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Regional Hydro-Chemistry of Hydrothermal Springs in Northeastern Algeria, Case of Guelma, Souk Ahras, Tebessa and Khenchela Regions

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Abstract: Hydrothermal units are characterized by the emergence of several large-flow thermo-mineral springs (griffons), each with varying temperature and physico-chemical characteristics depending on the point of emergence. It seems, however, that there is variability between the different systems, although it is not easy to characterize it because the variability within each system is high. The regional dimension of the chemical composition of thermal waters is, therefore, an aspect that has received very little attention in the literature due to the lack of access to the deep reservoir. In this study, we investigated the spatial variability, on a regional scale, in the characteristics of thermal waters in northeastern Algeria, and more specifically the hydrothermal systems of Guelma, Souk Ahras, Khenchela and Tébessa. Thirty-two hot water samples were taken between December 2018 and October 2019, including five samples of low-temperature mineral spring water. Standard physico-chemical parameters, major anions and cations and lithium were analyzed. The data were log-transformed data and processed via principal component analysis, discriminant analysis and unsupervised classification. The results show that thermal waters are the result of a mixture of hot waters, whose chemical profile has a certain local character, and contaminated by cold surface waters. These surface waters may also have several chemical profiles depending on the location. In addition to the internal variability in each resource, there are differences in water quality between these different hydrothermal systems. The Guelma region differs the most from the other thermal regions studied, with a specific calcic sulfate chemical profile. This question is essential for the rational development of these regional resources in any field whatsoever.

Keywords: hydrothermal springs; regional approach; chemical variability; multivariate analysis; Algeria

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1. Introduction

The purifying and curative virtues of thermal waters were already well known in ancient times all around the Mediterranean basin [1,2]. Greeks, Romans and Egyptians developed elaborate bathing rituals around thermal springs, often associated with religious and cultural practices. Public baths and thermal centers proliferated during the Middle Ages and the Renaissance for health and social purposes. With the technological advances of the industrial revolution, spas became more sophisticated and began to market by-products. In the 19th and 20th centuries, spas became fashionable destinations for the wealthy elite, and many towns invested in spa facilities. The mid-20th century saw a shift towards more

therapeutic and medical uses, with balneotherapy being recognized by medical circles, leading to the development of specialist clinics. Today, thermal waters are used in a variety of ways. While tourists still seek the relaxing and therapeutic properties [3–6], investment in geothermal energy potential is increasing [7,8], with a growing awareness of the need to protect these natural resources and minimize their negative impact on the environment, such as noise from power plants, risks of water pollution by saline fluids rich in elements such as boron, fluorine and arsenic, and the accumulation of heavy metal sulfides in river sediments [9–11].

The physico-chemistry of hydrothermal systems has been the subject of numerous studies since the late 19th century, but it reached its peak during the oil crisis of the 1970s [12], being brought back into focus by the current widespread increase in energy prices. The detailed analysis of modern hydrothermal systems has, however, generally advanced our understanding of deep hydrogeological processes, which has a wide impact in fields as diverse as geological engineering, environmental impact assessment or the protection and management of a local tourism resource. This is a difficult area due to the deep reservoirs of hot water and the impossibility, except in special cases, of accessing them to carry out measurements and sampling. In this context of understanding these hydrothermal systems, the surface sampling of hot springs is problematic due to the mixing of deep hot water with cold surface water, as well as the cooling of the water during ascent and potential re-equilibration with the host rock, both of which alter the geochemical information [13]. Given this challenging context, studies generally focus on local processes in a given hydrothermal system, including pollutants that may affect water quality [14–17], or concern the investigation of reservoir temperature using geothermometers, the location of recharge zones or water/rock interactions in the reservoir and groundwater mineralization [14,18–31]. The mineralization and temperature of thermo-mineral waters can be explained by the circulation of groundwater at different depths, but these waters have long been recognized for the stability of their chemical composition and their protection from any risk of surface pollution [14,25–27,32–34]. As hydrothermal systems are generally located along major faults, the question of the existence of "regional provinces" of thermal water quality arises but is rarely addressed, given the difficulties mentioned above, in particular the low volume of information, with each spring generally having very little temporal variability to enrich the pool of samples and data. The geographical connections of the various hydrothermal systems on a regional scale could complement our knowledge. In terms of analytical tools, multivariate statistical methods are frequently used to characterize groundwater quality and distinguish its geochemical signatures in the natural environment. They can be used to reveal, represent and interpret geochemical evolution [35], the origin of mineralization [36] and possible contamination elements in the water. Among these tools, the most common are discriminant analysis (DA), principal component analysis (PCA) and ascending hierarchical clustering (ACH) [37,38].

The aim of this study of hydrothermal systems in northeastern Algeria is twofold: to gain a better understanding of regional variability and the influence of mixing and surface water contamination on this variability and to investigate the relationships between the various thermal springs (griffons). In other words, the aim is to characterize the spatial variability in thermal water quality on a regional scale, despite the variability in surface water contamination and the spatially heterogeneous cooling of thermal waters as they rise.

2. Materials and Methods

2.1. Study Area

This study was carried out in northeastern Algeria, covering the local provinces of Guelma, Souk Ahras, Khenchela and Tébessa. It is located in the large basins of Chott Melhrir, Hauts Plateaux Constantinois, Oueds Medjerda, Seybousse and Mellègue. The temporary rivers that flow through these basins have their sources in the surrounding mountain ranges and receive water from the region's thermal springs along the way [3,15,39,40] (Figure 1). Thermal springs emerge following major tectonic accidents, according to neo-

tectonics on the thermal band, that is, zones of preferential water circulation marked by a series of griffons [41]. At our site, the Annaba and Constantine thermal bands [3] are involved. On these thermal bands, the thermal griffons are unevenly distributed and cluster around the intersections between these tectonic accidents trending N 115° and N 140°E and networks of conjugate faults of Quaternary age trending close to N 20° East. Geology and lithology are of crucial importance for understanding regional hydrothermal springs due to the acquisition of chemical characteristics by water/rock interaction. The study area belongs to the seismically active alpine structural domain. It comprises the terrestrial Atlas (Tellian) to the north, the Great Plains in the center and the Saharan Atlas to the south.

