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# Hydrochemical Differentiation of Salinisation Process of the Water in Endoreic Semi-Arid Basin: Case of Rémila Basin, Algeria

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Abstract: The aim of this study is to determine and treat a hierarchical basis of the various mechanisms responsible for the space variation of the water quality in a endoreic semi-arid basin. The water chemistry showed a large variability in space and time. The total dissolved solid (TDS) in water increases from upstream to downstream due to the effect of the arid climate, but also due to the water-rock interactions and the anthropic polution of surface water. The water chemistry changes progressively from bicarbonate calcic upstream to sulphated and chlorinated calcic in the median zone to chlorinate sodic in the Sebkha. Thermodynamic modelling showed the major role of evaporation in the evolution of the water chemistry. The result indicated calcite precipitation then gypsum precipitation as well as cations exchanges reactions. Statistical approach allowed to arrange processes that responsible for the hydrochemical variability according to their important. The increase of water salinity is due mainly to the aridity process. The differentiation between salty surface water (Sebkha) and deeper water (Chott) is the second process. The combined of the geochemical and statistical methods allowed to identify the main variability sources of the water composition and to classify them in this complex system.

Key words: Hydrochemistry, statistics, aridity, Sebkha, Chott, Algeria

### INTRODUCTION

The hydrochemistry of the semi-arid endoreic zones is marked by the phenomena of concentration of the solutions and salinisation under the influence of the evaporation. In this context, the other mechanisms responsible for the acquisition of the chemical quality of water are masked by the factor concentration<sup>[1,2]</sup> To appreciate the variety of mechanisms responsible for hydrochemical variations requires the identification and the hierarchical organization of the processes.

The mechanisms that responsible for the variation of water composition are often numerous and complex and depends on the geology, climatic and anthropology. The objective of this work is to study the geochemistry of ground water in the endoreic basin of Rémila in order to put in evidence the processes which affect the quality of water and finally to organize them by coupling the geochemical and statistical approaches. **Presentation of the study zone:** The endoreic basin of Rémila is located between the Atlas Tellien in the North and the Saharan Atlas in the South (Fig. 1). It is delimited to the North by Djebel Fedjoudj, to the South by Aures massif, to the West by Djebel Amrane and to the East by Sebkha. The massifs encircling that exceed 1000 m and peak in 2300 m at the top of Aures (Djebel Chélia). The low zone has a height of 830 m.

The climate is Mediterranean semi-arid<sup>[3]</sup>, the annual average of the precipitation is 330 mm and of the temperatures is 16°C. The potential evaporation of Penman is 1400 mm<sup>[4]</sup>. The river system is essentially formed by oued Bou el Freis and El-Gueiss that contribute to the recharge of the aquifer<sup>[4]</sup>.

**Geology and hydrogeology:** The Trias appears in the Southeast in the diaper of Khenchela and the limestone of the Cretaceous to the South and the North of the basin (Fig. 1). The sandstone of the Miocene is transgressed on the Cretaceous. The Quaternary is

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Fig.1: Geographic and geologic map of Rémila basin

formed by detritus formations that accumulated in the centre of the plain and based on a marly substratum.

The geometry of the Mio-plio-quaternary reservoir depends on the nature of sediment deposits that passes 280 m of thickness in the centre of the plain<sup>[4]</sup>.

The organisation of these deposits in sedimentary sequence, favoured the existence of the preferential horizon of water flow, characterized by an extreme lateral and vertical heterogeneity. The recharge of the basin is directly insured by the precipitation and by the side contributions of the Cretaceous and Miocene. The general drainage of water flows within a direction West-East. The permeability varies from  $10^{-3}$  m.s<sup>-1</sup> to $10^{-7}$  m.s<sup>-1</sup>, with an average of  $10^{-5}$  m sec<sup>-1</sup> [<sup>3,4]</sup>.

# MATERIALS AND METHODS

The water analyses were classified according to the increasing contents in chloride, witch considered as conservative element so can be used as hydrochemical tracer. The behaviour of the various major elements is studied by means of diagrams of concentration based on the ion chlorinate as factor of concentration  $(FC)^{[5,6,7,8,9]}$ .

The calculation of the balance states with regard to main salts that can be precipitated into this environment was realized with the model of Ionic association "Aqua"<sup>[10]</sup>. The chemical activity is calculation from the concentrations by using the law of Debye-Hückel. This model has already widely tested on numerous salty grounds<sup>[11, 12, 13, 14]</sup>. The pH, the temperature and the redox potential (Eh) was measured in the field. The balancing partial pressure of carbon dioxide (pCO<sub>2</sub>) was calculated from the measure of the pH and the alkalinity carbonate (Alcc).



Fig. 2: Piper diagram for water of Rémila basin



Fig. 3: Diagram of concentration of HCO<sub>3</sub>, Ca and Cl

**Concept of residual alkalinity calcite**<sup>[15]</sup>**:** Applied to the forming of the calcite (RA calcite) then some gypsum (RA calcite+gypsum) was used to verify the equivalence between the chemicals evolutions under the influence of the evaporation and the chemical composition of solutions

RAcalcite=Alkalinity - Calcium total (moL litre<sup>-1</sup>)

#### **RESULTS AND DISCUSSION**

The diagram of Piper (Fig. 2) shows an evolution of the chemical facies from bicarbonate-calcic in the South to chloride sodic near the Sebkha. In the median zone, the facies of water is sulphate and chloride calcic.

