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Assessment and Evaluation of the Conservative Character of the Calcite Residual Alkalinity in Drain Waters – A Case of Saline Soils Under an Arid Mediterranean Climate

Karim Ouamer-ali*(**)†, Youcef Daoud and Kaddour Djili****
*Institut National de la Recherche Agronomique d'Algérie (INRAA) - Division Sols et Gestion des Espaces Agricoles (S.G.E.A.), BP 200 Hassen Badi Avenue, El-Harrach 16200, Algeria
**Ecole Nationale Supérieure Agronomique (ENSA, ES1603), El-Harrach, Algeria
†Corresponding author: Karim Ouamer-ali

ABSTRACT

The residual alkalinity (RA) is a tool that allows to foresee the direction of evolution of concentrations of the different dissolved ionic species and consequently of the chemical facies of the solutions. The 13 samples of the studied water were collected from open drains of two sites located in the irrigated and semi-arid plains of the Cheliff Basin (Algeria). These samples cover a wide range of salinity (ionic power between 0.025 mol L^{-1} and 0.739 mol L^{-1} and show a neutral reaction to slightly alkaline from 7.04 to 7.63. The evolution of chemical composition of waters during their concentration shows that the activities of Na$^+$, Ca^{2+}, Mg^{2+}, K$^+$ and SO$_4^{2-}$ seem to evolve from a very divergent way regarding the concentration factor. The intensity of Na$^+$ ions activity is the one that predominates (R²=0.96). All the waters show an anionic chemical facies of chloride type and a cationic chemical facies of sodium type, and are saturated with respect to calcite. The alkalinity rises with the concentration factor, reaches a maximum, then decreases due to its non-conservative nature. The diminution of the RA$_{calcite}$ and the increasing activities of Ca^{2+} ions in a proportional way to the concentration factor (R²=0.87) confirms the conservative character of the RA$_{calcite}$ in these salted environments. Its sense of evolution can condition the observed salinization way in soils, which is of a neutral saline type. This process is less restrictive for the agricultural development of lands of that nature.

INTRODUCTION

Interpreting chemical balances of saline solutions require taking into consideration the geochemical processes (Keller et al. 1987, Morse & Arvidson 2002). The liquid phase composition results mostly from interactions within water, mineral and solid organic phases and the atmosphere (Andersson et al. 2007). De facto the dissolution and precipitation of solid phases play a decisive role, particularly for the regulation of chemical elements such as calcium and also the carbonates (Valles et al. 1990, Cross et al. 2013). The study of solubility of minerals corresponding to predominant solid phases of the so-called system should allow to define the balances between the different phases (Valles et al. 1989). If under-saturated initial solution regarding the calcite is concentrated through evaporation, as far as the equilibrium with the mineral is not reached, the calcium and the alkalinity behave like tracers of the concentration state of the solution (Ribolzi et al. 1993).

The concept of residual alkalinity (RA) derives from the notion of residual carbonates proposed by Eaton (1950). In environments where the calcite precipitate, Van Beek & Van Breemen (1973) defined the calcite residual alkalinity (RA$_{calcite}$). This is expressed by the difference between the alkalinity and the total concentration of the divalent cations in the soil solution in meq L^{-1}.

The RA is an interesting tool to foresee the direction of the evolution of the concentrations of the different dissolved elements and consequently of the chemical facies of the solutions (Valles et al. 1989).

In soil solutions, the capacity of cationic exchange contains a reserve of cation very often superior to the dissolved quantity, mainly when the solution of the soil is less concentrated. The ionic exchanges can alter the conservative aspect of RA (Ribolzi et al. 1993).

The aim of the present work is to evaluate the geochemical characteristics of drain waters of carbonate and salted soils of the Cheliff Basin irrigated plains (Algeria) and also to test the conservative aspect of RA$_{calcite}$ in these solutions diversely mineralized.