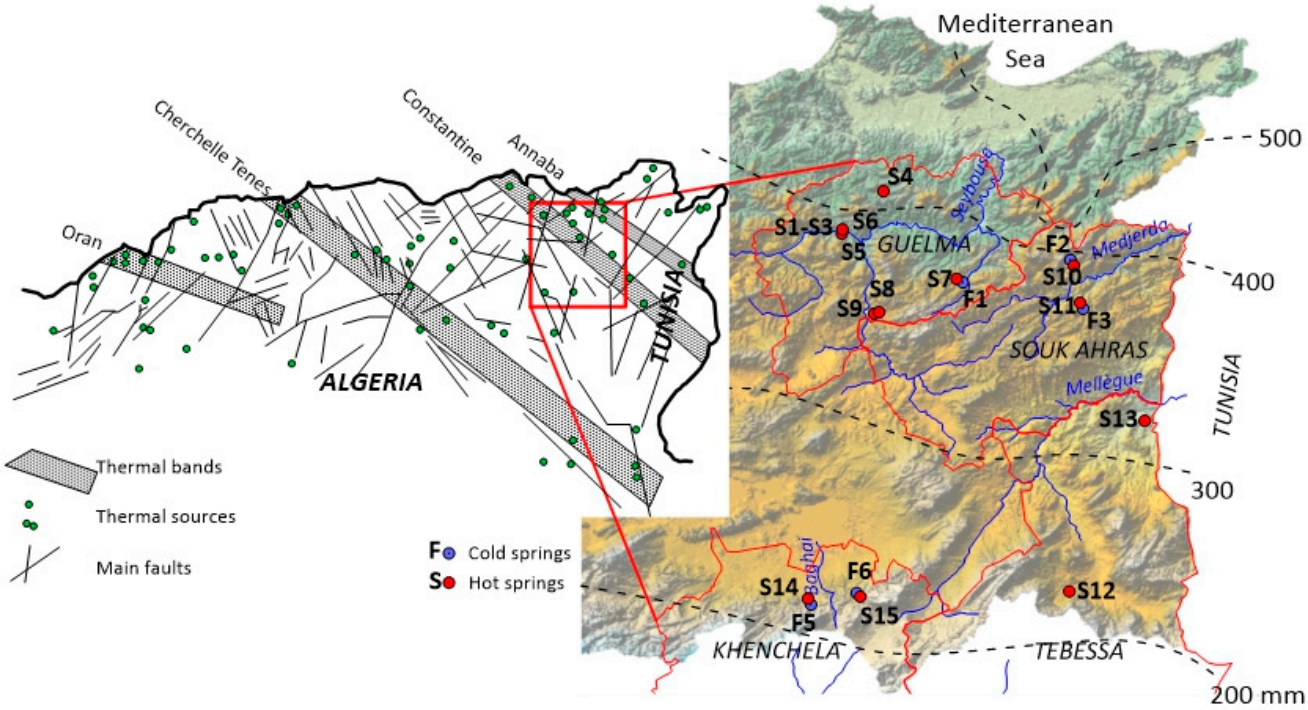


Figure 1. Thermal bands in northeastern Algeria (adapted from Verdeil [41]), the location of the study site and sampled thermal sources. The dashed lines represent rainfall isohyetes for 2021.

The complex geological structure is made up of superimposed allochthonous terrains (Figure 2). The formations are mainly carbonate and marl. The northeastern part consists of young Tertiary-age mountains resulting from the alpine orogeny [42]. The Guelma basin contains marls and carbonates deposited from east to west during the Mio-Pliocene, before the accumulation of Quaternary sediments [43]. It is bordered to the north and south by reliefs mainly in the Tellian domain (Meso-Cenozoic marls and carbonates [44]). The Souk Ahras region belongs to the Tellian domain made up of Secondaire–Tertiaire marl–limestone rocks and secondarily limestone rocks [45]. In the southern part of the Tébessa region, a stratigraphic sequence of alternating limestone, marl–limestone and clayey marl formations appears in the form of a series of synclines and anticlines [46,47]. The central part of the Tébessa–Morsott plain is made up of alluvial deposits, conglomerates, gravels and Plio-Quaternary and Quaternary sandstones. The presence of shallow groundwater is thought to be the result of a mixture of rainfall and upwelling of deeper groundwater along faults in the Cretaceous formations [48].

