Evaluation of groundwater mineralization processes in Moundou City (Southwestern Chad)

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ABSTRACT: This study aims to understand hydrogeochemical functioning of groundwater in Moundou city. This city is located in southwest of Chad between 16° 02' and 16° 12' East longitude and 8° 51' and 8° 60' North latitude. To carry out this study, 15 water points were sampled (8 wells and 7 boreholes,) from November 21 to 26, 2019; and chemical parameters analyzed are HCO_3^-, Cl^-, NO_2^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-. In order to determine origins and processes of mineralization of groundwater hydrochemical and statistical approaches were used. The results show through Chadah diagram, that groundwater presents 2 facies: a bicarbonate calcic and magnesian facies (HCO3-Ca-Mg) and a chloride calcic and magnesian facies (Cl-Ca-Mg). Results also show that main phenomena at origin of mineralization of waters are alteration of silicates, cationic exchanges, evaporation and anthropic activities.

KEYWORDS: Hydrochemistry, groundwater, mineralization, chemical facies, Moundou.

1 INTRODUCTION

Water is a natural resource of paramount importance, because it is essential to life on our planet and therefore, it constitutes an undeniable wealth for humanity. All beings and living organisms on earth need water for their survival and/or growth. It is necessary for all human activities and also plays a very important role in socio-economic development of human communities [1]. It should be noted that while water is one of most important and abundant compounds in ecosystem, freshwater resources are very limited. Although an estimated 70% of Earth's surface is occupied by water, only 3% of this water is fresh. Moreover, freshwater, whether renewable or not, is a resource that deserves special attention, since it is seriously threatened by human activities. Indeed, population growth accompanied by rapid urbanization causes numerous disturbances in natural environments [2], industrialization, abusive use of fertilizers and pesticides, as well as lack of awareness of population for protection of environment, lead to an imbalance of ecosystem and generate pollutants that can affect physico-chemical and biological quality of receiving aquatic environments [3].

In Africa, groundwater is largest and most important water resource ([4], [5]). Thus, groundwater is a preferred resource for supplying drinking water to populations, as it is free of pollution compared to surface water. Moreover, they are more resilient to climate variability than surface water [4]. Chad, one of largest countries in Central Africa with an area of 1284,000 km2, has significant exploitable groundwater resources that vary between 260 billion and 550 billion m3. The annual renewable water resources are estimated at 20 billion m^3 [6]. Unfortunately, latter is very unevenly distributed and access to drinking water remains limited despite efforts of the Chadian government. In Moundou city, situation is identical to that observed in other cities in Chad. Indeed, this city is also faced with problem of accelerated urbanization due to a growing population. In 2009, population was estimated at 15,015 inhabitants [7] and could reach approximately 380,000 inhabitants by 2030 [8]. This population growth is not without consequences on environment in general and on

groundwater resources in particular, especially in terms of quantity and quality. This rapid and significant growth of local population, coupled with rural exodus, is accompanied by an increase in production of large quantities of waste (solid or liquid), and when this waste is washed away during rainy season, it can alter groundwater table. It should be noted that chemistry of natural waters depends essentially on geological composition of environments crossed and residence time. However, it is very dynamic because it is largely controlled and modified by its contact environment. Thus, as soon as water comes into contact with an undesirable substance or a germ, its quality can be affected. Consumption of unsafe water is a threat to public health because it exposes people to a range of diarrheal diseases and chemical poisoning [9]. The greatest victims are young children and according to [10], each year more than two million people, mainly children under five, die from diarrheal disease. Faced with the inability of Chad Water Company (STE), main water Distribution Company, to provide good quality water, population of Moundou city uses traditional wells or human powered pumps to collect water from groundwater table to solve this problem, however quality of this water is not guaranteed. To ensure access to good quality water and to guarantee better management of this resource, it is essential to know hydrochemical processes that govern its mineralization. We hope that result of this work will provide necessary information for updating of hydrogeological maps of Chad.

2 PRESENTATION OF THE STUDY AREA

Economic capital of Chad, Moundou city is capital of department of Lac Wey and the region of Logone Occidental. Located 500 kilometers from N'Djamena, capital of Chad, it lies between 16° 02' and 16° 12' East longitude and between 8° 51' and 8° 60' North latitude (Figure 1). It is located on a relatively flat basin, with an average elevation of natural terrain between 390 and 400 m.
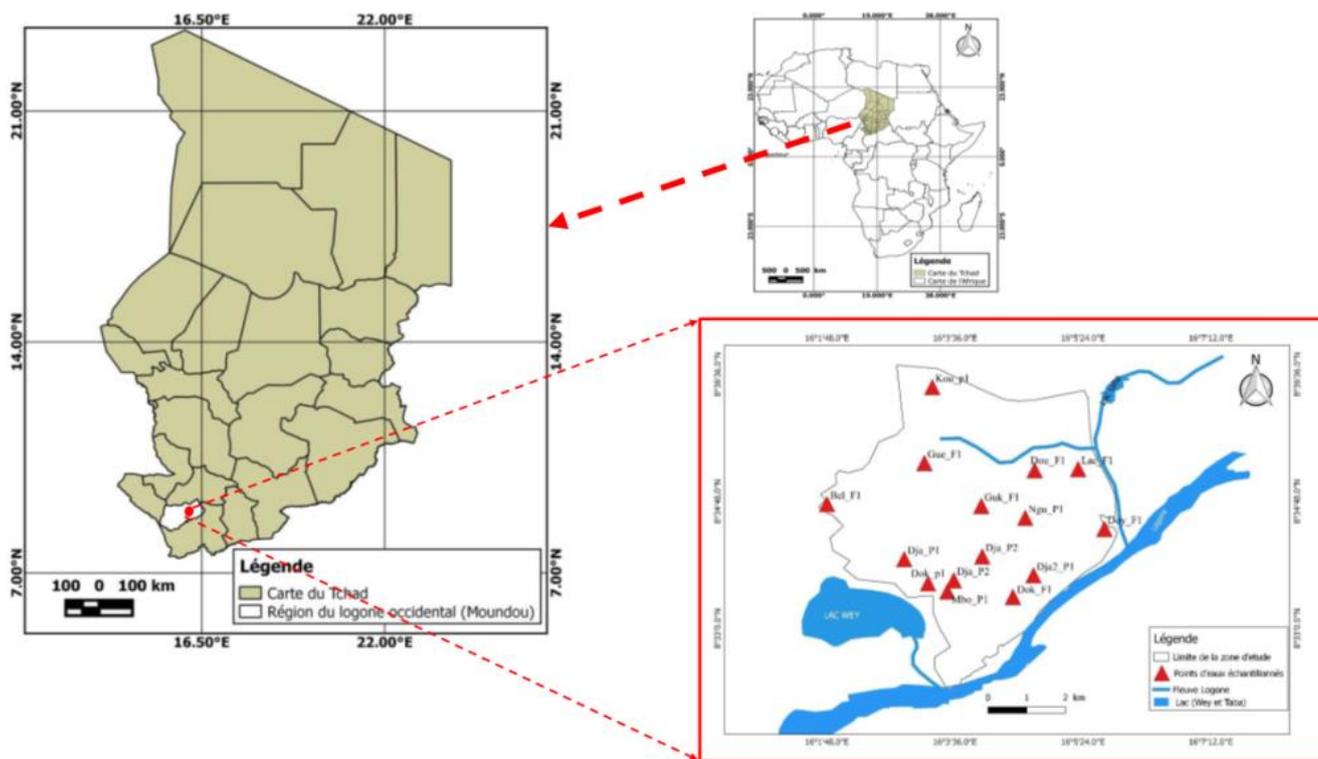