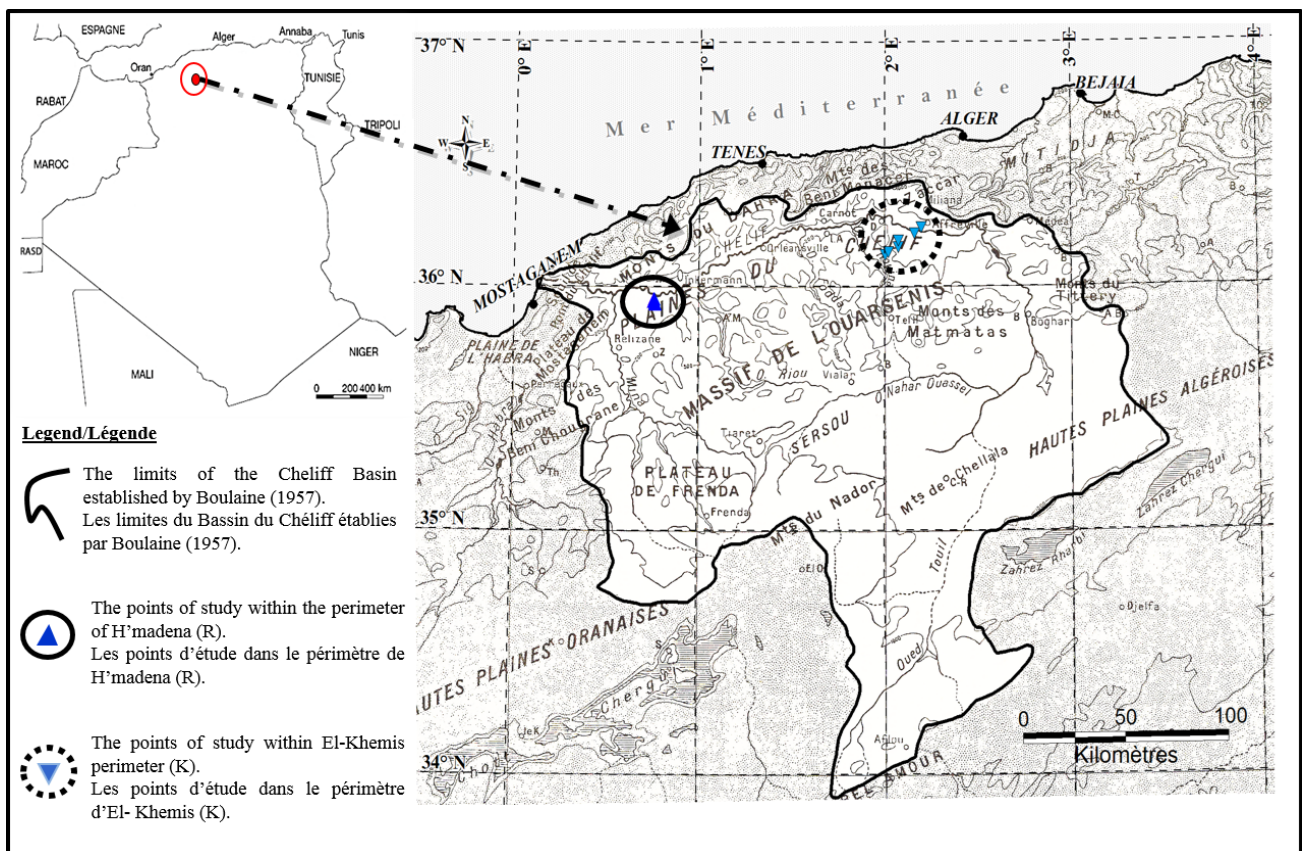## MATERIALS AND METHODS

Materials Used in the Study

Fig. 1: Geographical location of the study zones.

The samples of water studied were taken from the open drains. The first phase of sampling targeted drains from previous old perimeter of the studied station of saline soils in Hamadenas (1942 to 1961) now, a space in activity occupied by a private farm and by a research station in agronomy of the INRAA-H'madena (samples from R1 to R7). The second phase of sampling covered the drains of one part of the old parameter of study of the research station in agronomy of El-Khemis and also from agricultural lands in the area of Khemis Meliana (samples from K1 to K6).

These two sites of the study are located in the irrigated and semi-arid plains of Oued Cheliff which are situated in West of Algiers (Fig. 1). The samples cover a wide range of salinity, the soils are salted carbonated and clayey (Boulaine 1957, Daoud 1993, Hadj-miloud 2010).

Methods of Study

The water samples are filtered and kept at 4°C. The methods of analysis used are those described for the solutions of salted soils by the USSL (1954). The CE, pH and the temperature were measured on site with a multi-meter type device (MM40+) to a multisensor 5059P.