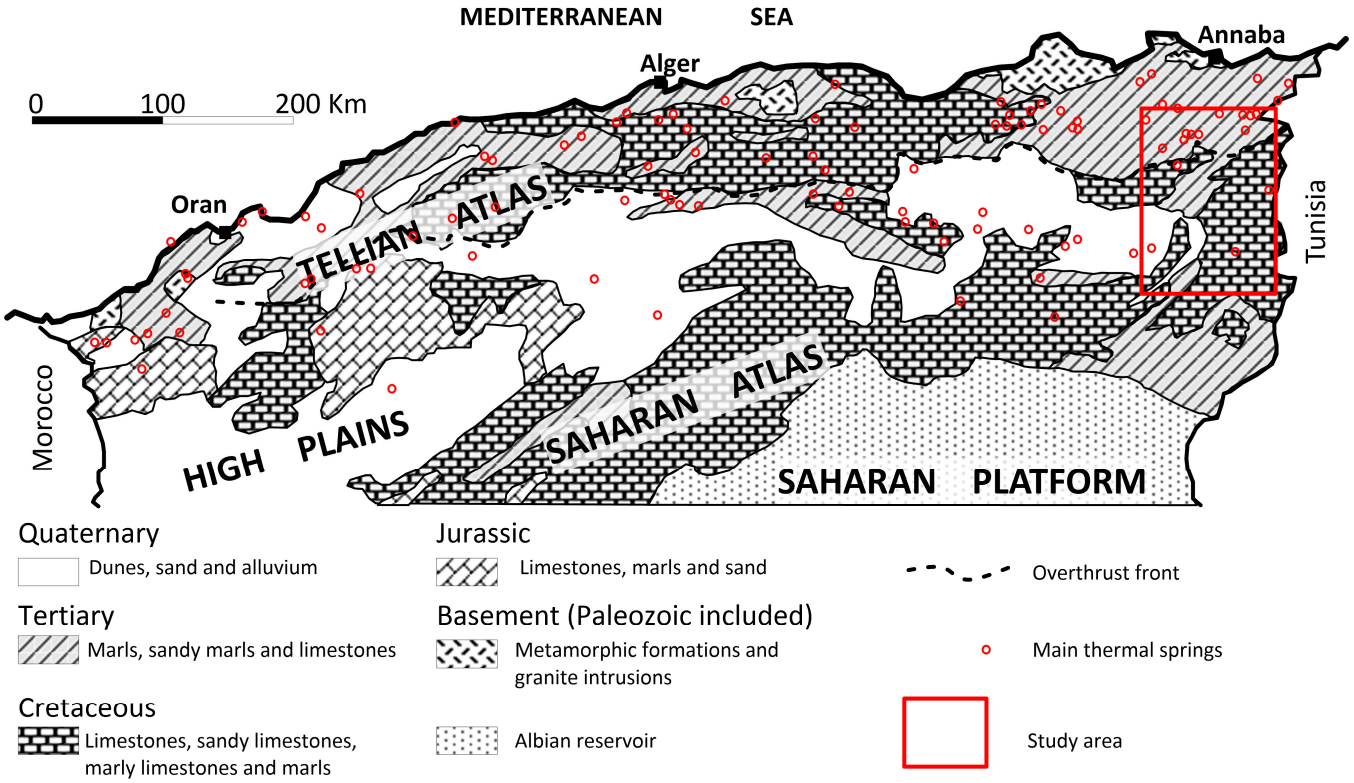


Figure 2. Lithological map of northern Algeria (adapted from Fekraoui and Kedaid [49]).

From a climate point of view, the study region features a rainfall gradient, from a mediterranean climate with cold, rainy winters in the north (500 to 600 mm rainfall from October to May), and dry, hot summers the rest of the year, to a semi-arid climate in the south, characterized by cold winters with rainfall ranging from 300 to 350 mm and dry hot summers. The remarkable amplitude of temperatures (from 5 °C in January to 40 °C in July) throughout the region results in high actual evapotranspiration, affecting both surface and shallow waters.

2.2. Sampling and Analytical Technics

2.2.1. Fieldwork

Samples were collected during 2 campaigns carried out in December 2018 and October 2019, and we obtained a total of 32 samples, 27 from hot springs and 5 from cold springs. The distribution of collections is shown in Figure 1, and some pictures are grouped in Figure 3. In the Guelma region, sampling concerned the springs of Hammam de Meskoutine (S1 to S3, S5, S6), Oueld Ali (S4), Guerfa (S8), Belhachani (S9) and N'bails (S7, F1). Two springs were sampled in the Khenchela region, namely the Hammam Salhine (S14) and Knif (S15), as well as the cold springs of Silene (F5) and Mosqué (F6). Two springs were also collected in the Souk Ahras region, the Hammam Driss and Tassa springs (S10, S11) and their cold springs (F2, F3), and finally, two reputed emergences from the Tébessa region in Hammamet (Youkous-les-Bains, S12) and the Hammam Sidi Yahia (S13) in Ain Zerga-Elméridj were sampled.

The classic physico-chemical characteristics of each sample were measured in situ (pH, electrical conductivity (EC), temperature (T)), and alkalinity was measured via titration with HCl (0.1 M) in order to provide reliable data for calculating the partial CO_2 pressure prevailing in the spring (not used in this study). Samples were collected in 150 mL containers (HDPE) previously acid-washed in the laboratory and then rinsed with ultrapure water and rinsed again three times on site with the water collected. Samples were filtered to 0.45 µm (cellulose acetate syringe filters) and then collected in duplicate, with one container acidified (pH < 2) with nitric acid (Ultrapur HNO_3 down to pH 2) for major cation analysis

and the other for major anion measurements. They were then stored at 4 °C, protected from light and transported to the Center of Geothermal Energy, Groundwater and Mineral Resources at Suleyman Demirel University in Isparta, Turkey.



Figure 3. Some pictures of hot springs and hammams in the study area: (**a**–**c**) Hammam Salhine of Tebessa, (**d**,**e**) Hammam Sidi Yahia of Tebessa, (**f**) Hammam Ouled Ali of Guelma, (**g**) Hammam Guerfa of Guelma, (**h**) Hammam Meskoutine cascade of Guelma and (**i**) Hammam Meskoutine Ain Chfa of Guelma.

