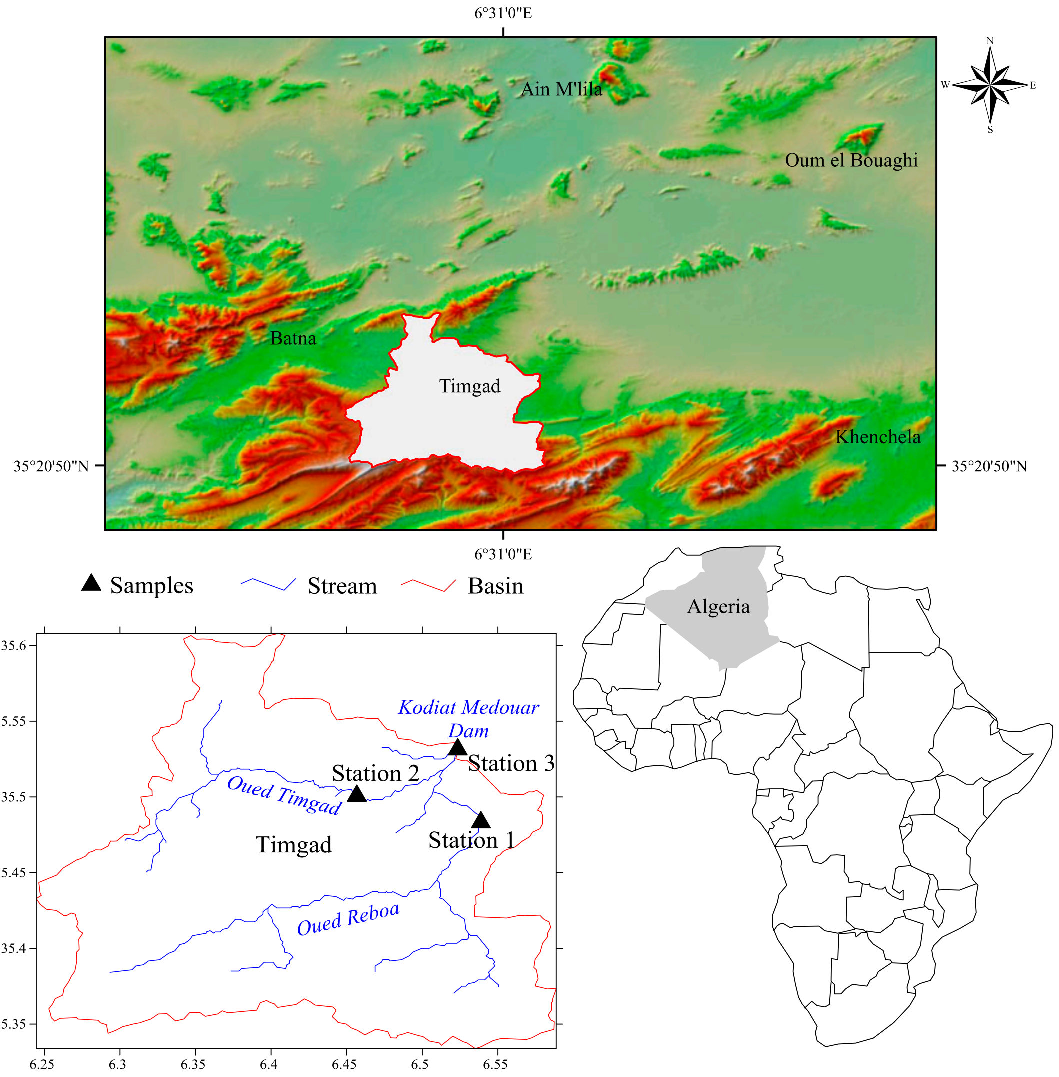

Fig. 1. Map showing the water sampling locations of the study area.

physical measurements [14]. The multivariate statistical techniques such as cluster analysis (CA) and analysis of variance (ANOVA) have been widely used as unbiased methods in analysis of water quality data to draw meaningful conclusions [15–22]. The multivariate analysis is widely used to characterize and evaluate water quality and it is useful for evidencing spatial variation caused by natural and anthropogenic processes [23–25].

