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Research Article

Study of the Hydrochemical Classification of Some Thermal Springs in the Region of Agadez (North-East of Niger)

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Abstract The thermal springs of the region of Agadez are exploited by the local population for various uses, mainly therapeutic. This study focuses on the quality of these thermal waters. The objective is to contribute to a deeper knowledge on these springs, particularly to determine the hydrogeochemical classification and therapeutic aspect of these waters. Twenty-six samples were collected and underwent a series of physico-chemical analyzes during two measurement campaigns, in March and August. The results of these analyzes were processed using a hydrochemical method that uses the Piper triangular diagram and a Multi-Variate Statistical Method including Principal Component Normalized Analysis (PCNA). The results of this study show that the temperature of the thermal springs varies between 26.3°C to 52.8°C with an average of 33.37°C during the dry season of March, and 26.7 to 54.8°C with an average of 34.91°C during the dry season of August. Three facies characterized the waters analyzed, with a predominance of sodium and potassium bicarbonate (53.84%), calcium and magnesium bicarbonate (30.77%) and sodium and potassium chloride (15.38%) during the two seasons. This classification makes it possible to orient the population towards the thermal springs according to the desired therapeutic virtues.

Keywords Agadez, thermal waters, hydrogeochemical, ACPN, therapeutic

Introduction

Groundwater is the largest reserve of liquid freshwater on the planet, about 8 to 10 million km^3, or between 98 and 99% of the total [1]. It is often stored in the upper layers (weathering) and/or flows along privileged pipes, which are essentially cracks or faults [2].

Thermal waters are groundwater that has been used for centuries in the treatment of various pathological conditions [3].

The chemical composition of water from the natural environment is highly variable. It depends, among other things, on the geological nature of the soil from which it originates and the reactive substances it may encounter during flow [4, 5].

The existence of thermal springs originates from the exploitation of mineral springs with recognized therapeutic virtues. The therapeutic indications were empirical: the major indication was the treatment of nervous disorders; it also treated stomach disorders, skin diseases, joint pain, poorly consolidated fractures and sterility. Thermal treatment is mainly due to the chemical composition and high temperature of the thermal waters [6].

The hydrochemical classification of thermal springs is based on the composition of characteristic mineral salts, i.e. on the presence and importance of various anions and cations since the salts are completely dissociated in the water.
The present study proposes, through geochemical tools, to make a contribution for a better understanding of the Hydrogeochemical Classification of the thermal waters of the Agadez region. Indeed, this area disposes several thermal springs which the riparian population uses for therapeutic purposes without medical indication. The thermal springs are traditionally operated.
The methodology applied to this study is based on the one hand on the determination of the hydrogeochemical classification of the groundwater from the Piper diagram and on the other hand by a standardized principal component analysis (SCA). This study would help guiding the populations on the therapeutic virtues related to each thermal spring.

2. Materials and Methods

2.1. Presentation of the study area

Agadez is a region that covers the northern part of Niger between longitudes 6° and 15° and latitudes 16° and 22° with an area of 667,799 km^2 (or 52.6% of the country's total area), it is the largest of the country's seven regions (figure 1).
The Agadez region has an extremely arid climate. The Ténéré desert is one of the driest areas in the world with an average of 12 mm of rainfall per year. Its Sahelo-Sahelian climate is characterized by the alternation of a short rainy season of about three months (July to September) and a nine-month dry season (October to June). The abundance of rainfall varies considerably from one year to the next. The maximum is generally observed in August, which alone accounts for 60% of annual precipitation. The western slopes of the Aïr Mount are a little better off, with about 150 mm of rain per year.
The Air Mount is a set of high crystalline and volcanic mounts emerging from an ancient basement. It is in fact an anticlinorium, made up of isoclinal folds leaning slightly to the east. The Precambrian basement zone of the Air is composed of deposits of folded and metamorphosed sedimentary rocks (gneiss, shales) and volcanic rocks dating from the Lower Proterozoic. These deposits, several kilometres thick, are intersected by granitoids dating from the Suggarian and by eruptive rocks that were put in place during the Pan-African orogeny 600 million years ago (or in the Paleozoic for the most recent).
In the Jurassic period, annular faults in the crystalline basement, located at an altitude of 500 to 1,000 m, allowed the surrection of granite peaks: Adrar Bous, Greboun (1,944 m), Mount Tamgak (1988 m), Mount Agalak, Mount Bagzane (2,000 m) and Tarouadji. These summits are sometimes topped by volcanic cones or domes of various types and ages. The existence of ancient volcanism is made tangible by the existence of hot springs with highly mineralized waters (Tafadeq, Iguluouf) [7].
Significant groundwater resources remain in the study area. These are mainly the Agadez sandstone aquifer, the Precambrian basement aquifer, the intercalary continental aquifer, the Namurian aquifer and alluvial aquifers [7].
Agadez sandstone aquifers : It is made up of two large groups: the Teloua sandstones (which contains the Teloua 1, 2 and 3 aquifers) and the aquifer sandstones (Tchirozerine 1 and 2) which is an alternation of clayey sandstones with analcimes glomerules and coarse conglomerate vacuolar sandstones.
Infill continental aquifer: this is a general captive aquifer with areas of open water near outcrops. It consists of lower Cretaceous sandstone and sandy-clayey continental deposits.
Namibian aquifer: it is a multilayered series of sandstones and clayey silts with a depth often exceeding 300 m. This Namurian aquifer is made up of the Tara aquifer at the top with a thickness of 25 to 50 m and the Guezouman aquifer at the base between 50 and 60m.
Precambrian basement aquifer: the basement of the basin is a foliated diorite with amphibole enclaves to which quartz and pegmatite veins are associated.
Alluvial aquifers: these are shallow aquifers buried under permeable soils with coarse sands; their renewal is ensured by rainwater.

2.2. Methodology

In this study two sampling campaigns were carried out, one in March 2018 and the other in August 2019. The physico-chemical analyzes were carried out on the thermal waters of Tafadek, Ingall, Tassinik, Ingiténe, Akakara, Teghazer, Agassara, Tozayate, Awlizdig, Taganjir, Tighraya, Tekarkar, Tiffadakéne, The choice of the above-mentioned sources is dictated by the fact that these sources are the best known and most used by the population. Water samples were collected in polyethylene bottles with a capacity of 1 litre. The samples were collected until overflow in bottles previously rinsed with ground water, then capped and labelled. They were then stored at 4°C in a cooler and taken to the analysis laboratory within 24 hours. The physical parameters such as pH, temperature, conductivity and turbidity were measured in situ using a multi-parameter cyber scan PC 300

The following parameters were analyzed: pH (hydrogen potential), EC (electrical conductivity); temperature (T°); calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), bicarbonate (HCO_3^-), nitrate (NO_3^-), nitrite (NO_2^-), fluoride (F^-), chloride (Cl^-), sulphate (SO_4^{2-}), sodium (Na^+).