2.2.2. Analyzed Parameters

In addition to the physico-chemical parameters analyzed on site, major anions and cations were analyzed, as well as lithium, often used as a marker for thermal waters as opposed to surface waters. Major anions were analyzed via ion chromatography and major cations and lithium via atomic adsorption. The data matrix comprises 32 observations and 12 parameters: T, pH, EC, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, $SO_4{}^{2-}$, $NO_3{}^-$, $HCO_3{}^-$ and Li. The analytical results are presented in the Supplementary Material in Tables S1 and S2.

2.2.3. Data Conditioning

The statistical methods used are based on the assumption of normality of the distribution of observations. Although this assumption is not an essential constraint, it is preferable to avoid a highly skewed, non-normal distribution with extreme values [50]. A Shapiro–Wilk normality test [51], suitable for small statistical distributions ($n < 50$), which is the case in our study, was performed for two major sources of variability, i.e., electrical conductivity (EC), representing mineral charge, and $NO_3{}^-$, reflecting possible surface

pollution. Quantile–quantile (QQ) plots were then constructed to visually compare the residuals of each distribution with a normal distribution with the same mean and standard deviation [52]. The diagonal of these plots represents the normality of the distribution. The closer the distribution points of the data studied are to the diagonal, the closer the distribution is to normality.

2.2.4. Principal Component Analysis

A principal component analysis (PCA) was performed by diagonalizing the correlation matrix in order to classify the various independent sources of variability and explore the underlying processes responsible for the variability in water characteristics [53]. PCA was used to identify relationships between different parameters and rank independent sources of variability. The procedure, which uses the correlation matrix, includes standardized (reduced-centered) variables that bypass the problems associated with numerical ranges and variable units by automatically scaling all variables to zero mean and unit variance. The n original variables are transformed into n principal components, i.e., macro-parameters that are a linear combination of the original variables. The eigenvectors linked to the principal components are orthogonal to each other in the data hyperspace and reflect independent associated processes.

2.2.5. Unsupervised Agglomerative Hierarchical Clustering

Unsupervised agglomerative hierarchical clustering was performed using the mean values of observations from each thermal province (Guelma, Souk Ahras, Tebessa and Khenchela) on the factor axes. Relative similarities between provinces were quantified using Euclidean distance, and the levels of similarity at which the sets merged were used to construct a dendrogram.

2.2.6. Discriminant Analysis

Finally, a discriminant analysis was performed to determine whether it was possible to differentiate thermal systems on the basis of water chemistry. This analysis imposed a non-zero variance constraint within the thermal system. All statistical treatments (Normality tests, PCA, DA and AHC) were performed with XLstat software 2019.2.2 (Addinsoft).

3. Results

Descriptive statistics for the dataset used are summarized in Table 1. The temperature of the hot thermal waters ranged from 34.5 °C (S13, Hammam Sidi Yahia) to 94.7 °C (S1, Hammam Meskhoutine). The electrical conductivity range of the sample was high, ranging from 531 to 16,850 µS cm^{-1}. For hot springs alone, the range extended from 609 (Hammamet, S12) to 16,850 µS cm^{-1} (Hammam Sidi Yahia S13). The electrical conductivity values of cold waters ranged from 531 µS cm^{-1} (F5 in the Khenchla region) to 736 µS cm^{-1} (F3 in the Souk Ahras region). The range of pH values measured was also wide, ranging from 5.71 (S15, Hammam Salhine), i.e., slightly acidic, to 9.88 (S8, S9, Hammam Meskoutine), i.e., clearly alkaline. Cold springs displayed pHs closer to neutrality, ranging from 7.09 to 7.49 (F5, Khenchela and F1, Guelma, respectively). Nitrate levels ranged from 0.69 to 1180 mg L^{-1}, the two extremes being measured in the Tebessa region on springs S12 and S13, respectively. At the Guelma site, values ranged from 17.27 mg L^{-1} (S4) to 165.85 mg L^{-1} (S7, Hammam N'Bail). A value of 135.67 mg L^{-1} was measured for Hammam Salhine (S14) in Khenchela, while thermal waters in the Souk Ahras region (S10, S11) showed low values. Nitrate levels in cold springs varied from region to region. In the Souk Ahras region, nitrates ranged from 2.98 mg L^{-1} (C2) to 63.26 mg L^{-1} (C3). In the Guelma region, the C1 source showed a high level of 46.47 mg L^{-1}, while in the Khenchela region, values ranged from 4.92 mg L^{-1} to 34.68 mg L^{-1}. Finally, the lithium concentrations measured were higher in thermal waters than in surface waters (0.01 mg L^{-1}). The Guelma and Tébessa regions presented the highest concentrations, 1.73 mg L^{-1} at Hammam N'Bail (S7) and 1.5 mg L^{-1} at Hammam Sidi Yahia (S13). Levels measured in the Khenchela

and Souk Ahras regions were intermediate, with 0.81 mg l^{-1} at Hammam Knif (S15) and 0.54 mg L^{-1} at Hammam Tessa (S11).

Table 1. Descriptive statistics for this study's parameters.