The aim of the present study is to analyze the 11 physico-chemical parameters in surface water samples from the Timgad watershed. The large data-set obtained was subjected to the CA, DA, and ANOVA multivariate techniques to evaluate information about the similarities and dissimilarities present among the different sampling stations, to identify water quality variables for spatio-temporal dissimilarity, and to ascertain the influence of the pollution sources on the water quality parameters.

2. Study area

Timgad Basin belongs to a heterogeneous geographical space located in highlands of the region of Constantine (Algeria). It is located between four large watersheds: to the north Rhumel Kebir and Seybouse, to the east Medjerdah, to the south Chot Hodna and Melghir, and to the west Summam. Administratively, it is located 35 km east of the city of Batna, Algeria (Fig. 1). According to the topographic map of Batna, scale 1/200.000 the study area ranges between Lambert coordinates $X1 = 233$, $X2 = 263$, $Y1 = 822$, and

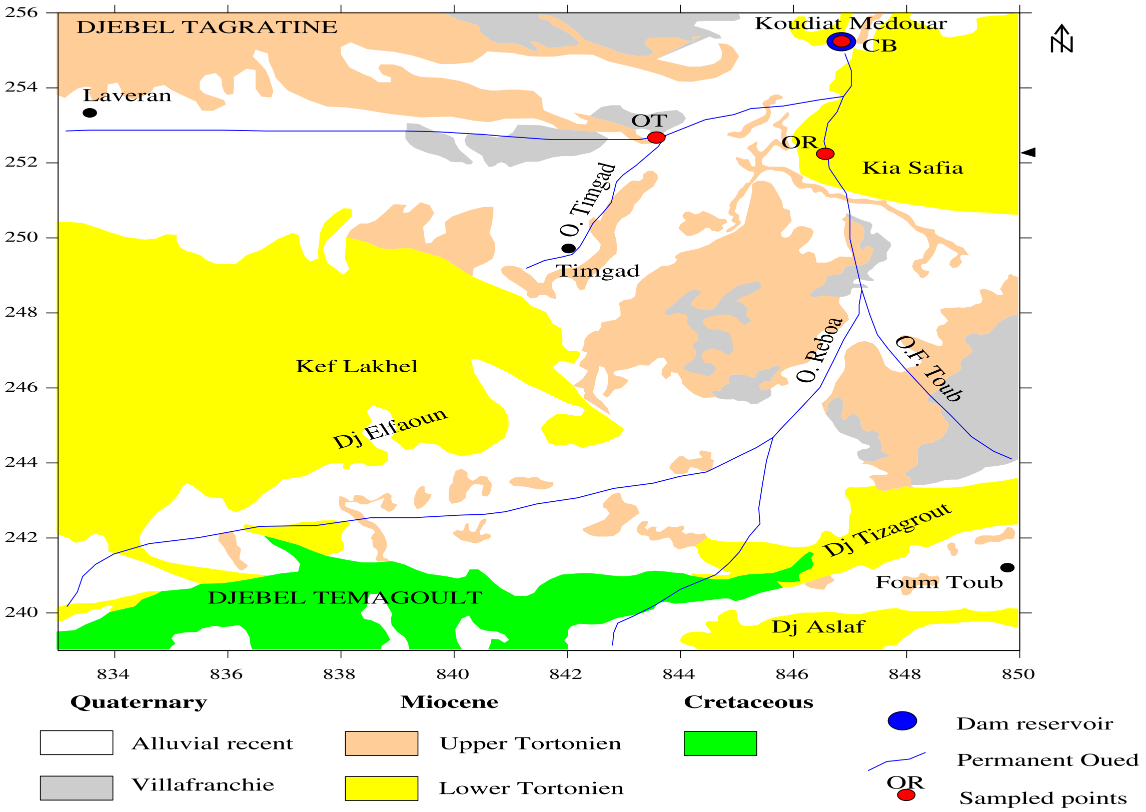

Fig. 2. Geology of the study area.