All these chemical elements were analyzed at the **Sociétés d'exploitation des eaux du Niger (**SEEN)

laboratory in Niamey. These analyzes were carried out using a spectrophotometer branded DR 1900 hach using the classical methods recommended by Rodier [8].

These data were processed by the hydrochemical method that uses the diagram software to determine the different hydrochemical facies of the sampled waters. They were then processed by the XLSTAT 2016 software to determine the mineralization of these waters by applying the statistical method of principal component analysis (PCA). This software is widely used in hydrochemistry to characterize the origin of the mineralization and the chemical facies of the waters and gives very good results [9, 10, 11, 12, 13, 14].

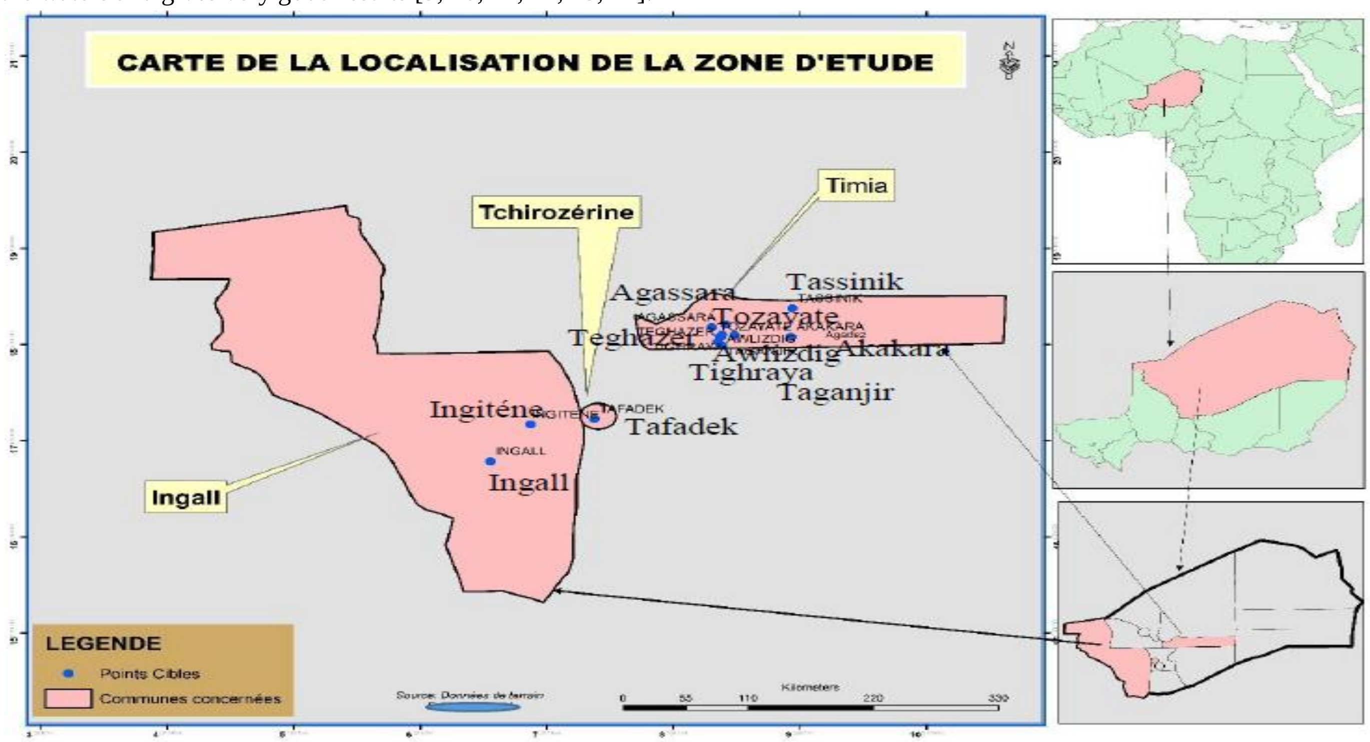


Figure 1: Location map of study

3. Results and Discussion

3.1. Results of the physico-chemical parameters

The results of the various physico-chemical analyzes carried out on the thermal springs of the Agadez region during the periods of March 2018 and August 2019 are presented in Table 1 and 2 respectively.

Table 1: Results of the physico-chemical parameters of the thermal waters of the region (March 2018)

Noms	pH	T°	CE	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	SO_4^{2-}	F^-	NO_3^-	Cl^-
Tafadek	8.5	52.8	1730	9	150	600	180	2300	230	4	3	130
Ingall	10.2	48	2800	7.5	100	800	170	3000	282	2	5	50
Ingiténe	9.7	34	830	7.5	152	750	171	2900	290	2.3	1.1	70
Akakara	8.8	32	435	27	20.04	97.06	40.17	300.73	67.2	20.9	63.86	49.34
Tassinik	7.5	28.3	6555	18.3	2	699.5	99	350	280.8	1.5	4	750
Tighraya	6.9	35.2	3200	6	98.04	1193.93	146.25	3666	147.84	18.5	63.86	231.46
Taganjir	9.6	29.3	7350	5	45.96	1050	121.68	2990.22	282.24	0.38	16.12	3500
Teghazer	7.2	27	2900	7	86.96	597.04	181.13	2290.16	97.92	1.95	1.86	136.03
Tiffadakéne	8.3	28.2	613	23	14.04	56.7	3.9	189.1	48.96	1.14	46	47.25
Tekarkar	7.8	26.3	212	21	15.96	13.11	3.12	101.26	12.96	0.96	17.98	23.075
Awlizdig	9.8	27	202	28	21.96	25.4	5.07	203.74	13.92	1.9	21.7	58
Agassara	8.2	34.8	230	29	6	19.09	5.85	114.68	22.08	0.57	3	17
Tozayate	7.3	31	370	30	12.96	27.5	5.07	210.45	2112	0.95	1.86	14.91

Table 2: Result of the physic-chemical parameters of the thermal waters of the region (August 2019)

Noms	pH	T°	CE	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	SO_4^{2-}	F^-	NO_3^-	Cl^-
Tafadek	7.5	54.8	2000	6	150	600	180	2300	230	4	2	130
Ingall	9.5	49	4000	9	92	800	170	3000	282	2	1.86	50
Ingiténe	9	36	850	7.5	100	750	171	2900	290	2.3	1.1	70
Akakara	8.5	32.5	433	27	20.04	97.06	40.17	300.73	67.2	20.9	63.86	49.34
Tassinik	6.5	35	6780	18.3	2	699.5	99	350	280.8	1.5	4	750
Tighraya	6.8	37.5	3230	6	98.04	1193.93	146.25	3666	147.84	18.5	63.86	231.46
Taganjir	9.6	29.3	7450	5	45.96	2512.08	121.68	2990.22	282.24	0.38	16.12	3500
Teghazer	7.9	30.2	2980	7	86.96	597.04	181.13	2290.16	97.92	1.95	1.86	136.03
Tiffadakéne	7.9	29	615	23	1404	86.02	3.9	189.1	48.96	1.14	46	47.25
Tekarkar	9.2	26.7	218	21	15.96	13.11	3.12	101.26	12.96	0.96	17.98	23.075
Awlizdig	9.8	27.2	202	28	21.96	32.89	5.07	203.74	13.92	1.9	21.7	58
Agassara	8.2	34.9	235	29	6	19.09	5.85	114.68	22.08	0.57	3	17
Tozayate	7.2	31.8	375	30	12.96	34.04	5.07	210.45	2112	0.95	1.86	14.91