The determination of alkalinity is realized using a titration (titling) of 10 mL of each sample of water by 0.01N HCl . The calculations were realized by applying a Gran function (Gran 1952).

The calculation of the distribution of the species in solution and the ionic activities was realized by the active software (Montoroi & Rieu 1987). The calculation of the activities of CO_3^{2-} was realized by the software from the pH values and also HCO_3^- activities. The saturation state of waters with respect to the calcite was calculated on the basis of a solubility product of $10^{-8.37}$ (Helgeson 1969).

The concentration factor was calculated by dividing the concentration of chlorine of water by the weakest concentration which was obtained for the sample K1 which is of 0.01251 mol L^{-1}. The $RA_{calcite}$ was obtained as follows:

$$RA_{calcite} \, (meq \, L^{-1}) = (Alkalinity) - 2(Ca^{2+}) \quad ...(1)$$

RESULTS

Chemical Composition of Drain Waters

The results of the chemical composition of drain waters taken from the study areas are presented in Table 1.

Table 1: Chemical characterization of drain waters.

Variables	Average	Median	Minimum	Maximum	Variance
I (mol/L)	0.230846	0.155000	0.025000	0.739000	0.04898
pH	7.243846	7.140000	7.040000	7.630000	0.04821
Ca^{2+} (mol/L)	0.002647	0.001120	0.000650	0.008110	0.00001
Mg^{2+} (mol/L)	0.004743	0.003800	0.001040	0.011300	0.00001
Na^+ (mol/L)	0.080840	0.048230	0.011500	0.259000	0.00574
K^+ (mol/L)	0.000377	0.000320	0.000037	0.000860	0.00000
Cl^- (mol/L)	0.112535	0.061230	0.012510	0.385000	0.01308
SO_4^{2-} (mol/L)	0.002941	0.002450	0.001510	0.005960	0.00000
CO_3^{2-} (mol/L)	0.000009	0.000007	0.000003	0.000021	0.00000
Alkalinity (meq/L)	0.036050	0.035600	0.015240	0.056800	0.00025
Q_{CaCO_3}	0.000000	0.000000	0.000000	0.000000	0.00000
$Q/Kps_{(calcite)}$	4.492769	1.783000	1.061000	14.269000	21.32892
$RA_{calcite}$ (meq/L)	0.000769	0.003000	-0.012000	0.007000	0.00003
Concentration factor (CF)	8.995615	4.894000	1.000000	30.775000	83.58127

A first evaluation allows to notice that they present an ionic force comprised between 0.025 mol L^{-1} and 0.7139 mol L^{-1} and a pH which varies between 7.04 and 7.63 (Fig. 2).

The evolution of the composition of waters during their concentration shows that the ionic activity of sodium rises in a proportional way to the concentration factor ($R^2 = 0.96$). Calcium activity rises also with the concentration factor in accordance with a lesser intensity than sodium ($R^2 = 0.87$); the activity of magnesium evolves a polynomial way with the concentration factor ($R^2 = 0.85$). Potassium evolves in a relatively independent way regarding the concentration factor, and finally the activity of sulphates seems to evolve in a relatively independent way with respect to concentration factor (Fig. 3).
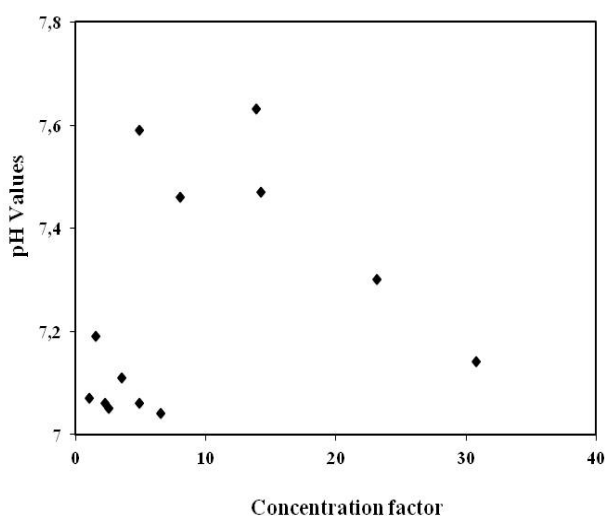

Fig. 2: Evolution of pH according to concentration factor.