$Y2 = 852$. It spreads out over an area of 590 km^2, the basin area is controlled by a dam of the same name with a capacity of 62 million m^3 where the flow direction is from south to north. It is fed up by thunderstorms and wastewater of neighboring cities and villages. The climate of the watershed is semi-arid, characterized by high temperatures and low rainfall. The average annual rainfall is about 370 mm, while the annual average temperature is around 15°C [26,27]. The geological study of Algeria (map 1,000.000) shows that the Miocene depression is located north of the Aures massif [28,29] where the synorogenic depression has an accident. This is showed by a few anticlines whose heart is formed by the upper cretaceous which constitutes the main outcrops of the Aures Mountains and Jebel Bouarif. The tertiary is constituted by alternating silicate clay and sandstone, which occupies the Tagratine reliefs, and by white and coarse sandstone outcrop in many places. The basin of the dam, Oued Reboa, and Oued Timgad are located in a land of marine origin from the Miocene (limestone lithothamnium) with terminal gypsiferous formation of lower Pontian, bud upper Miocene (Fig. 2).

3. Materials and methods

3.1. Sample collection and analysis

Water samples were collected in stopper-fitted polyethylene bottles and refrigerated at 4°C in order to be analyzed as soon as possible. Monitoring was done on 42 samples at the three stations and each station with 14 samples (station 1: Oued Reboa, station 2: Timgad, and station 3: Dam) (Fig. 1). Two samples for each month from June to December 2009 and just one sample in January and February 2010, total of 14 samples for each station are analyzed. Only high pure chemicals (AnalR Grade) and double-distilled water were used in preparing solutions for analysis [30]. The electrical conductivity (EC), pH, and the temperature (T) were measured at the site by digital portable water analyzer kit (CENTURY-CK-710). Subsequently, the samples were analyzed in the laboratory and the chemical constituents such as calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), chloride (Cl), Sulfate (SO_4), bicarbonate (HCO_3), and nitrate (NO_3) were determined. Ca, Mg, HCO_3, and Cl were analyzed by volumetric titrations. Concentrations of Ca

Table 1
Statistical summary of hydrochemical parameters

	EC	pH	*T*	Ca	Mg	Na	K	Cl	SO_4	HCO_3	NO_3
Station 1 (14 samples)											
Min	509.9	7.1	7.0	78.6	72.4	70.3	13.1	14.2	71.0	225.3	0.5
Max	752.0	7.7	23.0	120.9	103.9	80.0	39.6	42.6	184.4	373.3	2.6
Mean	642.6	7.6	19.0	100	91.2	74.6	25.5	31.1	157.9	267.7	1.2
SD	93.7	0.2	4.7	11.9	9	3.2	7.1	9.3	31.9	44.6	0.6
Cv	14.6	2.4	24.6	11.9	9.9	4.3	27.7	30.1	20.2	16.7	52.5
Station 2 (14 samples)											
Min	848	6.8	7	89.8	77.6	115	12.3	71	68.8	213.5	0.2
Max	1,534	7.9	25	168.3	154.5	162.8	99.3	184.6	186	646.6	3.6
Mean	1,251.5	7.4	18.9	117.1	105.2	135	65.6	118.4	160.1	442.3	1.3
SD	217.6	0.3	4.8	22.6	21.9	15	22.3	31.1	37.7	149.2	1.1
Cv	17.4	4.2	25.7	19.3	20.8	11.1	34	26.3	23.5	33.7	88
Station 3 (14 samples)											
Min	575.3	6.8	10	73.7	61.4	35.7	9.5	17.8	69	97.6	0.2
Max	784	7.9	25	100.2	92.8	108.8	39.6	32	149.9	189.1	0.8
Mean	682.3	7.5	20.9	86.7	79.2	52.4	26.1	22.4	119.8	143.0	0.5
SD	73.5	0.2	4.1	8.3	8.8	23.1	8.8	4.2	22.7	25.4	0.2
Cv	10.8	3.3	19.8	9.6	11.1	44.1	33.7	18.8	19.0	17.8	34.0

Notes: Min: minimum; Max: maximum; SD: standard deviation; Cv: coefficient of variation.
All values are in mg/L except pH, *T* (℃), and EC (μSiemens/cm).