The pH measured in situ gives the H^+ ion concentration of the water. It thus translates the balance between acid and base on a scale of 0 to 14 with the value 7 pH neutrality. This parameter conditions a large number of physico-chemical equilibrium, and depends on multiple factors, including temperature and origin of the water, it represents an important indication of the aggressiveness of the water and therefore the ability to dissolve limestone [15].

Figure 2 presents the variation of the pH of the thermal springs of the region of Agadez during the two periods of measurement campaigns. The pH varies from 6,9 to 9,6 with a mean of 8,073 and a standard deviation of 1,047 for the first campaign of March 2018 and from 7.2 to 9,8 with a mean of 8,012 and a standard deviation of 0,977 for the period of August 2019.

We note that the pH of August is slightly higher than that of March; this phenomenon is certainly due to the infiltration of rainwater. The pH values of some localities such as Ingal, Ingiténe, Akakara, Taganjir and Awlizdig have basic pH values far exceeding the WHO standard of quality water. However, these waters can be medically recommended for these values, mainly for people with ulcers. Figure 2 below shows the pH variation of the thermal waters.

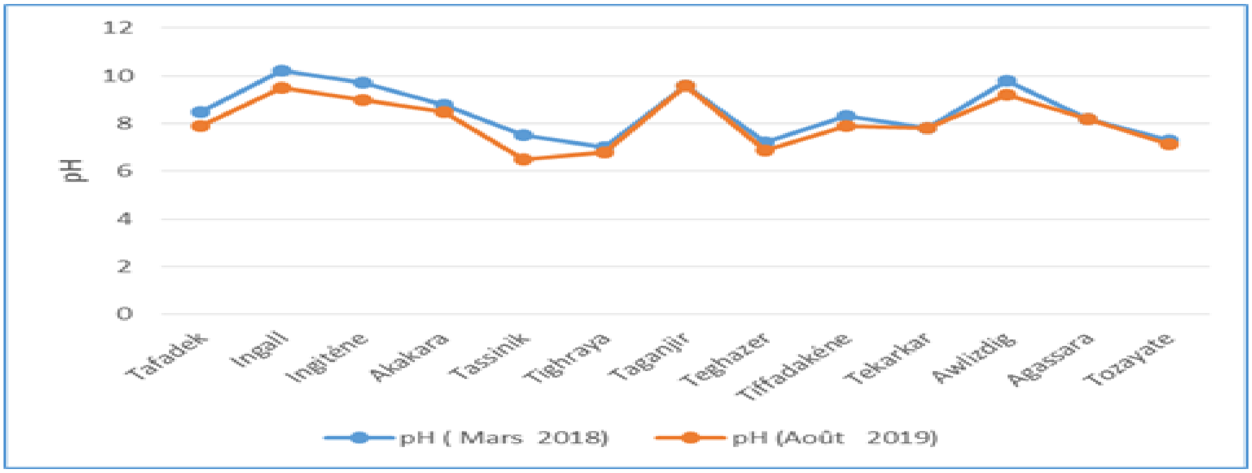


Figure 2: Variation of the pH of the thermal waters during the months of March 2018 and August 2019

It is important to know the temperature of the water with a good degree of accuracy, as this plays a role in the solubility of gases, in the dissociation of dissolved salts and in the determination of pH, for the knowledge of the origin of the water and any possible mixtures, etc. Generally speaking, the temperature of water is influenced by its origin [16]. During the month of March the temperatures of the thermal waters vary from 26,3°C to 52,8°C with a mean of 33,37°C and a standard deviation of 8,19°C, while in the rainy season they vary from 26,7 to 54,8°C with a mean of 34,91°C and a standard deviation of 8,33°C as shown in Figure 3. The spring of Tafadek, presents the warmest waters with a temperature of 52,8°C during the month of March and 54,8°C during the month of August. This spring can be classified as hyperthermal with temperatures above 50°C [17, 18, 19, 20]. It is the most renowned in the region of Agadez, given its high temperature. These waters are generally recommended in the treatment of rheumatic diseases. The localities of Ingall, Ingiténe, Akakara, Tighraya and Agassara, with temperatures between 30°C and 50°C, are classified as meso-thermal waters [20].

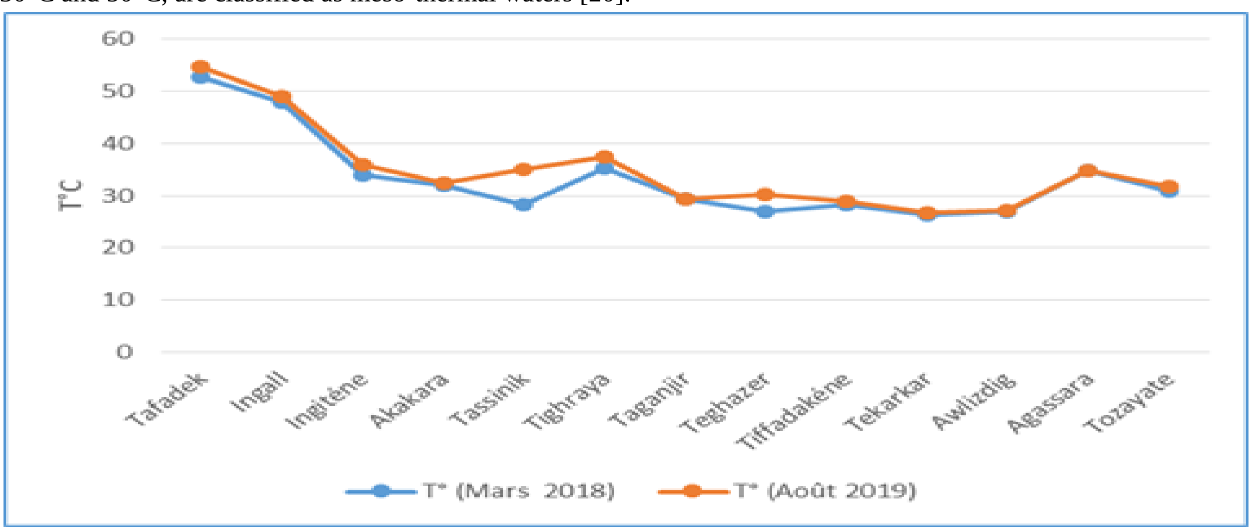


Figure 3: Temperature variation during the two campaigns (March 2018 and August 2019)

Figure 4 shows the variation in the electrical conductivity of the thermal waters of the Agadez region during the two measurement campaigns. These waters have electrical conductivities ranging from 202 to 7450 µS.cm^{-1} with a mean of 2166.769 µS.cm^{-1} and a standard deviation of 2475.935 µS.cm^{-1} during the Mars campaign. The waters show values from 212 to 7350 µS.cm^{-1} with a mean of 2000 µS.cm^{-1} and a standard deviation of 2417.08 µS.cm^{-1} during the August measurements.