Fig. 1. *Location of study area and spatial distribution of sampled water points*

Study area is subject to a semi-humid tropical climate of Sudanian type, and is characterized by two seasons: rainy season that extends from April to October and dry season that extends from November to March. Rainfall generally varies between 1000 and 1200 mm per year. Temperature in Moundou ranges from 15°C to 41°C with an annual average of 27°C. Dry season lasts approximately 5 months i.e. from November to end of March [11].

Regarding geology and hydrogeology knowledge is quite limited. Moundou city is located in Koros region which constitutes southern part of Chad [12], latter extends between crystalline massifs corresponding to border with Central African Republic and Chari floodplains. It is an area formed by 8 plateaus (Koros) resulting from an original plateau that has been cut by valleys occupied by permanent watercourses located between 100 - 500 m below plateau. Altitude of these plateaus can exceed +450 to +500 m, with a peak at +627 m (Koro de Bebangher) and Moundou city is located in hilly part of Koros region, at an altitude of +398 m. Geology of Moundou town,

as described by [12], is that of Doba-Salamat sub-basin (area corresponding to middle part of Logone and Chari river basins). Only Terminal Continental (TC) outcrops in study area, it is made up of sedimentary formations with variable lithology, ranging from sands to lateritic armoury, passing through clayey sandstones, sandy clays and mudstones. Maximum strength of Terminal Continental is in center of sub-basin and coincides with tectonic trough filled by Cretaceous materials. Lower part of TC, about 800 meters thick, consists of sands interspersed with beds of silts and clays. Upper part is formed by sandy-clay materials whose height varies between 70 m and 260 m. Continental Terminal (CT) is rich in water resources, including water table, which is subject of this study. Lithological sections (Figure 2) obtained from data sheets of four boreholes and a pressiometric borehole drilled by SETUBA Company [13] in Moundou city show a great heterogeneity of layers.
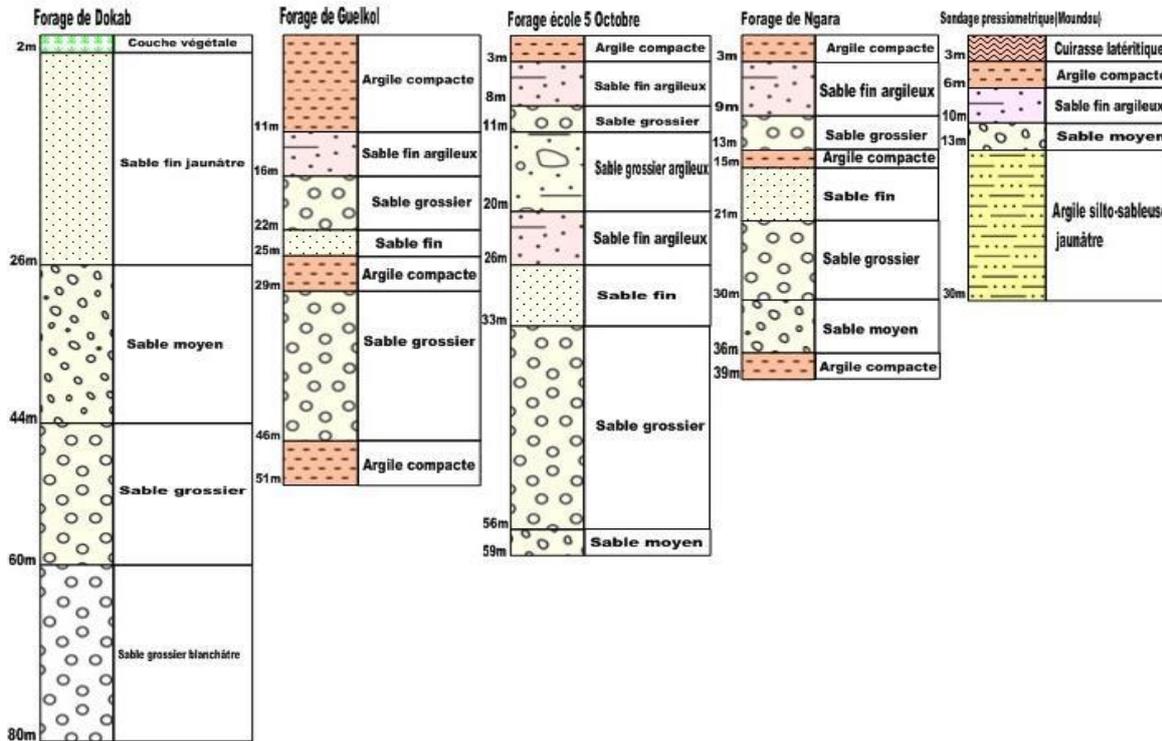