Parameter	Unit	Observations	Minimum	Maximum	Mean
T	°C	32	18.7	94.7	49.2
pH	-	32	5.71	9.88	7.08
EC	µs cm^{-1}	32	531	16,850	2886
Na^+	mg L^{-1}	32	9.53	4800	491
K^+	mg L^{-1}	32	0.24	81.2	15
Ca^{2+}	mg L^{-1}	32	51.74	2001	262
Mg^{2+}	mg L^{-1}	32	6.06	54.85	25.95
Cl^-	mg L^{-1}	32	14.13	6130	696
$SO_4{}^{2-}$	mg L^{-1}	32	12.47	1061	368
$NO_3{}^-$	mg L^{-1}	32	0.69	1180	71
$HCO_3{}^-$	mg L^{-1}	32	91.5	1671	469
Li^+	mg L^{-1}	32	0.01	1.73	0.42

Tests of the normality of the distributions (Table 2) highlighted the need to work with the logarithmic transform of the chemical parameters. The Shapiro–Wilk tests revealed that the raw distributions were not normal (test < 0.05), which the logarithmic transform clearly improved. The log ($NO_3{}^-$) transform was considered to be a normal distribution, while the log (EC) transform was close to it, as can be seen from the Q-Q plots (Figure 4). Further calculations were, therefore, based on log (concentration), log (EC), pH and T.

Table 2. The results of the normality test for the NO_3 and EC variables and their log-transformed distributions.

Parameter	Shapiro–Wilk Test
$NO_3{}^-$	<0.0001
Log ($NO_3{}^-$)	0.88
EC	<0.0001
Log (EC)	0.02

The correlation matrix between the parameters is shown in Table 3. From this matrix, we can see that electrical conductivity was highly correlated not only with chloride and sodium ions but also with lithium. Water temperature was positively correlated with potassium and sulfate content.

Table 3. The correlation matrix between parameters (major correlation values are in bold).

Variables	T	EC	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	$SO_4{}^{2-}$	$NO_3{}^-$	$HCO_3{}^-$	H^+	Li
T	1											
EC	0.31	1										
Ca^{2+}	0.33	**0.78**	1									
Mg^{2+}	0.36	0.39	**0.61**	1								
Na^+	0.31	**0.94**	0.66	0.21	1							
K^+	0.67	**0.85**	0.77	0.57	**0.81**	1						
Cl^-	0.33	**0.94**	0.66	0.25	**0.98**	0.82	1					
$SO_4{}^{2-}$	**0.66**	0.47	0.52	0.40	0.37	**0.63**	0.33	1				
$NO_3{}^-$	0.11	0.50	0.38	−0.17	**0.51**	0.35	0.41	0.44	1			
$HCO_3{}^-$	−0.07	**0.70**	0.60	0.27	0.64	0.50	0.63	−0.02	0.33	1		
H^+	0.03	0.21	0.05	−0.25	0.28	0.20	0.23	−0.06	0.27	0.16	1	
Li	0.59	**0.89**	0.72	0.42	**0.89**	**0.95**	**0.91**	0.54	0.36	0.53	0.24	1

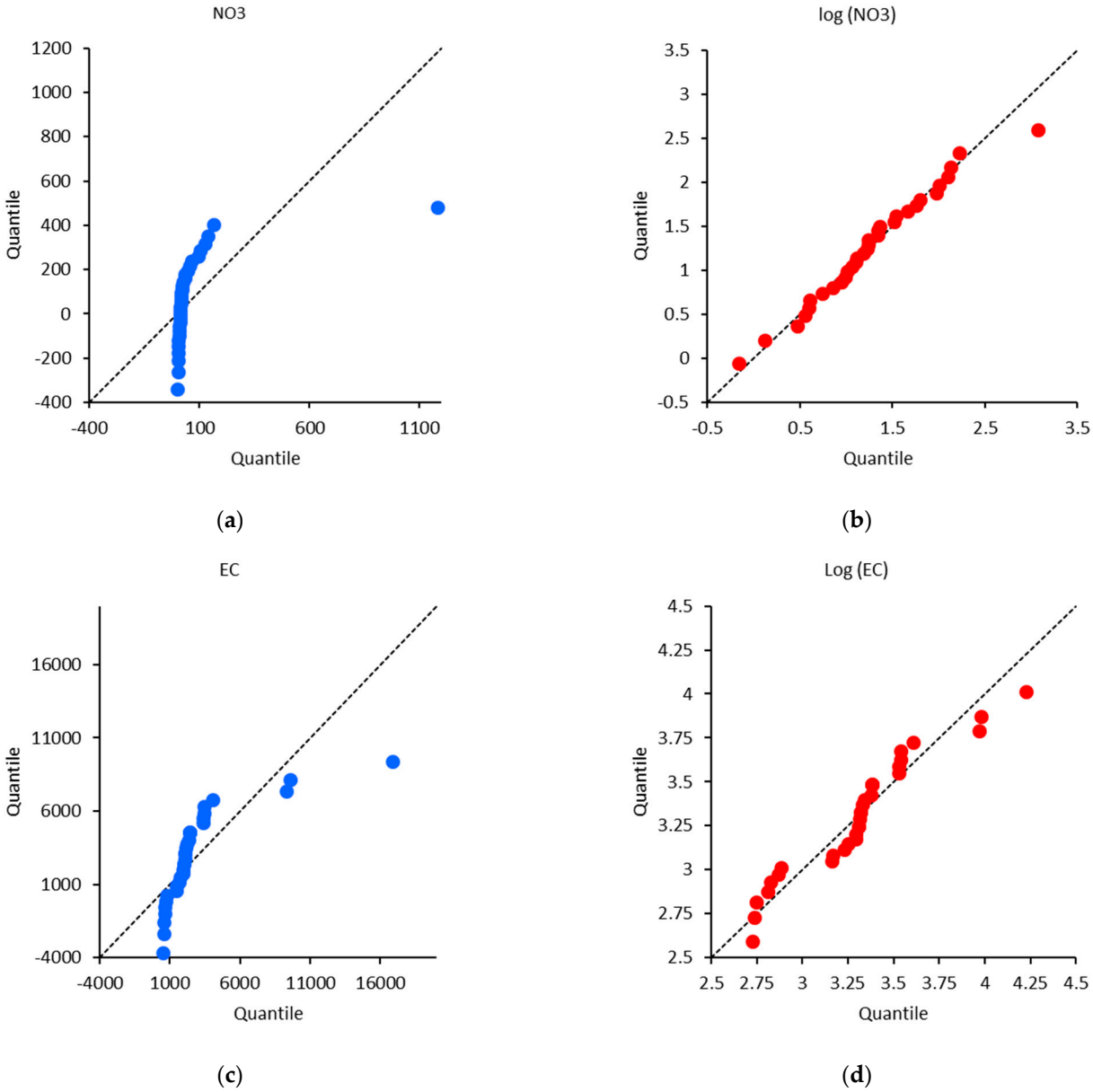
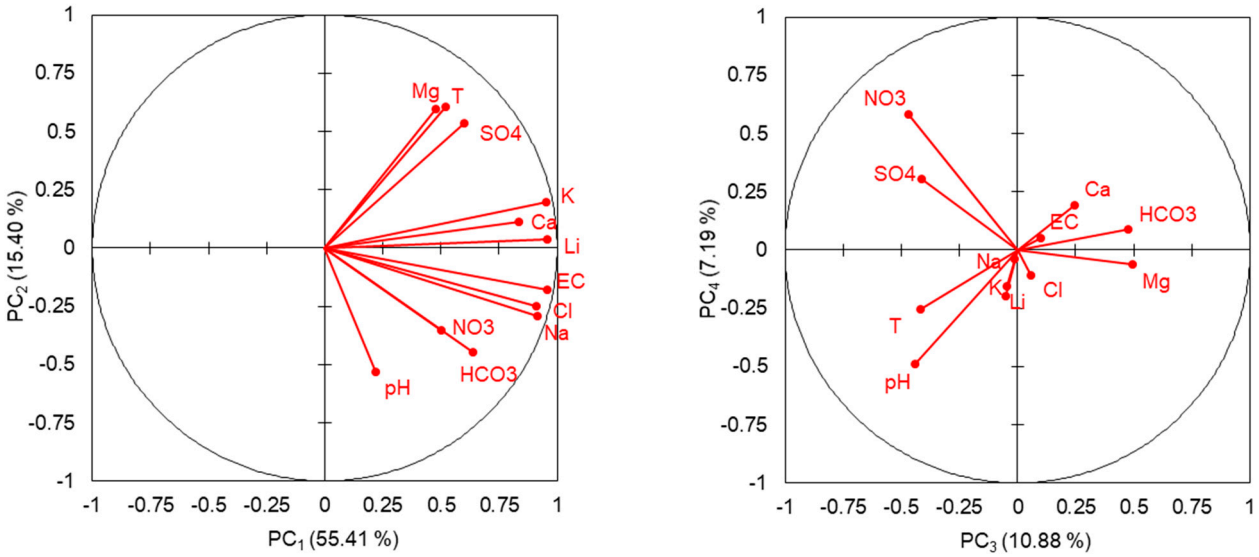