The thermal springs of Ingitene, Akakara, Tiffadakéne, Tekarkar, Awlizdig Agassara and Tozayate are strongly mineralized as a whole.

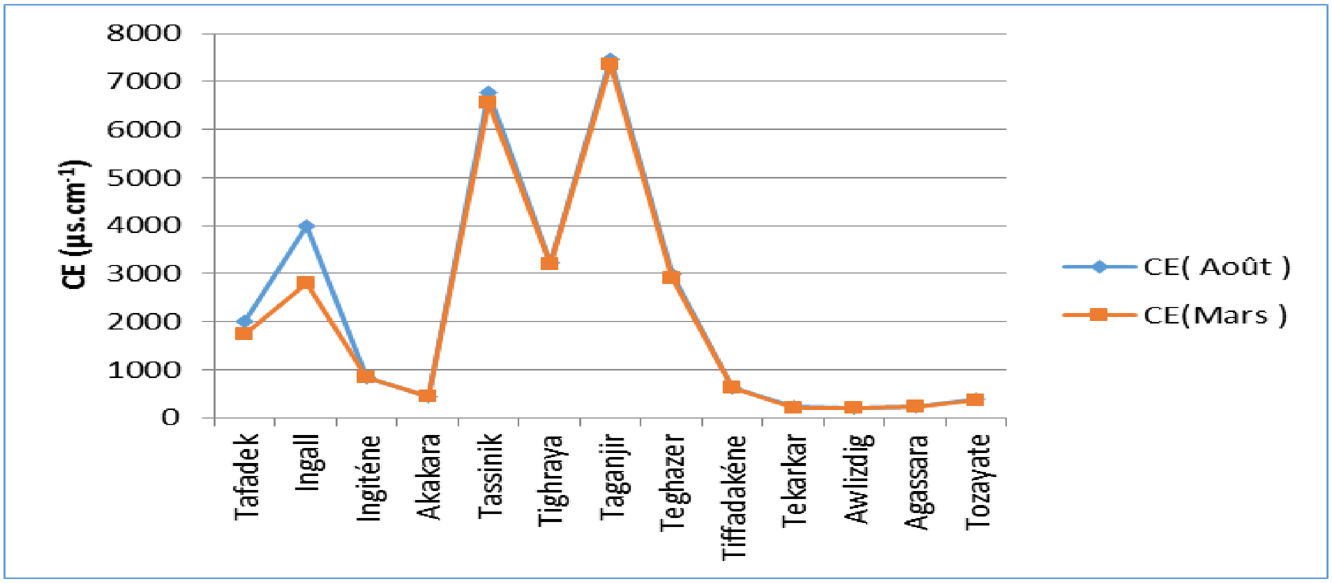


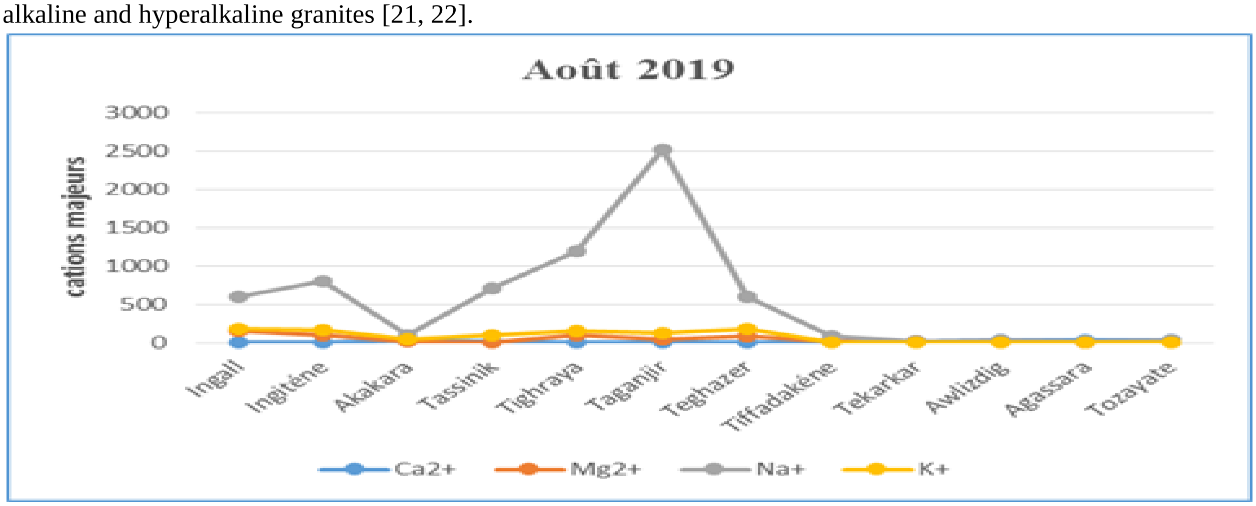
Figure 4: Variation in electrical conductivity during the two campaigns

Among the major cations, sodium is predominant in almost all thermal waters with 79.29%, followed by potassium with 11.4%, then magnesium with 6.8% and finally calcium 2.5% during the dry season. This predominance remains the same during the second measurement campaign, with 74.22% for sodium, followed by potassium with 14.49%, then magnesium with 8.04% and finally calcium with 3.24%. Calcium remains the least abundant cation in almost all the thermal springs of the Agadez region.