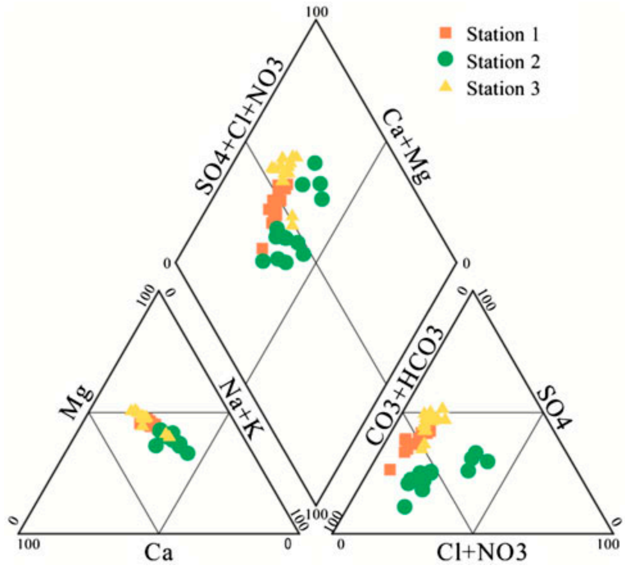

Fig. 3. Piper diagram for the three stations.

and Mg were estimated titrimetrically using 0.01 M 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 (Systronics Flame Photometer 128). The sulfate (SO_4) was determined by the turbidimetric method. The concentration of nitrate (NO_3) was analyzed by colorimetry with a UV–visible spectrophotometer using the spectroscan 60 DV model [31].

3.2. Data treatment and multivariate statistical method

Surface water quality data-sets were subjected to ANOVA and CA. ANOVA is a statistical technique to test for significant differences between means by comparing variances [32]. It tests for whether the variation within the mean value of hydrochemical element concentration for a categorical variable class is significantly less than the variation between the mean values of the different categorical variable classes. CA was used to determine if the samples can be grouped into statistically distinct hydrochemical groups that may be significant in the geologic context. A number of studies used this technique to successfully classify water samples [33–37]. Comparisons based on multiple parameters from different samples were made and the samples were grouped according to their "similarity" to each other. Classifications of samples according to their parameters are known as *Q*-mode classifications. In the present study, *Q*-mode HCA was used to classify the samples into distinct hydrochemical groups, and the Ward's linkage method [38] was used in this analysis. A classification scheme using Euclidean distance (straight line

Table 2
Analysis of variance for hydrochemical parameters

	df	Sum of squares	Mean square	*F*: ratio	*p*-level
Station 1					
EC	7	102,162	14,595	7.29	0.01
pH	7	0.35	0.05	4.61	0.04
T	7	272.50	38.93	20.31	0.00
Ca	7	1,748.10	249.70	16.18	0.00
Mg	7	972.00	138.90	9.29	0.01
Na	7	71.14	10.16	0.96	0.53
K	7	444.91	63.56	1.87	0.23
Cl	7	1,105.57	157.94	32.55	0.00
SO_4	7	12,618.60	1,802.70	18.02	0.00
HCO_3	7	20,767.10	2,966.70	3.51	0.07
NO_3	7	4.32	0.62	5.62	0.03
Station 2					
EC	7	455,058	65,008	2.43	0.15
pH	7	1.17	0.17	12.56	0.00
T	7	285.21	40.75	11.93	0.00
Ca	7	5,620.90	803.00	4.75	0.04
Mg	7	5,847.60	835.40	13.15	0.00
Na	7	1,858.30	265.50	1.49	0.32
K	7	6,296.50	899.50	28.98	0.00
Cl	7	11,937.90	1,705.40	16.58	0.00
SO_4	7	18,253.30	2,607.60	75.31	0.00
HCO_3	7	256,686	36,669.00	6.69	0.02
NO_3	7	16.30	2.33	27.39	0.00
Station 3					
EC	7	67,459	9,637	20.66	0.00
pH	7	0.14	0.02	0.18	0.98
T	7	216.71	30.96	37.15	0.00
Ca	7	874.46	124.92	37.29	0.00
Mg	7	979.66	139.95	29.37	0.00
Na	7	6,882.61	983.23	89.70	0.00
K	7	978.51	139.79	36.51	0.00
Cl	7	213.33	30.48	10.04	0.01
SO_4	7	6,537.00	933.90	29.50	0.00
HCO_3	7	7,767.60	1,109.70	10.66	0.01
NO_3	7	0.28	0.04	4.05	0.05