Figure 4. Quantile–quantile plots for parameters (**a**) NO_3^-, (**b**) log (NO_3^-), (**c**) EC and (**d**) log (EC). The dotted line is where the normal distributed pairs of quantiles are placed.

The information conveyed by the first factorial axes PC1 to PC4 is summarized in Table 4 and Figure 5. Axis 1 accounted for 55.4% of the information contained in the data, and its eigenvalue of 6.65 means that it concentrated more information than six initial variables [36]. The first factorial design alone accounted for 70.8% of the information. On the PC1–PC2 factorial plane, temperature was positively scored with all chemical quality characteristics, i.e., with mineral load, regardless of the chemical profile. The first factorial axis, therefore, represented water minerality. The second PC (15.41%) distinguished the different chemical profiles of the waters analyzed, with warm sulfated and magnesian waters positively scored and in opposition to cold bicarbonate and nitrate waters and, secondarily, sodium chloride. This second factorial axis was, therefore, an axis for the chemical facies of the solutions. Axis 3, on the other hand, opposed warm sulfated waters to cold bicarbonate calcic and magnesian waters. This was a water temperature factorial axis. As PC4 represented only 7.19% of the variance, it is difficult to attribute a clear significance to it in terms of associated processes.

Table 4. Eigenvalues and the percentage of variance explained by the first factorial axis, PC1 to PC4.

	PC1	PC2	PC3	PC4
Eigenvalue	6.65	1.85	1.31	0.86
Variance (%)	55.41	15.41	10.88	7.19
Cum. %	55.41	70.82	81.69	88.88



(**a**) (**b**)

Figure 5. Distribution of parameters (pH, T, log (EC) and log (concentration)) in score plots: (**a**) PC1-PC2 and (**b**) PC3-PC4.

The distribution of the 32 observations on the two main score plots PC1-PC2 and PC1-PC3 is shown in Figure 6. The points were scattered throughout the graphs thanks to the logarithmic transformation of the data, which reduced the weight of extreme values. Six groups can be distinguished: Group 1 included the cold waters of Guelma, Souk Ahras and Khenchla (F1, F2, F3, F5, F6) and the hypo-thermal (35 to 37 °C) waters from the Tebessa region (S12), all characterized by rather bicarbonate calcic chemical profiles). Group 2 included hot springs from the Guelma and Tebessa regions (S7, S13). Although far apart and not belonging to the same region, these two springs were characterized by high minerality and a chloride–sodium chemical profile. Group 3 comprised hot waters from the Guelma region (S1, S2, S3, S4, S5, S6, S8, S9). Group 4 contained thermal waters from the Khenchela (S14 and S15) and Souk Ahras (S10 and S11) regions; Group 5 was made up of hot springs from the Guelma and Souk Ahras regions. Finally, Group 6 consisted of hot springs in the Guelma and Khenchela regions (Figure 1) (S1 to S6, S14 and S15).