Fig. 2.   Lithological cross-section of boreholes drilled in Moundou town

A weak layer of compact clay can be seen in Ngara borehole and in 5 October School borehole; a layer of clay 11 meters thick can be seen in Guelkol borehole, and alternating layers of fine clayey sand have also been identified. Beyond a depth of 10 meters, we note presence of layers of medium and coarse sand, this depth corresponds to minimum depths of traditional wells in city. An alternation between coarse and medium sand layers and sometimes thinner compact clay layers is observed at a depth greater than 20 meters (example of lithological layers of Guelkol and Ngara). Piezometric map of groundwater table in Moundou city (Figure 3) was produced from piezometric data collected during June 2015 campaign on basis of twenty-nine (29) wells distributed more or less homogeneously throughout city [14], except for residential areas where no wells were found.
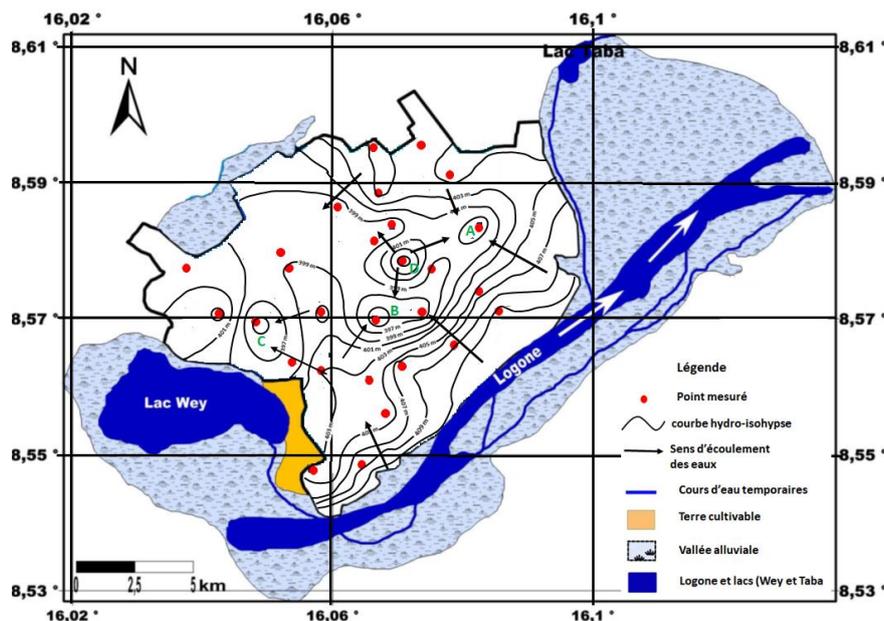
Fig. 3.   Piezometric map of Moundou city (June 2015)

This map provides a certain amount of information on the piezometric evolution of the water table and allows us to highlight some of its characteristics. Thus, it can be seen that, depending on orientation of treamlines, in eastern and southern parts of study area, water table flows from southeast to northwest. In North, it tends to flow from North-East to South-West on one hand and from North-West to South-East on other hand. In general, water seems to flow from peripheral neighborhoods to city center of. This observation is consistent with observations made by engineering consulting firm of French group Veolia during a study conducted in this area [11].

Overall, water table is close to surface of ground in vicinity of river (Logone) and becomes deeper as one moves away from it, towards city center. In addition, we note that near river isopiez curves are fairly close together, which suggests that river feeds groundwater table. The presence of piezometric depressions, A in northeast, B in center and C in west, as well as a pie zometric dome D in city central part, are certainly noted. However, current state of knowledge does not allow us to say whether domes correspond to recharge zones and depression to a zone of overexploitation of water table under city. The direction of water flow is linked to city's topography. In Moundou city, during wet season (rainy season), shallow water table is fed directly from rainfall, its level rises to ground level and its water then mixes with water that runs off.

From a hydrographic point of view, Moundou city is bordered in southeast (Figure 1) by Logone River (1,000 km long), one of country's main permanent watercourses. Logone River originates from convergence of two rivers: Vina and Mbéré, which originate on Adamaoua plateau in Cameroon, located at an average altitude of 1,200 meters. Logone receives on its right bank Lim from Mount Yadé [12]. At city level, there is also Lake Taba to northeast and Lake Wey to southwest. Although it has not been established, it seems that these two lakes also contribute to recharge of surface water table.

3   SAMPLING AND ANALYSIS

To carry out this study, a total of 15 water points were sampled (wells, boreholes,) between November 21 and 26, 2019 so as to have an overall picture of water (Figure 1). These points were located by Garmin GPS. pH and temperature were measured in situ with a device equipped with a mixed pH 323/SetB electrode and conductivity with the Lf 318/Set electrode conductivity meter. Samples for chemical analysis were filtered using millipore filters with a diameter of 0.45 μm, before being transferred to clean one-liter (1L) polyethylene bottles, which were previously rinsed at least three times with water to be collected, and bottles were filled to brim before being hermetically sealed to avoid air bubbles. A few drops of acid were added to samples for cation analysis. Samples were then placed in a cooler to be maintained at a temperature of 4° C before being sent to laboratory. Chemical analyses were performed at National Water Laboratory (LNE) of Ministry of Water and Sanitation. Analytical methods vary according to chemical elements: HCO_3^- and Cl^- were determined by the volumetric method; Na^+, K^+, Ca^{2+}, Mg^{2+}, were determined thanks to Photometer DR7100 and SO_4^{2-}, NO_3^-, NO_2^- by spectrometry (DR890). We have verified reliability of our results by calculating ionic balance of each water point, our values are between -3 and +5%.

4   PHYSICO-CHEMICAL CHARACTERISTICS OF THE WATER

4.1   PHYSICO-CHEMICAL PARAMETERS

Statistical parameters of each of physico-chemical variables (minimum, maximum, average, standard deviation and coefficient of variation) are calculated and summarized in table below (Table 1).

Table 1.   Statistical characteristics of physicochemical analyses

Paramètres	C25°C	pH	T°C	TDS	HCO_3^-	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	P_{CO2}
Unités	µS/Cm		°C	mg/L										atm
minimum	59,7	6,5	26,6	72	30,5	8	0,04	2,76	0,01	8	4	3,5	2,5	0,09
maximum	1999	8	31,7	1391	869	90	2,4	40,06	107,6	87,2	84	134,8	49,4	8,8
moyenne	775,6	7,3	28,5	540,9	329,5	30,9	0,4	14,6	28,4	39,9	35,5	48,5	11,7	3,0
Ecart - Type	662,9	0,5	1,5	446,0	286,2	19,8	0,7	13,8	33,3	28,3	28,2	51,1	11,9	3,0
Coefficient de Variation (%)	85,5	6,4	5,2	82,5	86,9	64,0	170,5	94,2	117,1	71,0	79,2	105,5	101,8	97,2

The coefficient of variation (CV) represents ratio of standard deviation to arithmetic mean. It is a parameter that measures dispersion of a series of observations of a variable around its arithmetic mean. If value of CV is less than 50%, observed variable has a homogeneous distribution around its arithmetic mean and if value of CV is greater than 50%, observed variable has a heterogeneous distribution around its arithmetic mean [15]. Calculation of CV shows that pH and temperature have a homogeneous distribution (CV < 50%) while Electrical Conductivity (EC), TDS and total ions analyses have a heterogeneous geographical distribution (CV > 50%).