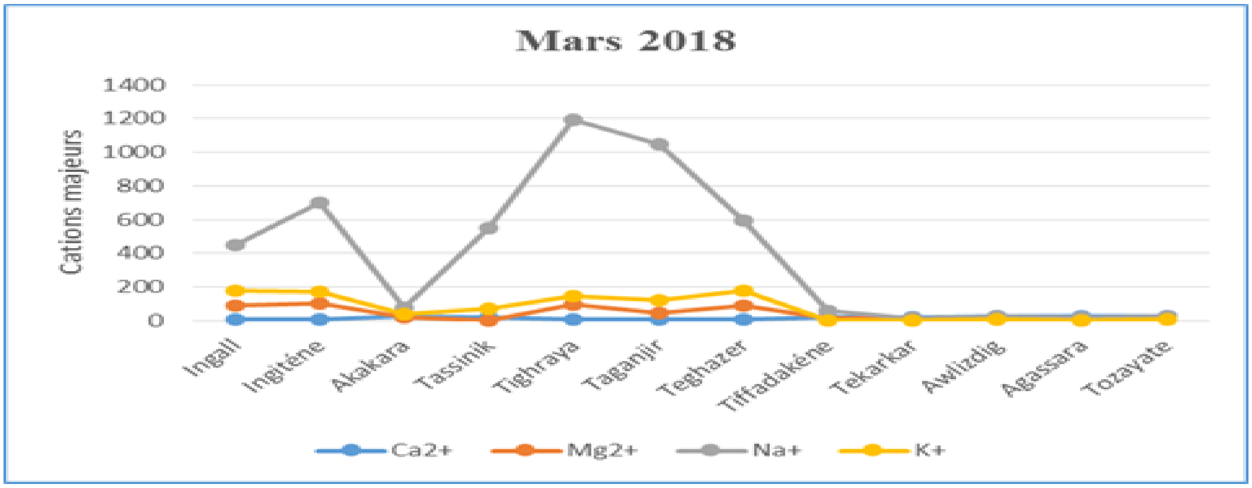
A significant amount of sodium was recorded during the two campaigns in the thermal waters of Tafadek (2512.06 $mg.L^{-1}$) as shown in Figure 5.

Sodium is an alkaline metal. Its origin can be natural (sea, land), human (in urine), or industrial (oil industry). Waters that are very rich in sodium become brackish and take on an unpleasant taste [15]. Waters with high sodium concentrations are used in the treatment of rheumatic and gynaecological diseases (such as chronic rebellious pelvic pain, painful after-effects of pelvic surgery) [17, 6].

The predominance of Na^+ ions in the analyzed waters may result from the hydrolysis of certain rocks such as alkaline and hyperalkaline granites [21, 22].



(a)



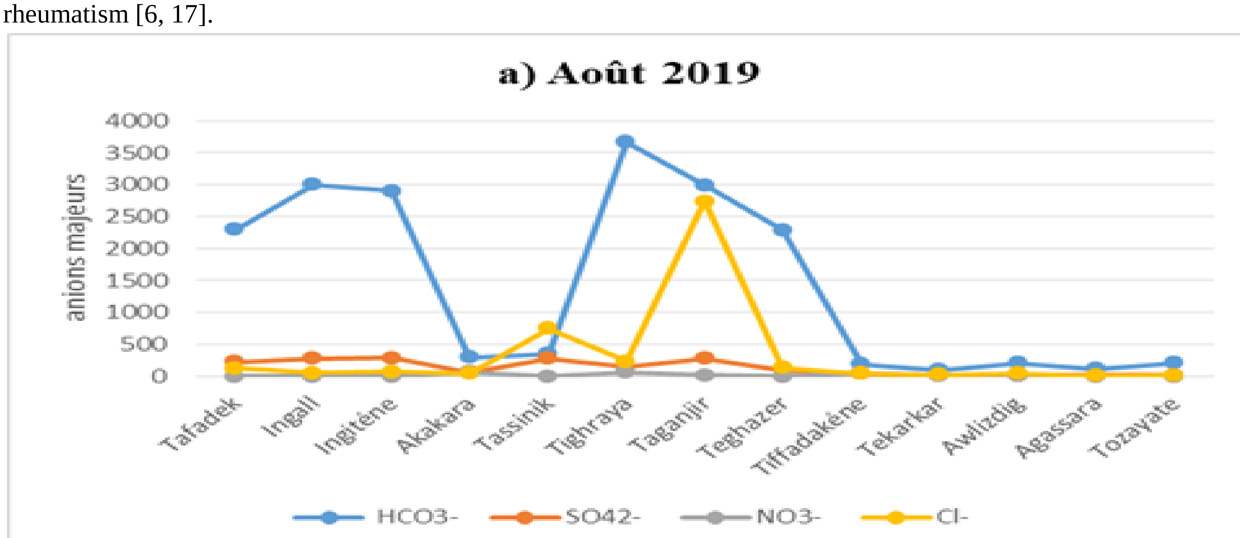
(b)

Figure 5: Predominance of major cations in the thermal waters of Agadez (a: August 2019 and b: March 2018)

Among the major anions (figure 6), hydrogen carbonate was the most abundant with 74.6%, followed by chloride ions with 17.23%, then sulphate ions with 7.2% and finally nitrates with 0.96% during the first season. This predominance remained the same during the second campaign, with 72.29% for HCO_3^- ions, followed by Cl^- ions with 19.71%, then sulphate ions with 6.97% and finally NO_3^- ions with 1.011%. The relatively high ion contents were observed during the month of August. These differences in values may be related to the infiltration of rainwater into the thermal waters.

The high concentrations of hydrogen carbonate ions recorded can be explained either by the dissolution of carbonates and/or the hydrolysis of silicates under the action of meteoric water more or less loaded with CO^2 according to the work of Rabilou [22].

These waters can be recommended for the treatment of diseases of the digestive tract, diabetes, phlebologies (chronic venous insufficiency, ulcers of venous origin, sequelae of thrombophlebitis of the lower limbs) and rheumatism [6, 17].



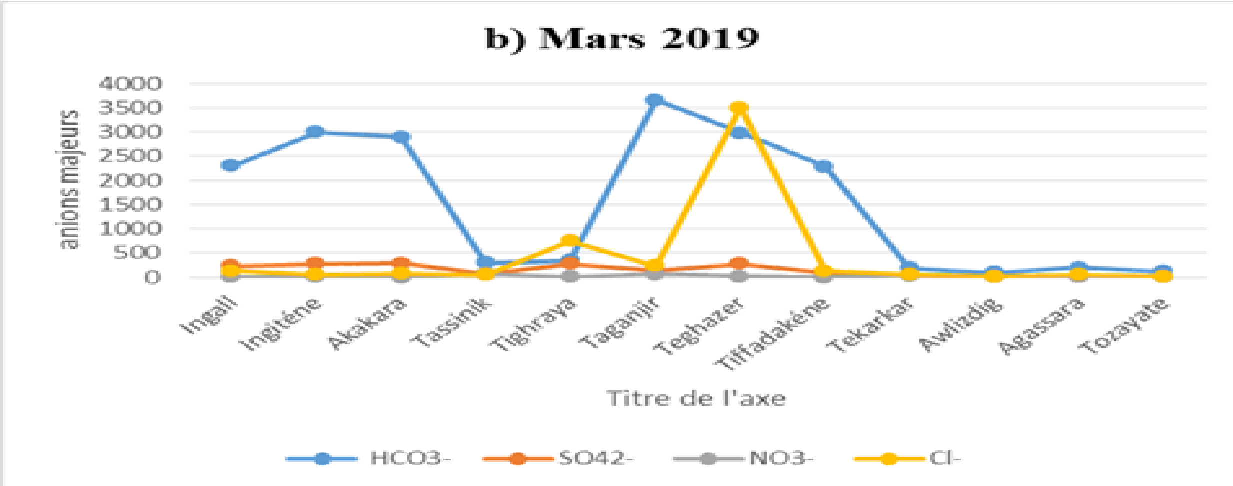


Figure 6: Predominance of the major anions of the thermal waters of Agadez (a: August 2019 and b: March 2018)