The Chemical Facies of Waters and the Saturation State with Respect to Calcite

All waters present an anionic chemical facies chloride type and cationic chemical facies sodium type, and are saturated with respect to the calcite (Fig. 4).

All waters present a saturation rating Q/Kps regarding the calcite superior to 1 (Fig. 5). So they are oversaturated over that salt. The values of the saturation rating Q/Kps are scattered around, and they are comprised between 1.06 and 14.27.

Alkalinity of Waters

It is determined by applying the function of Gran (1952). The different stages of the used approach are shown in Fig. 6. For this type of climate (arid) and for the range of values of the observed pH (values from 7.04 to 7.63) the total alkalinity (TA) corresponds to the carbonated alkalinity (Valles et al. 1990).

From the results indicated in Fig. 6(A,B,C), it is noted as the following:

$$TA \left(\frac{meq}{l}\right) = \frac{10^3 \times Veq \times C}{V_0} = \frac{10^3 \times 0.041 \times 0.01}{10} = 0.041 \quad ...(2)$$

Where, *TA* is the total alkalinity in meq L^{-1}, *C* is the titrant concentration eq L^{-1}, *Vo* is the volume of the sample (mL), and *Veq* (the equivalent volume) is the volume of the corresponding acid at the equivalent point in mL (-b/a = 0.015/0.368 = 0.041). Intuitively, *a* and *b* indicate real number obtained from the linear adjustment of the function of Gran (Fig. 6C) defined by y = 0.3687x - 0.0154.

The obtained results show that the alkalinity rises with the concentration factor; it reaches a maximum and then decreases (Fig. 7). The dispersion of alkalinity for broadly
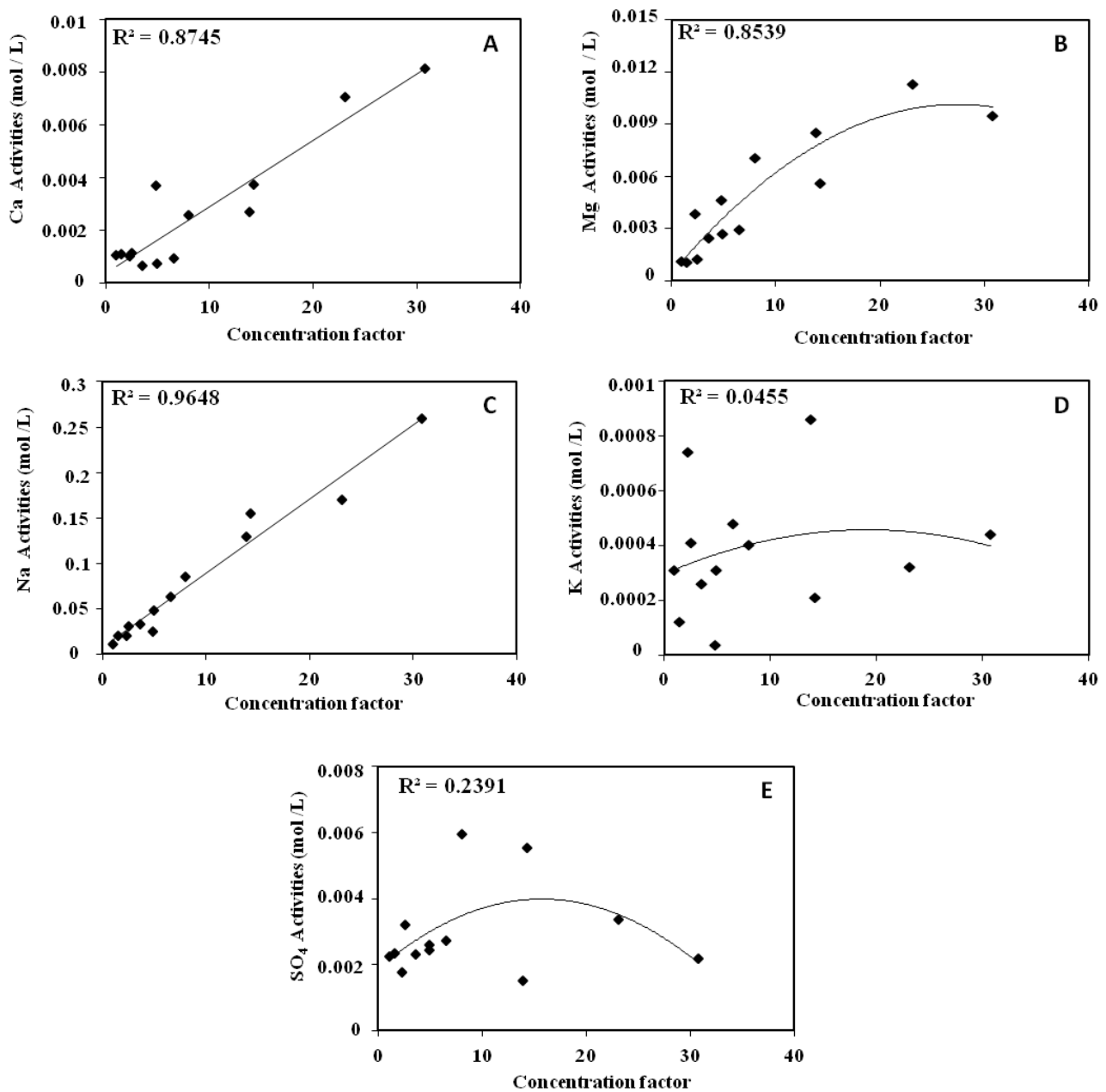
Fig. 3: Evolution of ionic activities of elements according to the concentration factor.
(A) Activities of Ca^{2+}(mol/L) according to concentration factor, (B) Activities of Mg^{2+}(mol/L) according to concentration factor,
(C) Na$^+$(mol/L) activities depending on the concentration factor, (D) Activities of K$^+$(mol/L) according to concentration factor,
(E) Activities of SO$_4^{2-}$ (mol/L) depending on the concentration factor