Electrical conductivity ranges from 59.7 µS/cm to 1999 µS/cm for all works combined (boreholes and wells), with an average of 775.6 µS/cm. Waters from wells are more mineralized than those from boreholes, in fact, the waters from wells have an average conductivity of about 1204.2 µS/cm, on other hand those from boreholes have an average conductivity of about 285.9 µS/cm. High mineralization observed in some water points (Dok-P2, Dja-P4, Dja-P6, Mbo-P7 and Dja-P8) can be explained by fact that catchment structures are made up of open wells and therefore without protection against all sources of external pollution that can influence its mineralization, on one hand, and on other hand, water table is shallow, so in addition to influence of pollution, it can also be subject to evaporation. Just like Electrical conductivity, total dissolved solids (TDS) also shows a wide variation (72-1391 mg/L). According to [16], a water is said to be soft if we have TDS< 1,000 mg/L; brackish for 1000 < TDS < 10,000 mg/L and saline for 10000 < TDS< 1,000,000 mg/L. According to this classification, three (03) water points (Dja-P6, Mbo-P7 and Dja-P8) can be qualified as brackish with a TDS higher than 1,000 mg/L. pH values vary between 6.5 and 8 with an average of 7.3; on average, pH of water is around neutral except for two wells, Doy-F6 and Dom-F1, which are slightly alkaline with respective pH values of 8. Temperature of water ranges from 26.6°C to 31.7°C with an average of 28.5°C. Average temperature of water from wells is equal to 27.5°C and is slightly higher than that of borehole water (average temperature: 29.7°C). In all cases, temperatures obtained are close to average annual temperature of region, which is 28°C. This means that water in study area is in thermal equilibrium with atmosphere

Chemical parameters analyzed in case of this study are also characterized by variations in concentration of ions: HCO_3^- (30.5 - 869 mg/L), Cl^- (8 - 90 mg/L), SO_4^{2-} (0.01 -107.6 mg/L), NO_3^- (2.76 -40.06 mg/L), NO_2^- (0.04 - 2.4 mg/L), Na^+ (3.5 - 134.8 mg/L), Mg^{2+} (4 - 84 mg/L), K^+ (2.5 - 49.4 mg/L, and Ca^{2+} (8-87.2 mg/l /L). This heterogeneity of physico-chemical parameters highlights fact that groundwater chemistry is regulated by several processes.

Statistically, as far as well water is concerned, for anions, the water is dominated by HCO_3^- ions which represent 83% of total anions followed by SO_4^{2-}, Cl^- and NO_3^- ions which represent respectively 7%, 6% and 4% of total anions. Percentage of NO_2^- ions is 0%. For cations, waters are dominated by Na+ ions which represent 36% of total cations followed by Ca^{2+}, Mg^{2+} and K+ ions which represent respectively 29%, 26%, and 9% of total cations. The anions in the borehole water are dominated by HCO3- ions which represent 73% of the total anions followed by Cl-, SO_4^{2-} and NO_3^- ions which represent respectively 18%, 6% and 3% of the total anions. Percentage of NO_2^- ions is 0%. Cations are dominated by Ca2+ ions which represent 45% of total cations followed by Mg^{2+}, Na^+ and K^+ ions which represent respectively 31%, 14%, and 10% of the total cations.

4.2   CHEMICAL FACIES

To get an overview of the different types of water in relation to the geochemical processes that control the mineralization of groundwater, the water points were plotted on the diagram of [17]. This diagram is a modified version of Piper's diagram [18] and was produced using Diagramme software [19]. Chadah's diagram is constructed from the percent difference in milliequivalents between alkaline earths (Ca^{2+} +Mg^{2+}) and alkalines (Na^+ + K^+), expressed as reaction percent contents, on the X-axis, and the percentage difference in milliequivalents between weak acid anions (HCO_3^- + CO_3^{2-}) and strong acid anions (Cl^- + SO_4^{2-}), also expressed as percentage reaction contents, on the Y axis. Percentage differences of milliequivalents of coordinates (X and Y) are then extended in main sub-areas of study of diagram, this is what allows to define character of whole groundwater.

Thus four (04) main types of water can be defined from this diagram: $NaHCO_3$, $CaHCO_3$, $NaCl$ and $Ca-Mg-Cl$, based on relationship between alkaline earths (calcium and magnesium), alkali metals (sodium and potassium), weak acid anions (carbonate and bicarbonate) and strong acids (chloride and sulfate). In Figure 4, a total of fourteen (14) water points or approximately 93% of total water sampled is located in Zone 5, where alkaline earths and weak acid anions dominate both alkali metals and strong acid anions. Waters are of calcic and magnesian bicarbonate type. This type of water is characteristic of fresh waters generated by alteration of silicate minerals
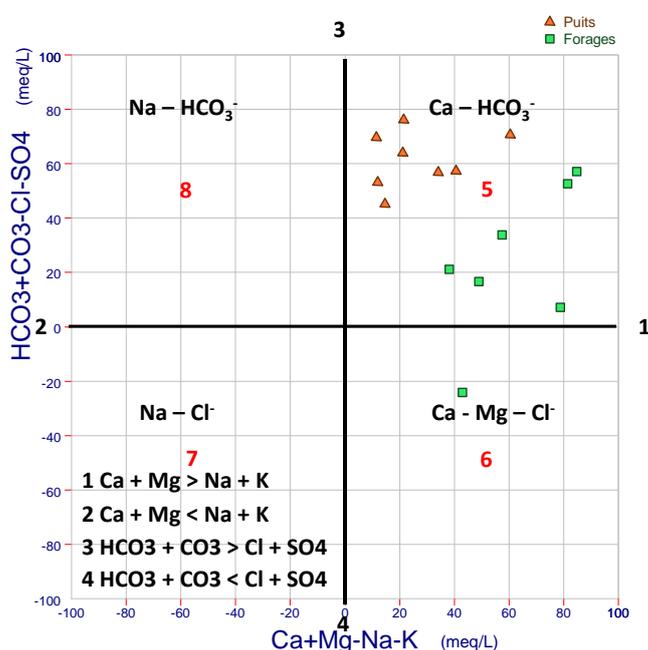

Fig. 4.   Diagram of Chadah (1999)

One (01) water point or about 7% of total water sampled is in zone 6, where alkaline earth metals dominate alkali metals and strong acid anions dominate weak acid anions. This water, which is of chloride-calcium-magnesium type, probably results from reverse base exchange process. This water point may also be influenced by anthropogenic activities and/or evaporation.