**Diagram of concentration:** The element concentration diagram (based on the ion  $Cl^{-}$ ) is presented in (Fig. 3 and 4). The FC corresponds to the value in



Fig. 4: Diagram of concentration of Ca, Na, SO<sub>4</sub> and Cl

chloride of the sample divided by the value into chloride of the most diluted sample.

**The sodium:** In diluted water, log (FC) varies from 0 to 0.5, the concentration of sodium (Na<sup>+</sup>) increases, but slightly less quickly than chloride (Fig. 4). For more concentrated water, log (FC) lies between 0.5 and 1.5, the content of Na<sup>+</sup> evolves in a similar way of  $CI^{-[16,17]}$ . This is probably due to a fixation of Na<sup>+</sup> by the capacity of cationic exchange (CEC)<sup>[18]</sup>.

**The alkalinity:** In diluted waters, log (FC) understood between 0 and 0.5, the alkalinity decreases and then stabilized (Fig. 3). Beyond log (FC) superior to 0.5, we note an important dispersal of points. The alkalinity decreases and the content in  $Ca^{2+}$  increase (less than the chloride) towards the heights values of FC. This evolution suggests a precipitation of calcite with  $Ca^{2+}$  dominating Alcc, from witch we conclude an negative RA calcite<sup>[6,7,8]</sup>. The state of saturation of the solutions towards the calcite will allow us to confirm this hypothesis. The dispersal of the alkalinity results mainly from the spatial variability of pCO<sub>2</sub>, connected to the gas exchanges between waters and their environment<sup>[5,16]</sup>.

**The pH:** The pH is stable (Fig. 3). This is in agreement with an evolution in the neutral salt way<sup>[19]</sup>. The strong dispersal of points must be attributed to the spatial variability of the  $pCO_2$ .

**The calcium:** The concentration of  $Ca^{2+}$  increase more quickly than the alkalinity but slightly less than the tracer (Fig. 3). This process is in agreement with the precipitation of the calcite in this geochemical context. Besides the concentration under the influence of the evaporation, the phenomena of exchanges of cations between clay-humic complex and the solution of the ground surface increase the desorption of  $Ca^{2+}$  during

The oblique line corresponds to the theoretical balance water / calcite The dotted line represents pCO2 atmospheric



Fig. 5: Diagram of balance of the solutions with the calcite



Fig. 6: Diagram of balance of the solutions with the gypsum

the concentration of the solutions due to absorption of the sodium<sup>[20,21]</sup>. For log (FC) = 1.7,  $Ca^{2+}$  is stable. It can be affected by the successive precipitation of calcite and gypsum.

**The sulphate:**  $SO_4^{-2}$  increases, less quickly than Cl<sup>-</sup> (Fig. 4) until the value of log (FC) = 1,7; beyond this value,  $SO_4^{-2}$  seems to be controlled by the precipitation of gypsum.

**Balances minerals-solutions:** The diagram of concentration leads us to various hypotheses on reactionnels mechanism: precipitation of calcite, precipitation of calcite and gypsum, Practically, all the waters are in balance or supersaturated towards the calcite (Fig. 5). The forming of this mineral can explain the control of calcium and the alkalinity in solution<sup>[1,6,7]</sup>.

Concerning the state of balance with regard to the gypsum, the solution aims towards the balance (Fig. 6). The forming of this mineral thus controls the sulphates ions. In conclusion, these two results confirm the hypotheses advanced from the study of the diagrams of concentration.

**Statistical multivariées analyses:** The principal components analysis (ACP) was applied to discriminate, the factors which influence most the



Fig. 7: ACP of water Rémila basin (Space of the variables)



Fig. 8: ACP of water Rémila basin (Space of the individuals)

variability and the hydrochemical classes<sup>[22,23]</sup> then to organize them according to their important order.

**Geochemical analyse:** The results of the principal component analysis (ACP) concerned twelve physic-chemical parameters:  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$ ,  $Cl^-$ ,  $SO_4^{-2}$ ,  $NO_3$ ,  $HCO_3^-$ , electric specific conductivity (IT), mineralization (Min), dry residue (RS) and pH that carried out on 174 samples (drillings, well, Chott and Sebkha) is presented in (Fig. 6, 7 and 8).

The factorial axis I (Fig. 7) expresses 49 % of the variance. This axis indicates the concentration of the solutions. The axis II express 17 % of the variance and oppose variables such as  $HCO_3^-$ ,  $Ca^{2+}$ ,  $SO_4^{-2}$  to  $Na^+$  and  $CI^-$ . This axis defined two opposed hydrochemical systems: surface water (Sebkha) against ground water



Fig. 9: ACP of water Rémila basin (Space of the variables)

(Chott). (Fig. 7 and 8). The axis III (Fig. 9) represents 9 % of the variance and groups together the variables  $K^+$ ,  $NO_3^-$  and pH. This axis translates the anthropogenic pollution (agricultural or urban).

## CONCLUSION

This study shows the interest of the coupling between the geochemical and statistical approaches (ACP) for the analysis of the chemical composition of water in a semi-arid endoreic complex system.

In Rémila basin, the salinisation is the main process and its importance masked the other sources of chemical variability. In that case, the associated mechanisms are: calcite, gypsum precipitation and anthropogenic pollution.

The use of the statistical methods (ACP), allows us to identify the others processes and to classify them. The study underlines the hydrochemical differentiation between the salt evolution of surface waters (Sebkha) and ground water (Chott) in the same hydrochemical region.

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