similar concentration factors mainly due to the spatial variability of pCO$_2$ and exchanges with the clay-humic complex (Ribolzi et al. 1993).

The non-conservative nature of the alkalinity in drain waters will be the result of dissolution-precipitation phenomena of calcium carbonate (Cross et al. 2013).

The calcite residual alkalinity (RA$_{calcite}$) is calculated for all waters as they are all saturated with respect to the calcite (Fig. 5). The values of RA$_{calcite}$ decrease in a proportional way compared to the concentration factor (R^2 = 0.87), while the ionic activities of calcium rise in a proportional way compared to the concentration factor (R^2 = 0.87) (Fig. 8).
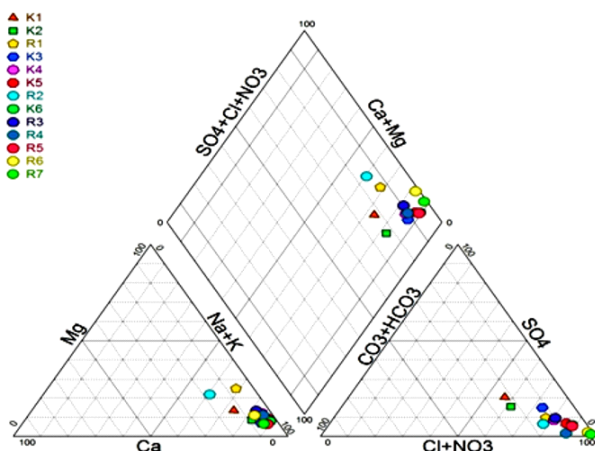
Fig. 4: The chemical facies of waters as per the
de Piper diagram.

Fig. 5: Saturation state of waters according to calcite.

So $RA_{calcite}$ has a conservative nature in those salted areas. The ionic exchange phenomenon seems not to be important to clear the conservative nature of the $RA_{calcite}$. The absorbing complex is probably close to balance with solutions in contact (Ribolzi et al. 1993).

DISCUSSION

Analysed drain waters show an ionic power ranging from 0.025 mol L^{-1} to 0.739 mol L^{-1} and a pH ranging from 7.04 to 7.63. The waters are in this case diversely mineralized and have a reaction which is close to neutrality to slightly alkaline. The evolution of the composition of waters during the concentration shows that ionic activities of sodium and calcium rise in a proportional way to the concentration factor. The activity of magnesium evolves in a polynomial way with the concentration factor. The ionic activities of potassium and sulphates evolve in a relatively independent way regarding concentration factor.