5   GROUNDWATER MINERALIZATION PROCESS

5.1   GIBBS DIAGRAM

To gain insight into hydrogeochemical processes that control chemistry of major ions in groundwater, [20] proposed a scatter plot that takes into account three important natural mechanisms, namely: (1) atmospheric precipitation, (2) rock weathering and (3) evaporation. Thus, TDS were plotted as a function of Na+ / (Na^++ Ca^{2+}) +) for cations and Cl^- / (Cl^-- HCO_3^-) for anions (Figure 5).
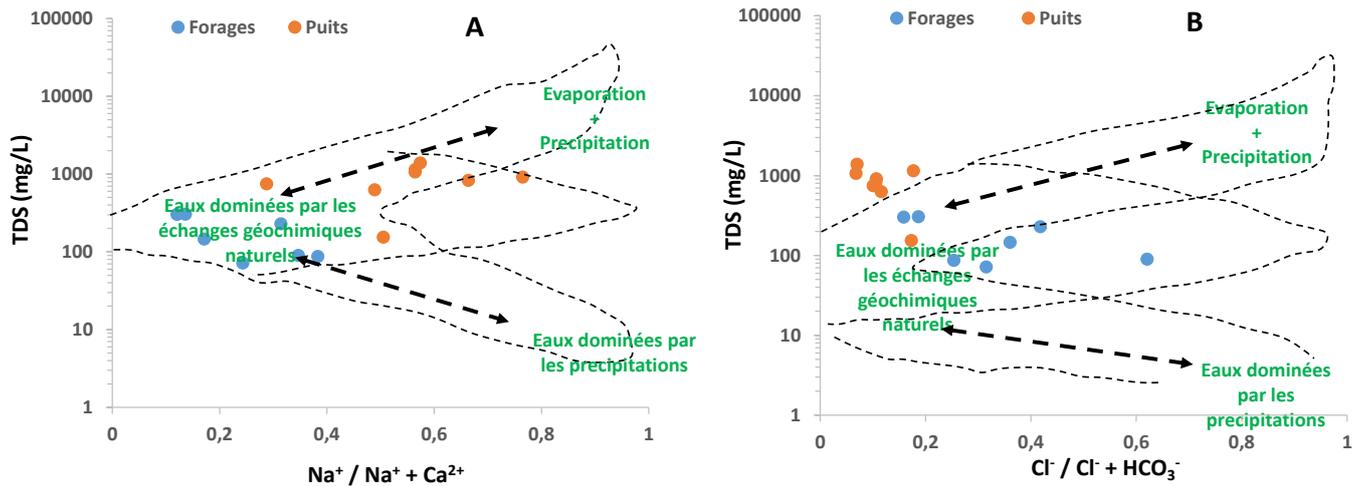
Fig. 5.   Groundwater chemistry expressed as a function of rainwater chemistry, rock matrix and evaporation

Figures 5A and 5B show that most of water points have relatively low $Na^+/ (Na^+ + Ca^{2+})$ and $Cl^-/ (Cl^- + HCO_3^-$ relative ratios (less than 0.4) and relatively low TDS as well (less than 400 mg/L); for these water points we can say that rock weathering is the main mechanism that controls water chemistry. There are points that have ratios that increase together with TDS, this indicates that water chemistry is controlled not only by rock weathering but also by evaporation-precipitation. In our case, precipitation phenomenon remains very limited because majority of water is under-saturated or saturated with respect to carbonate minerals and evaporites (Figure6). Among these points are Dok-P3, Ngu-P5, Dja-P8 and Mbo-P7 which are all open wells. In Figure 5B, we can also see that a number of points that are essentially open wells have a relatively high TDS (> 600 mg/L) and a relatively low $Cl^-/ (Cl^- + HCO_3^-)$ ratio (less than 0.2), which suggests that water chemistry is probably influenced by anthropogenic activities. Among these water points, we have almost all well water points except Kou-P1.

5.2   MINERAL PHASE SATURATION INDICES

In order to determine degree of equilibrium between water and minerals and to appreciate at same time phenomena of dissolution and precipitation of minerals present in groundwater, saturation indices (SI) of groundwater with respect to mineral phases (Aragonite ($CaCO_3$), Calcite ($CaCO_3$), Dolomite (Ca, Mg (CO_3) 2) and Gypsum ($CaSO_4$. H_2O) were calculated using geochemical computer model PHREEQC [21]. Saturation index is defined by the following equation:

$$IS = Log\ PAI\ /\ Ksp \tag{1}$$

With PAI and Ksp which represent respectively product of ionic activity and constant of solubility product.

When IAP <Ksp, i.e. SI < 0 the groundwater is undersaturated with respect to a given mineral phase, thus leading to dissolution of mineral. Whereas with IAP>Ksp, i.e. SI > 0 water is rather supersaturated with respect to a determined mineral phase, thus leading to precipitation of mineral. When SI is equal to zero, water is saturated with respect to mineral considered ([22], [23]). This means that mineral is in equilibrium with groundwater, and thus will tend neither to precipitate nor to dissolve. SI evaluation is therefore useful in understanding geochemical processes, plus it is able to determine origin of dissolved ions in groundwater [24]. Calculated SI values (Table 2) for calcite varies between -1.29 and 0.48 with an average of -0.25, that of aragonite varies between -1.43 and 0.34 with an average of -0.39. For, gypsum and dolomite values vary, between -6.34 and -1.68 and between -2.97 and 0.79, with averages of -3.10 and -0.77 respectively.

Table 2.   Saturation indices for some minerals and P_{CO2}

Nom des échantillons	Calcite	Aragonite	Gypse	Dolomie	$P_{CO_2} 10^{-2}$	CAI-1	CAI-2
Dom-F1	0,21	0,07	-5,48	-0,04	0,129	0,41	0,41
Gue-F2	-1,05	-1,19	-3,24	-2,44	0,09	-0,61	-0,61
Bel-F3	-1,02	-1,16	-4,36	-2,57	0.082	0,23	0,23
Dou-F4	-1,29	-1,43	-6,34	-2,97	0,104	0,50	0,50
Guk-F5	-0,97	-1,11	-2,99	-2,11	0,371	0,63	0,63
Doy-F6	0,48	0,34	-2,8	0,78	0,211	0,45	0,45
Lac-F7	-0,52	-0,66	-2,81	-1,31	1,995	0,42	0,42
Kou-P1	-0,61	-0,75	-3,39	-1,86	2,44	-1,71	-0,31
Dok-P2	-0,28	-0,42	-2,09	-0,35	5,306	-3,88	-0,36
Dok-P3	-0,1	-0,24	-2,25	-0,35	3,016	-2,21	-0,24
Dja-P4	0,05	-0,09	-2,47	-0,02	4,114	-4,25	-0,44
Ngu-P5	0,34	0,2	-2,28	0,32	2,993	-1,37	-0,13
Dja-P6	0,45	0,31	-2,18	0,79	4,486	-1,06	-0,21
Mbo-P7	0,37	0,23	-1,68	0,55	8,456	-5,66	-0,36
Dja-P8	0,17	0,03	-2,14	0,02	8,797	-5,31	-0,35

Relationship between saturation indices and TDS (Figure 6) allows us to determine saturation state defined by band between saturation indices -1 and 1. Zone located above this band represents oversaturation state while undersaturation state is located below this band [25].