Note: df: degrees of freedom; *F*: ratio.

distance between two points in *c*-dimensional space defined by *c* variables) for similarity measurement, together with Ward's method for linkage, 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. All 11 hydrochemical variables measured (consisting of EC, pH, T, Ca, Mg, Na, K, Cl, SO_4, HCO_3, and NO_3) were used in this analysis. For statistical analysis, all variables were log-transformed and more closely correspond to normally distributed data. Subsequently, they were standardized to their standard scores (*z*-scores) as described by Güler et al. [39]. Hydrochemical results of all samples were statistically analyzed by using the software STATISTICA® [40].

4. Results and discussion

4.1. Hydrochemical characteristics of surface water

The hydrochemical properties of surface water samples collected from the Timgad Basin are shown

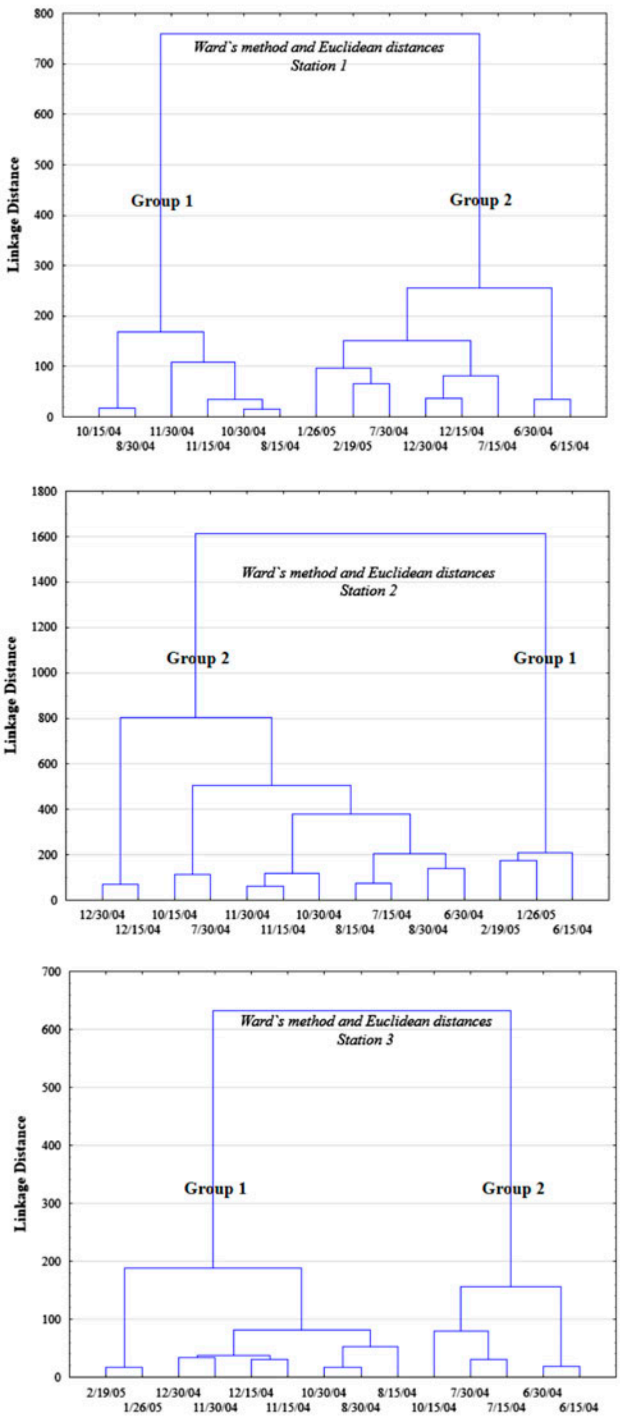

Fig. 4. Dendogram of *Q*-mode CA.