Figure 7 shows the variation of F^- ions in the thermal springs of the Agadez region during the two measurement campaigns. The F^- ions vary from 0.38 $mg.L^{-1}$ to 20.9 $mg.L^{-1}$ with a mean of 4.38 $mg.L^{-1}$ and a standard deviation of 6.875 $mg.L^{-1}$ during the 1st campaign and vary from 0.38 $mg.L^{-1}$ to 21.9 $mg.L^{-1}$ with a mean of 5.627 $mg.L^{-1}$ and a standard deviation of 7.66 mg.L-1 during the 2nd campaign. Very high levels were observed at the Akakara hot springs (20.9 $mg.L^{-1}$ and 21.9 $mg.L^{-1}$) and the Tighraya hot springs (18.5 $mg.L^{-1}$) as shown in Figure 7. The fluoride-rich waters are very often used by those suffering from dental caries.

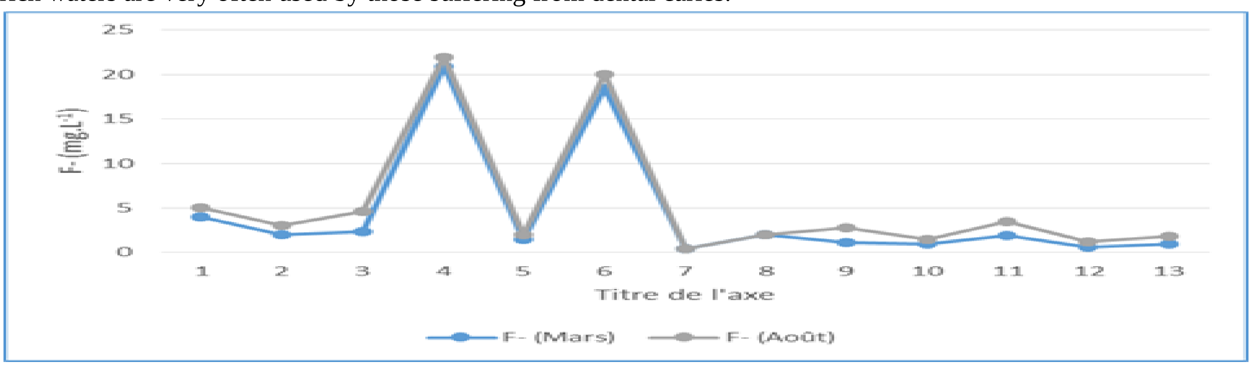
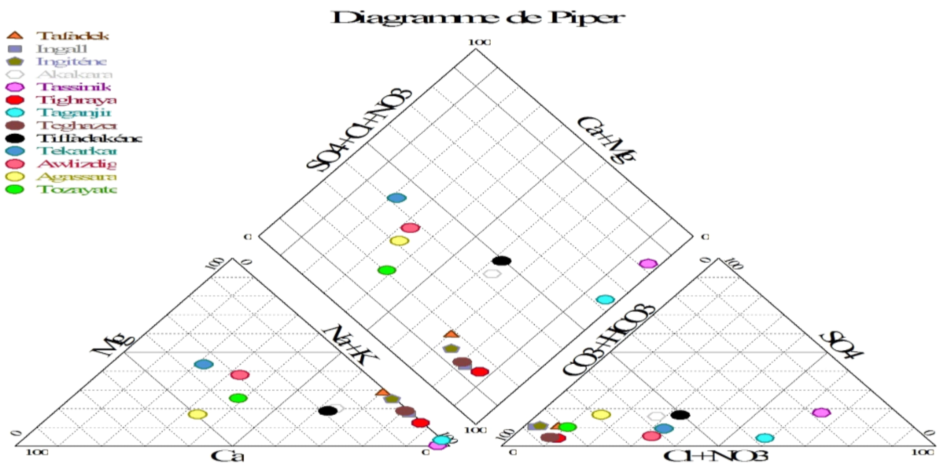


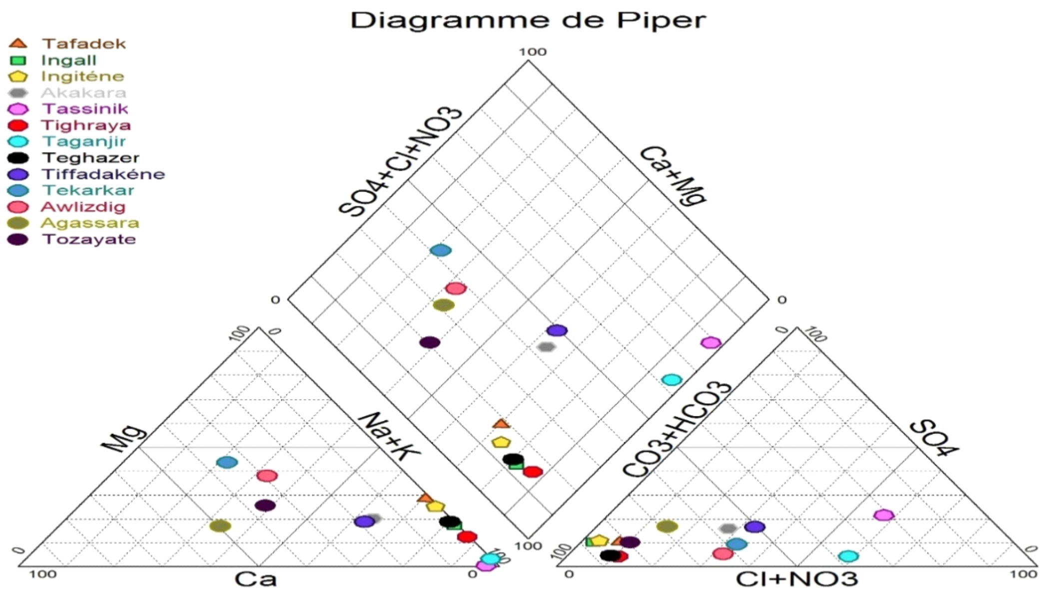
Figure 7: Predominance of fluoride ions in thermal waters (August 2019 and March 2018)

3.2. Hydrogeochemical facies

From the hydrogeochemical point of view, figure 8 presents the Piper triangular diagram showing the different groundwater facies of Tafadek, Ingall, Akakara, Tassinik, Ingite, Tighraya, Taganjir, Teghazer, Tiffadakéne, Tekarkar, Awlizdig, Agassara and Tozayate. The thermal waters constitute a memory that brings to the surface indications about the deep reservoir. Their geochemical study represents a reconnaissance tool which, in a complementary way to the other approaches (geological, geophysical, hydrodynamic, etc.), makes it possible to better determine their origin, the underground circuit used and the possible mixtures with the cold surface waters [23] The Piper diagram provides the same result as a classical characterization of the chemical composition by the main anion or cation. However, it has the advantage of defining at the same time a certain number of water families and clearly highlighting the evolution of the mineralization.