We note that eleven (11) water points (or 73%) are saturated and four (04) points (or 27%) are undersaturated with respect to calcite. For dolomite, six (06) water points sampled are under saturated and nine (09) points are saturated with respect to this mineral; this represents 40% and 60% of total points sampled respectively. For aragonite, four (04) water points are under saturated and eleven (11) water points are saturated with respect to this mineral, representing respectively 27% and 73% of total points sampled. As for gypsum, it was found that all sampled points (i.e. 100%) are saturated.
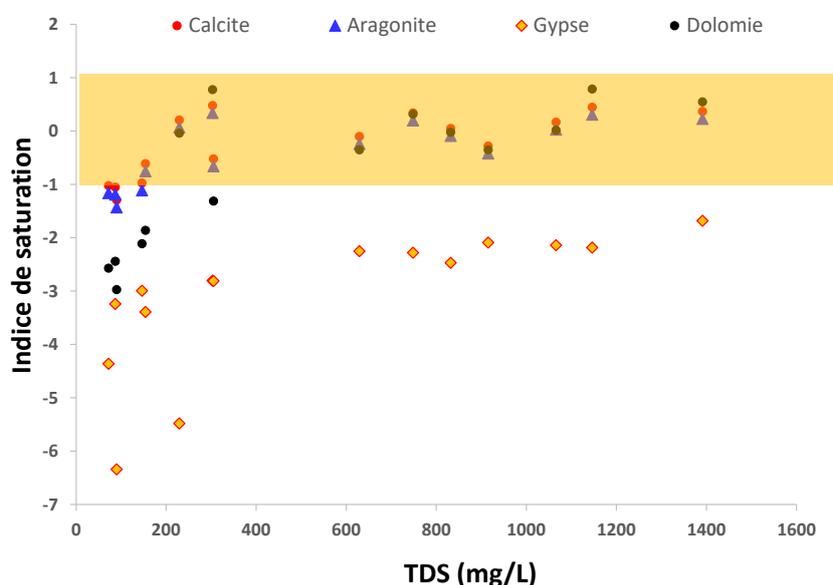

Fig. 6.   Saturation index (SI) versus TDS

5.3 BASE EXCHANGE INDEX

During flow, the chemical composition of water can undergo changes due to the phenomenon of ion exchange. This ion exchange is defined as a process of replacement of one chemical element by another at the solid material interface when the composition of the water changes due to pollution, acidification, or displacement of the interface of two types of water with distinct characteristics [26].

Direct and reverse ion exchange can be expressed as equations (2) and (3), respectively below:

$$2Na^+ + CaX_2 = 2NaX + Ca + \qquad\qquad (2)$$

$$Ca^+ + 2NaX = CaX_2 + 2Na^+ \qquad\qquad (3)$$

Where X indicates the soil exchange ion [27].

Base Exchange Indexcan be highlighted through graph representing $Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-}$ as a function of $Na^+ - Cl^-$ (Figure 7). If we consider that cation exchange plays an important role in process of water mineralization this should be reflected in a strong linear relationship between variables with a slope of - 1 [28].
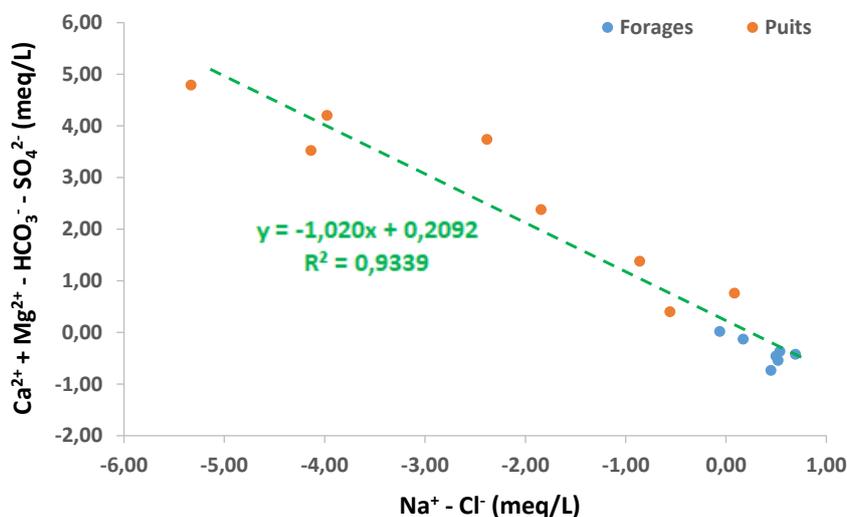

Fig. 7.   Graphical representation of $Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-}$ according to $Na^+ - Cl^-$

In our case (Figure 7), we notice that most of water points are distributed along a straight line with a slope of -1.02 and present a good correlation (0.93), this confirms that there is an ion exchange process. This shows that cation exchange is one of hydrochemical processes that influence the quality of water in Moundou city. However, fact that there are a few points distributed above and below linear trend suggests that mineralization of water depends on other processes besides ion exchange.

To confirm presence of cation exchange, we used chlor-alkali indices proposed by [29]. Schoeller's indices, such as CAI-1 and CAI-2 were calculated using equations below:

$$CAI\text{-}1 = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \qquad\qquad (4)$$

$$CA2\text{-}1 = \frac{Cl^- - (Na^+ + K^+)}{SO_4^{2-} + HCO_3^- + CO_3^{2-} + NO_3^-} \qquad\qquad (5)$$

In these equations all ions are expressed in meq/L.

When there is an exchange between Na^+ or K^+ ions of water with Mg^{2+} or Ca^{2+} ions of rock, it indicates that there is a direct ion exchange. Amounts of Na^+ or K^+ ions will decrease in water and both indices (CAI-1 and CAI-2) above will be positive. In contrast, reverse ion exchange will produce negative indices [30]. If values of chloroalkaline indices are zero, it means that no ion exchange process is promoted. Values of CAI-1 and CAI-2, in this study range from -3.63 to 0.93 and -0.64 to 0.92 respectively (Table 2). At level of Figure8, it can be seen that eight (08) sampled water points (i.e. 53%) have negative CAI 1 and CAI 2 values and for seven (07) sampled water points

(i.e. 43%) these values are positive, which means that both direct and reverse ion exchange processes play an important role in water mineralization.

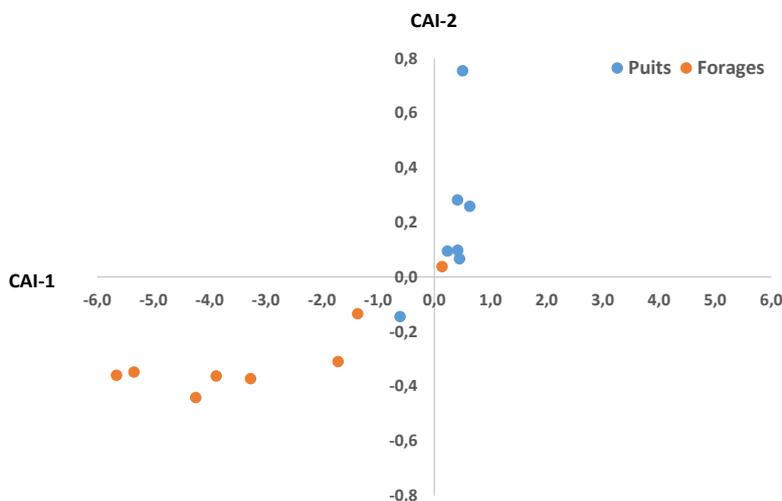It also confirms fact that cation exchange is an important geochemical process in groundwater of Moundou.