The results of the discriminant analysis, i.e., the prediction of whether a given sample belongs to a region, are summarized on the confusion matrix shown in Table 5. All samples were well classified, which means that it is possible to discriminate the region of origin of the samples on the basis of the physico-chemical parameters analyzed.

Agglomerative hierarchical clustering (AHC), based on the averages of the coordinates of observations per region over the first four PCs, revealed that sources from the provinces of Khenchela and Tebessa were very similar. Next came sources in the Souk Ahras region, which were similar to those in the first two regions, while sources in the Guelma region were the least-related, showing the greatest dissimilarity with the other regions (Figure 7).

Table 5. Confusion matrix for the discriminant analysis.

From/to	Guelma	Khenchela	Souk Ahras	Tebessa	Total	% Correct
Guelma	17	0	0	0	17	100%
Khenchela	0	6	0	0	6	100%
Souk Ahras	0	0	6	0	6	100%
Tebessa	0	0	0	3	3	100%
Total	17	6	6	3	32	100%

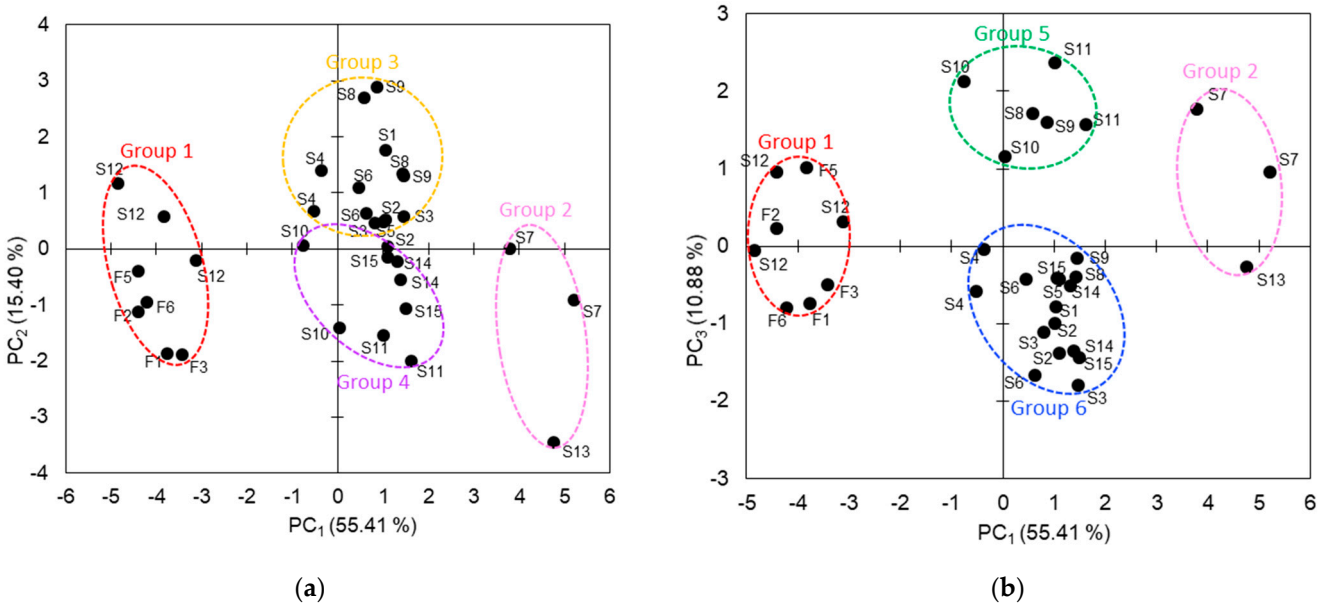


Figure 6. Sample distribution on factorial plots: (**a**) PC1-PC2 and (**b**) PC1-PC3 (see text for group correspondence).

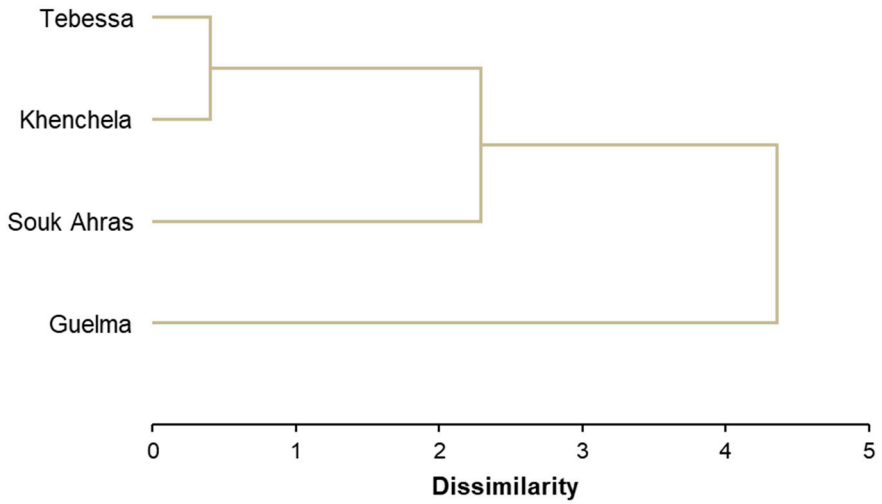


Figure 7. Dendrogram based on the coordinates of the centroids of each region on the first four principal components.