All waters present an anionic chemical facies chloride type and also cationic chemical facies sodium type and are saturated with respect to the calcite

The obtained alkalinity values via Gran method (1952) are between 0.015 meq L^{-1} to 0.0268 meq L^{-1}, they evolve in a polynomial way with the concentration factor and they confer a non-conservative nature to alkalinity. The $RA_{calcite}$ values are between 0.003 meq L^{-1} and 0.007 meq L^{-1} for positive values and are between -0.012 meq L^{-1} and -0.003 meq L^{-1} for negative ones.

These waters are in equilibrium with pCO_2 of the atmosphere (360 µatm) CO_{2aq}, HCO_3^- and CO_3^{2-} are instantaneous and continuo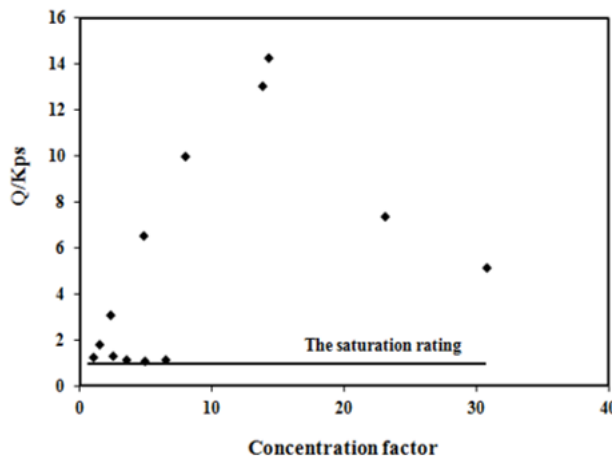us balance. The carbonated balances that exist in drain waters are governed by the following equations (Morse & Arvidson 2002):

$$CO_{2aq} = K_0\, pCO_2 \quad K_0 = 2.839 \times 10^{-2}\, mol\, kg^{-1}\, atm^{-1}$$

$$...(3)$$

$$CO_{2aq} + H_2O \leftrightarrow HCO_3^- + H^+$$

$$K1 = \frac{(HCO_3^-)(H^+)}{(CO_{2aq})} = 1.422 \times 10^{-6}\, mol\, kg^{-1}$$

$$...(4)$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

$$K_2 = \frac{(CO_3^{2-})(H^+)}{(HCO_3^-)} = 1.081 \times 10^{-9}\, mol\, kg^{-1}$$

$$...(5)$$

In natural conditions, variations in alkalinity are mainly due to the dissolution or the precipitation of calcium carbonate (Kim et al. 2010, Cross et al. 2013). In the range of pHs of analysed waters (7.04 - 7.63) the HCO_3^- ion largely predominates over the CO_3^{2-} ion and also over CO_{2aq} (Garrels & Christ 1967).

The diminution of the $RA_{calcite}$ when the concentration factor rises and its negative sign for concentration factors ≥ 13.83 explains the nature of the salinization mechanism of soils of these plains (Barbiero et al. 2001).