in Table 1. The pH values varied from 6.8 to 7.9 indicating that the surface water was slightly alkaline. All samples show that the values of the temperature were lower than the value fixed by WHO (25°C) [41]. The average value of pH is 7.5, indicating an alkaline nature. EC values of the surface water samples ranged from 509.9 to 1,534 µS/cm. All samples are within the desirable limit (1,500 µS/cm) except one sample in the second station (30 October 2004).

In the three stations, the mean values of magnesium are 91.2, 105.2, and 79.2 mg/L and the mean values of calcium are 100, 117.1, and 86.7 mg/L, respectively (Table 1). All surface water samples exceeded the desirable limit of Mg for drinking water (50 meq/L) and most samples exceeded the desirable limit of Ca (75 mg/L). The alkaline earth elements (Ca + Mg) exceed the alkali metals (Na + K) in all water samples.

The value of bicarbonate varied from 97.6 to 646.6 mg/L and it is the dominant ion in the first and second station (Table 1). High HCO_3 concentration is caused by the presence of carbonate rock in the study area. The value of sulfate varied from 68.8 to 186 mg/L and it is the dominant ion in the third station. All samples are within the desirable limit of SO_4 (200 mg/L). The chloride concentration varied from 14.2 to 184.6 mg/L. From the results, it is observed that all surface waters are within the standard desirable limit prescribed by WHO (200 mg/L). The concentration of NO_3 ranged between 0.2 and 3.6 mg/L in the three stations and all water samples are within the desirable limit for nitrate (50 mg/L).

Chemical data of the water samples are also presented by plotting them on a Piper trilinear diagram (Fig. 3). Piper diagram provides a convenient method to classify and compare water types based on the ionic composition of different water samples. This diagram reveals the different types of waters in the Timgad Basin. Two main water types have been identified on the basis of major ion concentrations (Fig. 3). The first is $MgHCO_3$ water type which is represented by the samples of the first and the second station. The second is $MgSO_4$ water type which is represented by the samples of the last station. Most of the surface water samples contain a high amount of HCO_3 and plotted points cluster toward the alkalinity apex with secondary trends toward SO_4 (Fig. 3).

The temporal variation of the parameters in the three stations is tested using ANOVA. Relationships among the considered variables were tested using Pearson’s coefficient as a nonparametric measure with statistical significance set priori at $p < 0.05$ [42,43]. The results of ANOVA shows that all parameters are significant except for Na, K, and HCO_3 in the first station and EC in the second, also pH and NO_3 in the last station ($p > 0.05$) (Table 2).

Table 3
Mean parameter values of the three principal water groups

		Station 1		Station 2		Station 3	
		Group 1	Group 2	Group 1	Group 2	Group 1	Group 2
EC	µS/cm	581	704	901	1,347	596	730
pH		7.5	7.6	7.3	7.4	7.5	7.5
T	˚C	17	21	12	21	23	20
Ca	mg/L	95.53	104.48	140.54	110.68	78.39	91.25
Mg	mg/L	86.97	95.49	128.39	98.91	70.45	84.02
Na	mg/L	74.96	74.19	142.13	133.01	67.42	44.04
K	mg/L	21.56	29.43	47.40	70.55	21.56	28.58
Cl	mg/L	24.31	37.84	142.13	111.87	20.35	23.54
SO_4	mg/L	141.67	174.14	143.47	164.68	97.52	132.16
HCO_3	mg/L	254.70	280.77	293.72	482.77	123.22	153.94
NO_3	mg/L	1.10	1.26	2.57	0.95	0.56	0.43

4.2. Cluster analysis

From the output of the Q-mode HCA (Fig. 4), a total of two clusters of times in each station was recognized to the level of clustering. EC seems to be a major distinguishing factor with concentrations increasing in all major ions following the order: group 1 and group 2 (Table 3).