Fig. 8.   Relationship between CAI-1 and CAI-2 of groundwater

53% of water points in this study have negative CAI-1 and CAI-2 values and for 43% of water points these values are positive, meaning that both normal and reverse ion exchange processes play an important role in water mineralization.

5.4   PARTIAL PRESSURE OF CO2 (PCO2)

Groundwater P_{CO2} values were calculated using PHREEQC program. They are found to range from 0.078 to 8.255 10^{-2} atm (Table 2). These values are higher than the atmospheric P_{CO2} which has a value of $10^{-3.50}$ atm [31], suggesting that groundwater is in contact with soil CO_2. Latter comes from root respiration and decomposition of soil organic matter. Carbon mineralization occurs in an open system.

Furthermore, in Figure 9, we can see that for most of water points, pH values increase as partial pressure of CO_2 decreases. This behavior can be explained by a relatively long residence time of water in aquifer on one hand, and by importance of physical and chemical reactions that take place between water and minerals in aquifer on the other hand. To this we can add probable presence of biological reactions of micro-organisms that produce CO_2.
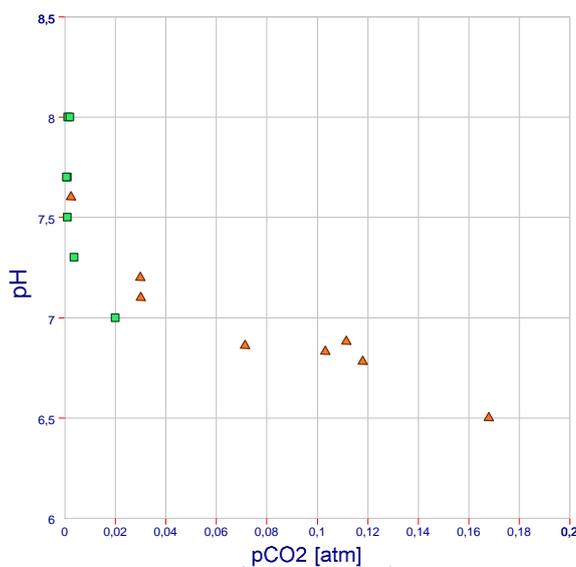

Fig. 9.   Relationship between pH and PCO2 of groundwater

It is also noted that presence of CO_2 in water from soil facilitates hydrolysis of silicate minerals and formation of HCO_3^- ions, which are most dominant ions in our waters. This explains fact that water is dominated by HCO_3^- ion and that it sometimes becomes more and more alkaline. It is also noted that consumption of CO_2 following hydrolysis of silicates leads to an increase in HCO_3^- ions and consequently basicity of waters [32].

6 MULTIVARIATE STATISTICAL ANALYSIS

6.1 PRINCIPAL COMPONENT ANALYSIS (PCA)

Multivariate statistical techniques such as correlation coefficient, Principal Component Analysis (PCA) and Hierarchical Ascending Classification were used to further characterize water types in our study area, based on a wide variety of measured parameters. Chemical data were statistically analyzed using computer software Statistical Package for Social Sciences (IBM SPSS Statistics 21).

Eigenvalues of factors are grouped in Table 3 and finding is that first two factors F1 and F2 account for 78.94% of variance expressed. These factors group together maximum of variance expressed and are sufficient to reflect information sought.

Table 3.   PCA results using varimax rotation with Kaiser normalization.

Parametres	F1	F2	F3
c25C	**0,64**	0,53	0,50
pH	-0,80	-0,34	-0,10
TC	-0,84	-0,01	-0,02
TDS	**0,70**	0,57	0,43
HCO3	**0,68**	**0,56**	0,47
Cl	0,12	**0,97**	-0,05
NO2	-0,07	-0,05	**0,93**
NO3	0,51	0,23	**0,66**
SO4	**0,81**	0,24	0,10
Ca	0,48	**0,55**	**0,57**
Mg	**0,67**	**0,65**	0,29
Na	**0,72**	**0,51**	0,38
K	**0,77**	0,26	0,20
PCO2	**0,74**	0,28	0,55
Valeurs propres	9,71	1,34	1,03
% de la variance	69,34	9,60	7,37
% cumulés	69,34	78,94	86,31

Factor 1, which alone accounts for 69% of total variance (Table 3), contains high loadings of Electrical Conductivity, TDS, P_{CO2}, and ions such as Na^+, Mg^{2+}, K^+, Ca^{2+}, SO_4^{2-}, NO_3^- and HCO_3^-. Grouping of these variables shows that Factor 1 expresses main source of mineralization of aquifer water. Majority of ions very often come from hydrolysis of silicate minerals. However, we note influence of anthropic activities in acquisition of mineralization of water, especially in presence of NO_3^- ion. To search for origin of these ions, we were interested in analysis of correlation matrix (Table 4). When two variables have a correlation coefficient R ≥ 0.7 they can be considered strongly correlated and for R between 0.5 and 0.7 they are considered moderately correlated [33].

Table 4.   Pearson correlation between physicochemical parameters.

Paramètres	c25C	pH	TC	TDS	HCO3	Cl	NO2	NO3	SO4	Ca	Mg	Na	K	PCO2
c25C	1													
pH	-0,75	1												
TC	-0,47	0,70	1											
TDS	0,96	-0,78	-0,59	1										
HCO3	0,95	-0,77	-0,59	0,99	1									
Cl	0,55	-0,43	-0,17	0,61	0,60	1								
NO2	0,37	-0,07	0,05	0,32	0,36	-0,08	1							
NO3	0,81	-0,54	-0,54	0,75	0,78	0,24	0,40	1						
SO4	0,71	-0,72	-0,47	0,77	0,74	0,29	0,14	0,35	1					
Ca	0,82	-0,58	-0,51	0,89	0,91	0,56	0,40	0,83	0,49	1				
Mg	0,89	-0,79	-0,56	0,97	0,96	0,68	0,22	0,65	0,77	0,86	1			
Na	0,96	-0,80	-0,58	0,96	0,95	0,57	0,28	0,72	0,76	0,75	0,89	1		
K	0,76	-0,53	-0,51	0,78	0,77	0,29	0,07	0,57	0,80	0,67	0,73	0,73	1	
PCO2	0,89	-0,78	-0,63	0,91	0,92	0,36	0,48	0,76	0,74	0,79	0,81	0,92	0,72	1

On this basis, we note in particular that electrical conductivity correlates very well with HCO_3^- (R=0.95,) Ca^{2+} (R=0.82), Mg^{2+} (R=0.89), SO_4^{2-} (R=0.71), Na^+ (R=0.96) and K^+ (R=0.76), thus confirming that this group of elements is strongly involved in mineralization. In any case, this suggests that EC is mainly controlled by these ions. The strong correlation between Ca^{2+} and Na^+ (R=0.75) is probably due to basic ionic exchanges with clay matrix (as we have seen previously).