4. Discussion

4.1. Origins of Chemical Signature Diversity

In Figure 5, some points representing samples in the first two score plots, PC1-PC2 and PC1-PC3, are close to those of other groups, all parameters considered. For example, some points in Group 3 are closer to Group 4 than to other points in Group 3. This can be attributed to the internal variability in each group, which depends in particular on

the variability in thermal water mixtures with more superficial waters during ascent to the surface. The temperature reflects the depth of the reservoir and the rate of ascent of the water flow to the surface [31]. In northeastern Algeria, the geothermal gradient is between 3.9 and 4.4 degrees per 100 m [27]. Nitrates, on the other hand, are of external, anthropogenic origin. They are one of the most obvious markers of contamination of thermal waters by surface water during the ascent of warm waters [54]. Temperature and nitrate parameters are opposed along factorial axes 2 and 4 (Figure 5), which account for around 22.5% of sampling variability. This opposition reflects the mixing process. The different outlet temperatures of thermal waters cannot, therefore, be attributed solely to water flow ascent velocities and circulation times [55] but also to local mixing conditions with surface waters [54,56]. The fact that contamination of thermal water by cold surface water appears in the first factorial axes, accounting for almost a quarter of the total variance, all parameters and all samples combined, shows the importance of this phenomenon. In detail, given this opposition between the parameters' temperatures and nitrates being carried by two orthogonal factorial axes, thus representing independent processes, the difference between factorial axes 2 and 4 conveys the information of a variable surface water signature according to geographical area. Nitrate-laden surface water has a carbonate chemical profile in some areas and a sulfate profile in others. Such spatial variability in the chemical composition of surface waters is an additional source of variability, complicating the analysis of results.

4.2. A zoning for Thermal Waters Systems

The second factorial plot PC1-PC3 (Figure 6) shows a better separation of these sources into groups 5 and 6, a result which underlines the need to cross more than two sources of variability, i.e., more than two factorial axes, for a good multiparametric discrimination of waters. The results of the discriminant analysis, with 100% discrimination on the basis of only three discriminant functions, show, beyond the internal variability in each group, the specificities of each province based on (1) the lithological nature of the host reservoir, (2) the circulation depth and ascent speed and (3) the mixtures with surface waters along the way. To assess the degree of similarity between the four thermal provinces, it is necessary to neutralize the variability internal to each of them. This was carried out by basing the hierarchical clustering on the coordinates of the centroids of each region, i.e., on the barycenters of each thermal region on the four main factorial axes. According to this classification (Figure 7), the characteristics of the waters in the Tebessa and Khenchela regions are similar. In particular, these waters have a dominant sodium chloride chemical profile, as do the waters in Souk Ahras province and Hammam N'Bail (S7) in Guelma province. The chemical profile of these waters contrasts with that of springs S1 to S6, S8 and S9 in the Guelma region, which have a calcic sulfate chemical profile. This regional distinction is reflected in their different therapeutic properties [14,15,27,54,57]. Sulfated thermal waters are effective at treating kidney ailments. In addition, when they also contain calcium and magnesium, they successfully treat dermatological conditions such as eczema and burn scars [58–60]. When they contain only calcium, they are used to treat certain metabolic diseases. Chloride- and sodium-bearing thermal waters are said to have a growth-stimulating effect and are, therefore, ideal for treating developmental disorders, as well as enuresis [61]. The result obtained in Figure 7 is consistent with the geography of the area studied. Indeed, the Guelma spa region is furthest to the northwest of the study area (Figure 1), while the Khenchela and Tebessa regions are geographically and geologically closer, both belonging to the Saharan Atlas geological domain.

5. Conclusions

In this study, various statistical methods were used to investigate the variability in the chemical compositions of hydrothermal systems in northeast Algeria. This study revealed a diversity of chemical profiles (sodium chloride, calcium sulfate, calcium bicarbonate) with a regional distribution or depending on the origin of the water (deep or surface). When

hot water rises to the surface, mixing with surface water is another source of variability in the sampling. For each hydrothermal system, the proportion of hot deep water to cold surface water, which varies according to the vent, generates chemical variability within each hydrothermal system. However, the observed variability in chemical composition is not just due to simple differences in mixing proportions but also to the varying chemical composition of the surface water in different regions. This work has taken advantage of the complementary nature of the various available statistical tools. Checking the normal nature of frequency distributions is useful because most methods assume that the distribution of parameters is normal. However, this assumption is generally not very restrictive for the methods used here. PCA has made it possible to not only separate the different sources of variability, taking all parameters together, but also to concentrate the information. It was, thus, possible to eliminate non-essential information by discarding the minor factorial axes. The clustering carried out on the average values per geographical sector of the first factorial axes offers the advantage of showing the similarities and differences, all parameters considered, between the different geothermal sectors of this large thermal region. In short, the complementary nature of these different mathematical tools enables comparisons to be made between the different hydrothermal sectors, i.e., to overcome this intra-hydrothermal system variability and study the inter-hydrothermal system variability. The chemical facies of the thermal waters of the four provinces differ, with those of Tebessa and Khenchela being close and fairly close to those of Souk Ahras, while those of Guelma are very different in their calcium sulfate composition. This study validates the statistical tools used, and a more exhaustive collection of the numerous thermal springs in northeastern Algeria should enable us to significantly refine our knowledge of the diversity of the waters, the mechanisms responsible for the acquisition of chemical characteristics and the regional distribution of this diversity.

Supplementary Materials: The following supporting information can be downloaded via this link: https://www.mdpi.com/article/10.3390/earth5020011/s1, Table S1: Physico-chemistry of thermal springs; Table S2: Physico-chemistry of cold springs.

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