4.2.1. Station 1

The first group, made up on August, October, and November, has low salinity (mean EC = 581 µS/cm) and abundance orders Mg > Ca > Na > K and $HCO_3 > SO_4 > Cl > NO_3$ (Table 3). The second group 2, made up of June, July, December, January, and February, has mean value of EC of 702 µS/cm which is greater than that of the first group. The cation composition is dominated by Mg and Ca, with anion composition varying from dominantly HCO_3 to dominantly SO_4 + Cl (Table 3). These waters are classified as HCO_3-alkaline earth water type. Most of the HCO_3, has present in the two groups, has mean concentrations of 254.7 mg/L and 280.77, respectively. It is probably derived from the dissolution of carbonate.

4.2.2. Station 2

The Group 1 is composed of June (6/15/2004), January, and February. This type of water is relatively fresh with a mean EC of 901 µS/cm. The order of abundance of major ions is Mg > Ca > Na > K and $HCO_3 > Cl > SO_4 > NO_3$ (Table 3). Group 2 is represented by June (6/30/2004), July, October, November, and December. The order of abundance of major ions in this group is Mg > Na > Ca > K and $HCO_3 > SO_4 > Cl > NO_3$ (Table 3). EC (mean 1,347 µS/cm), and is significantly greater than that of group 1.

4.2.3. Station 3

The Group 1 encompasses August, October (10/15/2004), November, December, January, and February. This type of water is relatively fresh with a mean EC of 596 µS/cm which is a characteristic of less saline water. Group 2 includes June, July, and October (10/30/2004). The mean EC for this group is 730 µS/cm. In the two groups, the cation composition is dominated by Mg and Ca, with anion composition varying from dominantly SO_4 to dominantly HCO_3 + Cl (Table 3).

4.3. Hydrochemical evaluation

The different compositions of water types result from several hydrochemical processes. Interactions between water and rocks are the main processes controlling hydrochemical characteristics of surface water in the studied area. These processes generally include chemical weathering of minerals, dissolution–precipitation of secondary carbonates, and ion exchange between water and clay minerals [44].

The dissolution of calcite and dolomite generally accounts for the calcium and magnesium concentration in the water. The mineral dissolution that controls the water chemistry can be inferred from the variation in chemical compositions. Because calcite and dolomite are dominant in the study area, the chemical reaction controlling water quality can be expressed by the following equations:

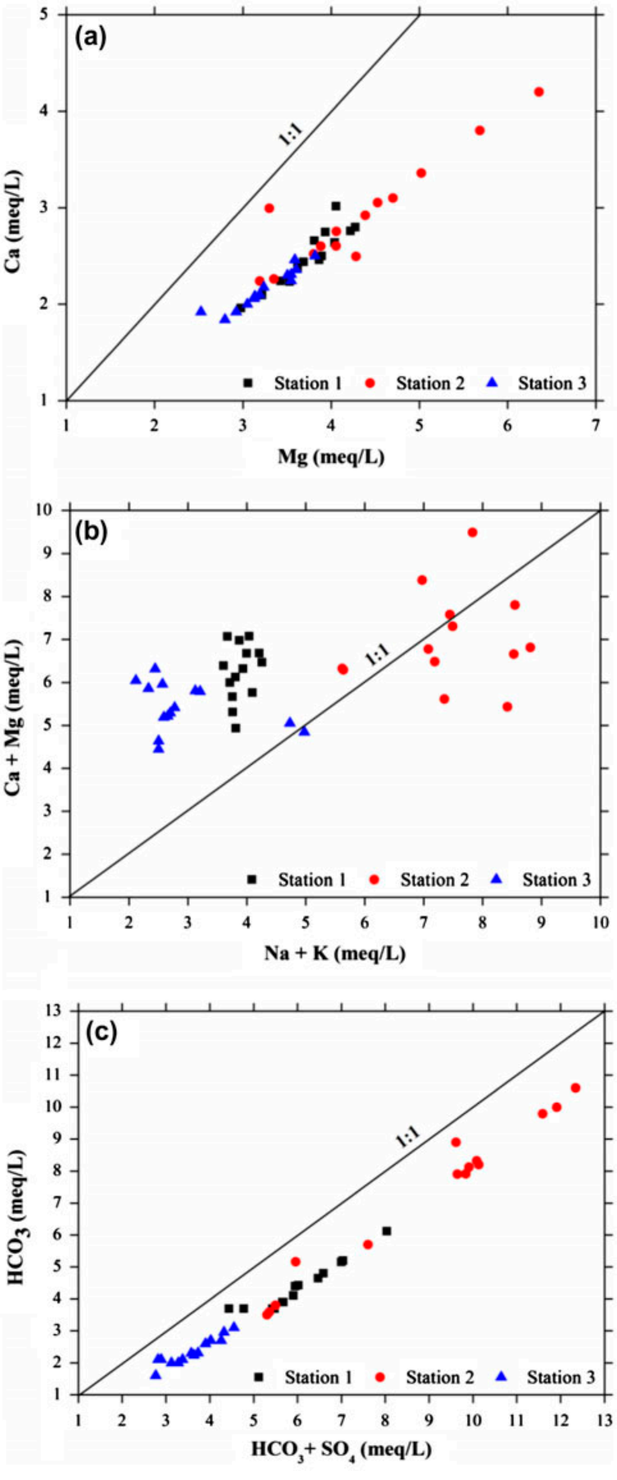

Fig. 5. Major ion relationship: (a) Ca vs. Mg (b) (Ca + Mg) vs. (Na + K), and (c) HCO_3 vs. (HCO_3 + SO_4).

$$CaCO_3\,(\text{calcite}) + CO_{2(g)} + H_2O \rightarrow Ca^{2+} + 2HCO^{3-} \quad (1)$$

$$CaMg\,(CO_3)_2\,(\text{dolomite}) + 2H_2O + 2CO_2 \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3 \quad (2)$$

The study of the Ca vs. Mg ratio of surface water from these stations also supports the dissolution of calcite and dolomite (Fig. 5(a)). Dissolution of dolomite should occur if the ratio Ca/Mg = 1, whereas a higher ratio is indicative of greater calcite contribution [45]. Fig. 5(a) shows that most of water samples of the three stations have ratio smaller than 1, which indicates dissolution of dolomite.

The graph of Ca + Mg vs. Na + K shows that alkaline earths exceed alkalies in most of the samples. Further, the observed low ratio of (Ca + Mg)/(Na + K) and relatively high contribution of alkaline earths toward the total cations suggest that coupled reactions involving carbonate, silicate weathering, and anthropogenic inputs control the solute acquisition process (Fig. 5(b)).

Most of water samples shows that high ratio of $HCO_3/(HCO_3 + SO_4)$ (>0.5) (Fig. 5(c)) which signifies that carbonic acid weathering was proton producer in these waters [46]. The HCO_3 is derived from both natural dissolution of carbonate rocks and anthropogenic input. High HCO_3 concentration could result from dissolution of CO_2 gas likely formed by the anoxic biodegradation of organic matters in domestic sewage and wastewater. Bicarbonate may also be derived from the dissolution of carbonates and/or silicate minerals. Sulfate in aquatic systems is derived from the anthropogenic sources because the area is associated with agriculture for more than 80% and SO_4 is also a major constituent of fertilizers [47].

5. Conclusion

In this study, selected statistical methods CA and ANOVA were used to determine the spatio-temporal variations of hydrochemical elements and to identify the origin of these elements in surface of Timgad watershed, East Algeria. The overall evaluation during the study period showed that the surface in the area is alkaline in nature. The ANOVA results indicate that all parameters are significant except for Na, K, and HCO_3 in the first station and EC in the second, and pH and NO_3 in the last station ($p > 0.05$). For this purpose, 42 samples of surface waters at 3 stations were collected. Two groups found by *Q*-mode HCA at each station. The major ion chemistry (Mg, Ca, HCO_3, and SO_4) in the three stations is derived from the anthropogenic sources and the water–rock interaction.

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