Of course, weight of NO_3^- is not as high as that of other ions, but the good correlation between NO_3^- and EC (0.81) and TDS (0.75) underlines the importance of NO_3^- in global mineralization of water on one hand and influence of anthropic activities in acquisition of mineralization of water on other hand. We also note a strong correlation between NO3- and Na+ (R=0.72), and HCO_3^- (R=0.78) and a moderate correlation between NO_3^- and K^+ (R=0.57) and NO_3^- and Mg^{2+} (R=0.65), which suggests that these ions probably have an anthropic origin, apart from their natural origin. F2 factor alone explains 9.60% of total inertia of cloud, it is characterized by dominant weight of Cl- associated with Na^+, Ca^{2+}, Mg^{2+} and HCO_3^- ions.

The Cl^- ion can be used alone to highlight influence of evaporation on water as well as it can be used jointly with Na+ as indicators of pollution, especially in urban areas. These two ions have an average correlation of about 0.57 (Table 4) and have values that are sometimes high, especially in this freshwater context, suggesting that their origin is not exclusively natural. Furthermore, these high values are mostly found at relatively mineralized water points. In Table 4, strong correlations observed between Na^+ and HCO_3^- (0.95), Ca^{2+} (R=0.75), Mg^{2+} (R=0.89) and the average correlations observed between Cl^- and HCO_3^- (0.60), Ca^{2+} (R=0.56), Mg^{2+} (R=0.68) are probably due to influence of anthropogenic activities coupled with evaporation. Finally, F3 factor, which explains 7.37% of total variance, contains NO_3^-, NO_2^- and Ca^{2+} ions.

F3 factor is an indicator of surface inputs and degradation of water quality. Nitrates (NO_3^-) and nitrites have a superficial origin and indicate pollution of anthropic origin. This indicates presence of anthropogenic mineralization of superficial origin.

Both nitrite and nitrate ions can originate from domestic wastewater discharges, organic matter degradation, latrine influence or animal excrements.

6.2   HIERARCHICAL ASCENDING CLASSIFICATION (HAC)

Hierarchical ascending classification (HAC) is a classification technique that aggregates observations, from most similar to most dissimilar. For this study, we used Ward's aggregation method [34] and Euclidean distance, combination of which produces groups of samples distinct from each other [35]. The dendrogram of samples in Figure 10 allows a classification of water points according to their similarity. Dendrogram of samples in Figure 10 allows classification of water points according to their similarity. Thus, two groups of water C1 and C2 emerge, which are in turn subdivided into two subgroups according to their degree of mineralization and/or their chemical composition.
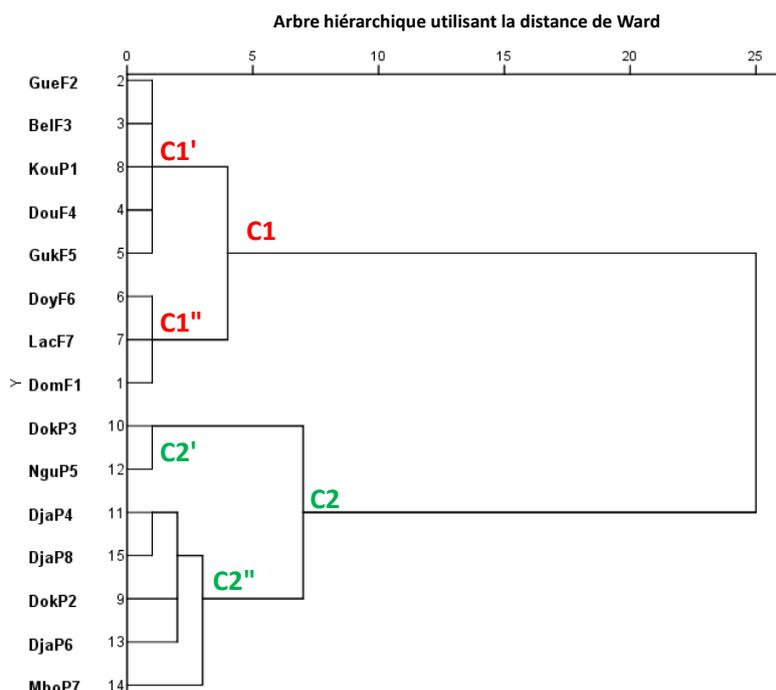
Fig. 10.   Dendrogram of water samples from Moundou city

Class C1 groups together least mineralized waters, there are sub-classes C1' and C1", with conductivities varying from 59.7 to 285 μS/Cm and from 396 to 497 μS/Cm, these waters are of calcium bicarbonate type. Mineralization of these waters is essentially of natural origin; it represents dominant class (54%). In the C2 class, two sub-classes can be distinguished:

The sub-class C2' which corresponds to moderately mineralized waters with a conductivity that varies between 675 and 813 μS/Cm. Waters are of bicarbonate calcium and magnesium type. It represents about 13% of the totality of water points.

The sub-class C2" corresponds to all waters characterized by a strong mineralization with conductivity values that vary between 1275 and 1999 μS/Cm. Waters are of soda-potassium bicarbonate and magnesium type. It represents about 33% of the totality of water points.

7   CONCLUSION

Study of hydrochemical characteristics of groundwater of Moundou city was by combining hydrochemical methods and multivariate statistical analysis. It is a study that aims to understand hydrochemical functioning of groundwater and results obtained show that pH revolves on average around neutrality with an average value of 7.26 but some samples may be slightly basic as in case of (Doy_F6 and Dom_F1 which have a pH of 8. Electrical conductivity varies between 59.7 to 1999 μS/cm, well waters are more mineralized with an average conductivity of about 1204.2 μS/cm compared to boreholes which have an average conductivity of about 285.9 μS/cm. This large variability in conductivity indicates the presence of several processes responsible for mineralization of Moundou waters.

The classification of water from Chadah diagram allows identification of two groups of water: bicarbonate calcic and magnesian type and chloride calcic and magnesian. Results obtained through various diagrams allowed us to identify different processes responsible for mineralization of groundwater in our study area. Thus, Gibbs diagram indicates that alteration of silicates represents the main process involved in evolution of groundwater, to which is added phenomenon of evaporation. Results also show that basic exchange processes between alkaline earths and alkalis, as well as contributions linked to anthropic activities, are responsible for mineralization of groundwater in Moundou city. The identification of different processes involved in acquisition of water chemistry, highlighted by hydrochemical approach, was confirmed by Principal Component Analysis.

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