(a)



(b)

Figure 8: Diagram of Piper of the thermal waters of Agadez (a: August 2019 and b: March 2018)

The thermal springs studied in the region of Agadez were divided into three facies 53.8% of the waters were sodium bicarbonate and potassium, 30.7% of the waters were calcium bicarbonate and magnesian, 15.3% sodium chloride and potassium. In the cation triangle 69.23% of the waters were concentrated in the sodi-potassium pole and 30.77% of the waters no cation dominates. In the anion triangle 84.61% were concentrated in the bicarbonate pole and 15.38% were concentrated in the chloride pole. These results are almost identical to those found by the work of Illias (2018) [26], which finds in the Timia area (Agadez area) bicarbonate waters with a calcium content of 52% and sodium and potassium bicarbonates with 42%.

This bicarbonate predominance can be justified by the high levels of bicarbonate recorded in the thermal waters of the Agadez region.

Sodium and potassium bicarbonate facies are used in the treatment of digestive tract diseases (gastric dyspepsia, chronic colopathies, chronic inflammatory bowel diseases), rheumatic diseases (osteoarthritis of the limbs, chronic vertebral pain, sciatica, cruralgia, cervico-brachial neuralgia, chronic musculoskeletal disorders linked to chronic tendinopathies or tendino-bursopathies, cold phase algodystrophies syndromes.), sequelae of thrombophlebitis of the lower limbs [6, 17].

Calcium and magnesian bicarbonate facies are used in the treatment of diabetes, rheumatic and dermatological diseases.

Sodium and potassium chloride facies are mainly used in rheumatology [6].

According to our different types of facies (table 3) we can direct each patient to the sources according to the disease from which he or she suffers. So it would be good to classify each thermal spring in its field of treatment.

Table 3: Possible treatment from the facies

Name of villages	facies	Possible treatment
Tafadek, Ingiténe, Teghazer, Ingall et Tighraya	Sodium and potassium bicarbonates	Digestive tract, rheumatism, sequelae of thrombophlebitis of the lower limbs
Tekarkar, Awlizdig, Agassara et Tozayate	Calcium and magnesium bicarbonates	Diabetes, rheumatism and dermatology
Tassinik et Taganjir	Sodium and potassium chlorides	Rhumatism

3.3. Study of the mineralization of the thermal waters of Agadez: main component analysis

The principal component analysis was carried out on 26 samples (13 for the 1st campaign and 13 for the 2nd campaign) and on 12 parameters (pH, EC, T°, F^-, $SO_4^{2-,}$ NO_3^-, K^+, Na^+, Ca^{2+}, Mg^{2+}, HCO_3^- and Cl^-). This analysis makes it possible to calculate the eigenvalues, the variances expressed for each factorial axis, their accumulation, the correlation coefficients between all the parameters taken in pairs, as well as the participation of each parameter in the constitution of the factorial axes. The results of this analysis are presented in Table 4 for the correlation matrix and Table 5 for the eigenvalues for the March measurements, Table 6 for the correlation matrix and Table 6 for the eigenvalues for the August measurements. Table 4 shows that electrical conductivity is highly correlated with Na^+ (0.826) and Cl^- (0.801), temperature is highly correlated with Mg^{2+} (0.654), magnesium is highly.

correlated with K^+(0.858) and HCO_3^- (0.820), sodium is highly correlated with HCO_3^- (0.744), SO_4^{2-} (0.712), and Cl^- (0.869), potassium is highly correlated with HCO3- (0.882) and SO42- (0.794), sulfate ions are highly correlated with HCO_3^- (0.696), fluorine is highly correlated with NO3- (0.826). No correlation is observed between: T°, EC, Na^+, Cl^-, K^+, HCO_3^-, SO_4^{2-} , NO_3^- , F^- and Ca^{2+}. Table 6 shows good correlations between the electrical conductivity EC and the elements Na^+(0.810), K^+ (0.626) and Cl^- (0.777), there is a strong correlation between Mg^{2+} and K^+(839), HCO_3^-(0.894), F^-(0.650) and NO_3^-(0,701) there is a strong correlation between sodium and the elements HCO_3^- (0.704), SO_4^{2-} (0.630) and Cl^-(0.872), there is a significant correlation between potassium ions and the elements HCO_3^-(0.866) and NO_3^- (0.717).

Table 4: Correlation matrix between the different variables taken two by two (March 2018)

Variables	T°	pH	CE	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	F^-	NO_3^-	Cl^-
T°	**1**											
pH	0.215	**1**										
CE	-0.020	-0.071	**1**									
Ca^{2+}	-0.378	-0.092	-0.581	**1**								
Mg^{2+}	**0.654**	0.165	0.055	-0.780	**1**							
Na^+	0.109	0.258	**0.826**	-0.758	0.346	**1**						
K^+	0.534	0.019	0.494	-0.920	**0.858**	0.591	**1**					
HCO_3^-	0.464	0.188	0.452	-0.934	**0.820**	**0.744**	**0.882**	**1**				
SO_4^{2-}	0.461	0.225	0.705	-0.767	0.594	**0.712**	**0.794**	**0.696**	**1**			
F^-	0.096	-0.157	-0.093	-0.033	0.105	0.010	0.094	0.183	-0.077	**1**		
NO_3^-	-0.214	-0.081	-0.128	0.124	-0.191	-0.013	-0.235	-0.023	-0.292	**0.826**	**1**	
Cl^-	-0.174	0.288	**0.801**	-0.393	-0.081	**0.869**	0.197	0.326	0.480	-0.164	-0.049	**1**

Table 5: Eigenvalue sand percentages expressed for the main a March 2018

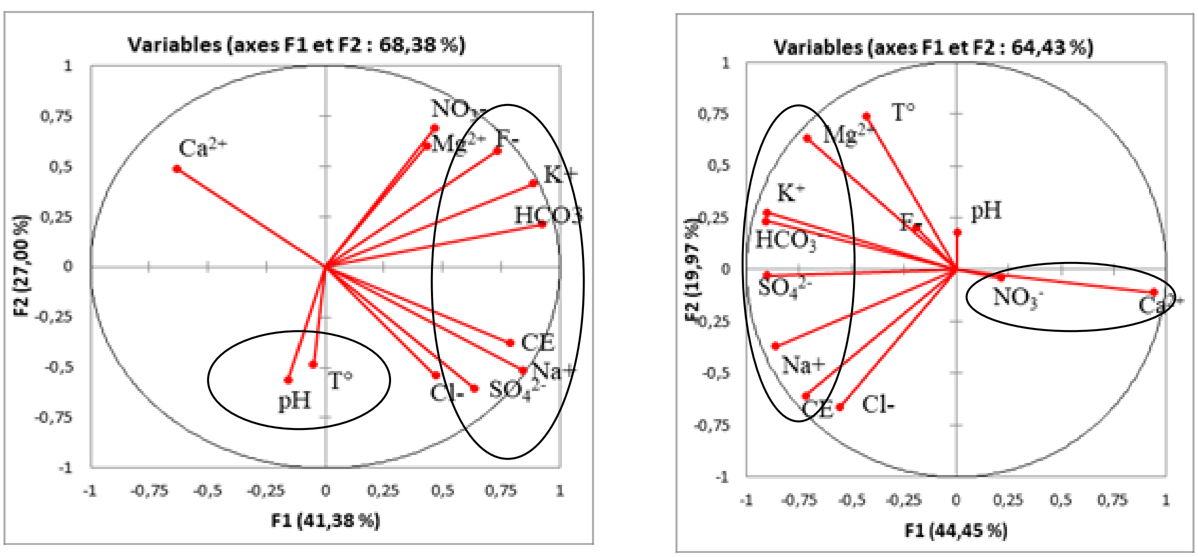
	F1	F2
Eigenvalues	5.779	2.597
Variability (%)	44.454	19.974
cumulated %	44.454	64.427

Table 6 : Correlation matrix between the different variables taken two by two (August 2019)

Variables	T°	pH	CE	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	SO_4^{2-}	F^-	NO_3^-	Cl^-
T°	**1**											
pH	0.109	**1**										
CE	-0.061	-0.115	**1**									
Ca^{2+}	-0.360	-0.146	-0.604	**1**								
Mg^{2+}	-0.256	-0.333	0.234	-0.180	**1**							
Na^{+}	0.215	0.232	**0.810**	-0.762	0.353	**1**						
K^{+}	-0.315	-0.418	0.626	-0.294	**0.839**	0.520	**1**					
HCO_3^-	-0.142	-0.178	0.566	-0.488	**0.894**	**0.704**	**0.866**	**1**				
SO_4^{2-}	0.519	-0.051	0.587	-0.472	-0.001	**0.630**	0.220	0.208	**1**			
F^-	-0.038	-0.294	-0.016	-0.173	**0.650**	0.045	0.580	0.519	-0.097	**1**		
NO_3^-	-0.280	-0.357	0.071	0.100	**0.701**	0.054	**0.717**	0.484	-0.044	0.524	**1**	
Cl^-	-0.069	0.437	**0.777**	-0.542	0.112	**0.872**	0.334	0.486	0.427	-0.211	-0.111	**1**

Table 7: Eigenvalues and percentages expressed for the main axis (August 2019)

	F1	F2
Eigenvalues	4.966	3.240
Variability (%)	41.381	27.002
cumulated %	41.381	68.383



(a) (b)

Figure 9: Space of variables in the factorial designs a) F1 x F2 and b) F1 x F2 for basement waters during March 2018 and August 2019 respectively

Factor F_1 (Figure 9.a) is defined by EC, Na+, SO_4^{2-}, Cl^-, HCO_3^-, K^+ , F^- and Ca^{2+}, Mg^{2+} (Figure 9). This axis represents 44.45% (Table 3) of the total variance, and reflects the natural overall mineralization of the waters. The elements that define this factor come from a long solution time following "water-rock" contact. These elements, which present continuous variations over long periods, characterize the mineralization of the water. The grouping of these elements around this axis shows that they would be put in solution by the same phenomenon which is hydrolysis. The Na^+, HCO_3^- and F^- ions could come from the hydrolysis of silicates and rocks that may contain fluoride ions (muscovite, tourmaline, micaschist...) which would reflect the residence time of the water in the reservoir. Indeed, hydrolysis being a slow process, the F1 factor reflects the conditions of acquisition of the water chemistry. The F_1 factor thus expresses the phenomenon of mineralization-residence time. The grouping of the majority of the variables around this axis shows the influence of alteration-hydrolysis in the solution of the ions.

The factor 2 is determined by the temperature (T°), pH, NO_3^- and Mg^{2+} (figure 9.a) Ca^{2+}. The presence of the NO_3^- ion could have a mainly anthropogenic origin either by leaching of applied fertilizers, or by domestic wastewater discharges or by the degradation of organic matter. For the waters of the August 2019 season (figure 9.b), the factor F1 represents 41.38% of the total variance, (Table 5) is defined by Ca^{2+}, NO_3^-, SO_4^{2-}, K^+, Na^+, HCO_3^-, EC, and Mg^{2+} the factor F_2 represents 27% of the total variance, (Table 5) is determined by temperature (T°), pH, F^- and Cl^-. The Cl^- and SO_4^{2-} ions could come from rainwater infiltration. The grouping of temperature with the elements of the F2 factor could explain their natural origins (water-rock contact or residence time).

In view of the results of the principal component analyzes, it appears that two main mechanisms govern the mineralization of thermal waters in the Agadez region: rainfall by infiltration during the August 2018 campaign and the residence time, as well as the different reactions that could take place in the aquifer during the March 2019 campaign. The abundance of hydrogen carbonate ions in the thermal springs of this aquifer shows that they mainly come from the dissolution of silicate rocks and they provide information on the residence time of the water in the aquifer [13, 24-25]. PCA has made it possible to identify ions of atmospheric origin (Cl^- and SO_4^{2-}) and of anthropogenic origin due to the contribution of nitrate ions. These results are similar to the work of Illias (2018) [26] who worked in one part of our study area (Timia), they are also similar to those of [27, 28, 29, 30].

4. Conclusion

The study of physico-chemical parameters has shown the great chemical variability of the thermal waters studied. The waters with the highest temperature are those of Tafadek during both seasons (52.8°C and 54.8°C) classifying this source as hyperthermal. The waters studied were generally in conformity with the standards recommended by the WHO. However, there were high levels of fluoride ion, chloride, nitrate and bicarbonate during the two campaigns. The classification of the chemical analysis results obtained from the Piper triangular diagram allows the identification of three groups of waters. Sodium and potassium bicarbonate waters (53.845%), calcium and magnesium bicarbonate waters (30.76%) and sodium and potassium chloride waters (15.38%). Bicarbonate waters are revealed as the predominant ions. The therapeutic aspect of these waters is due to the presence of abnormally high ions as well as the type of sodium and potassium bicarbonate facies. Principal Component Analysis (PCA) indicated that the mineralization of the waters studied was governed by two phenomena: the residence time mineralization of the water, the phenomenon of oxidation-reduction in the aquifer and rainfall. The prospects of our work would lead us to estimate the temperature of these sources for geothermal exploitation through the application of chemical geothermometers.

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