In fact, Daoud (1993) and Hadj-miloud (2010) showed that the salinization way observed in soils within these plains is a neutral saline type. This neutral saline way is less restricting for agricultural development of that kind of lands (Cheverry 1974, Cheverry & Robert 1998, Houha et al. 2008).
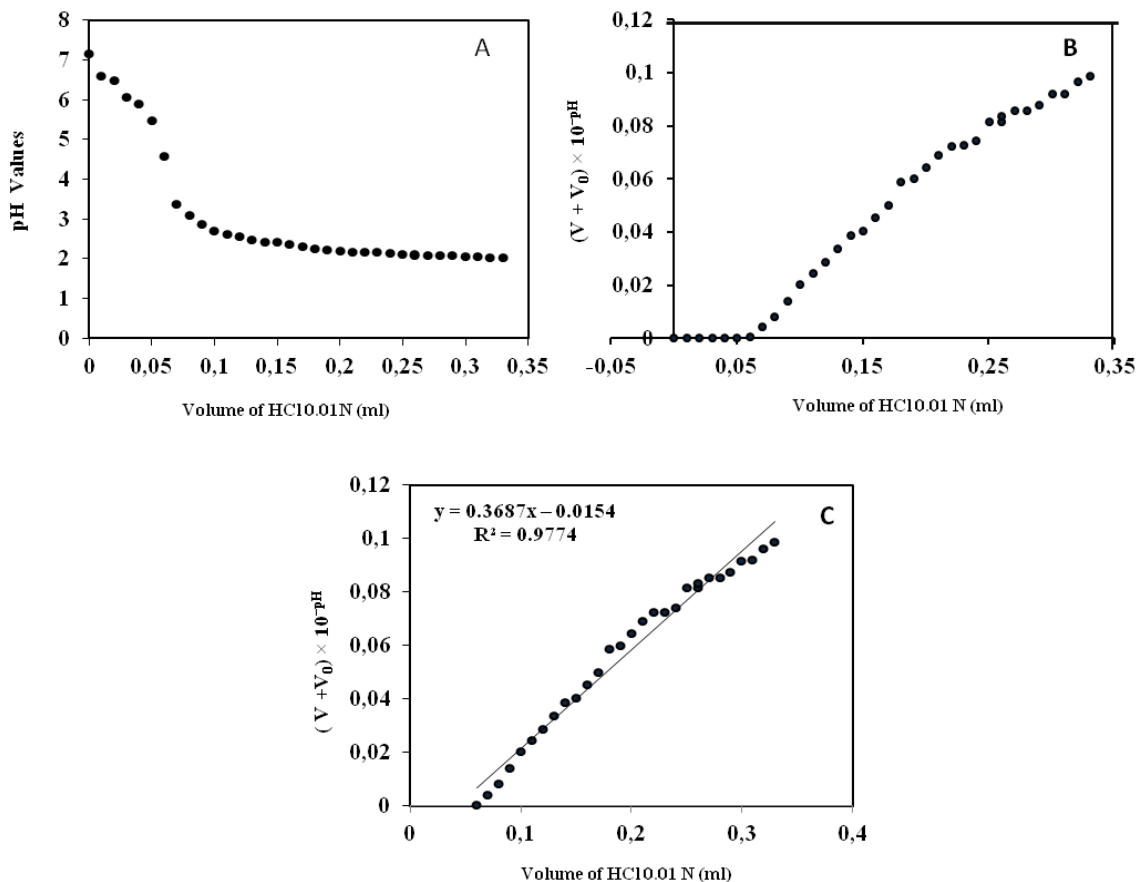
Fig. 6: Steps for the determination of the total alkalinity of waters. (A) The titration curve of water using the acid chloride, (B) Application of the Gran function 1952, (C) Adjustment of the linear part of Gran function.
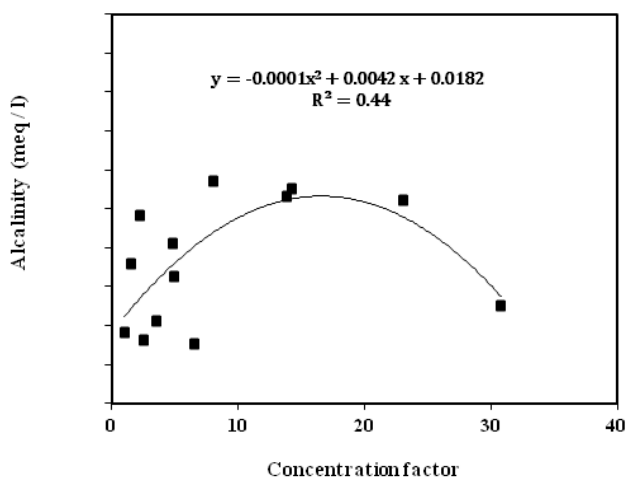

Fig. 7: Evolution of total alkalinity depending on the concentration factor.

CONCLUSION

The evolution of calcite residual alkalinity ($RA_{calcite}$) is proportional to the chlorine ions. In fact, it is conservative contrary to the total alkalinity. The $RA_{calcite}$ seems not to be affected by interactions with soil constituents in accordance with the concept of residual alkalinity (RA) applied to the precipitation of calcite; once the saturation is reached we do observe a rise in calcium content and a diminution in RA. From that point, it is possible to say that the rule of the $RA_{calcite}$ which allows a kind of qualitative prevision of the calcium behaviour and of the carbonated alkalinity is then verified.

The diminution of the $RA_{calcite}$ according to the level of salinity, expressed by the concentration factor, shows that the precipitation of the calcite in those environments, under salted and arid Mediterranean climate, prevents the evolution of soils towards the alkaline way and make easier their agriculture development via irrigation and drainage.
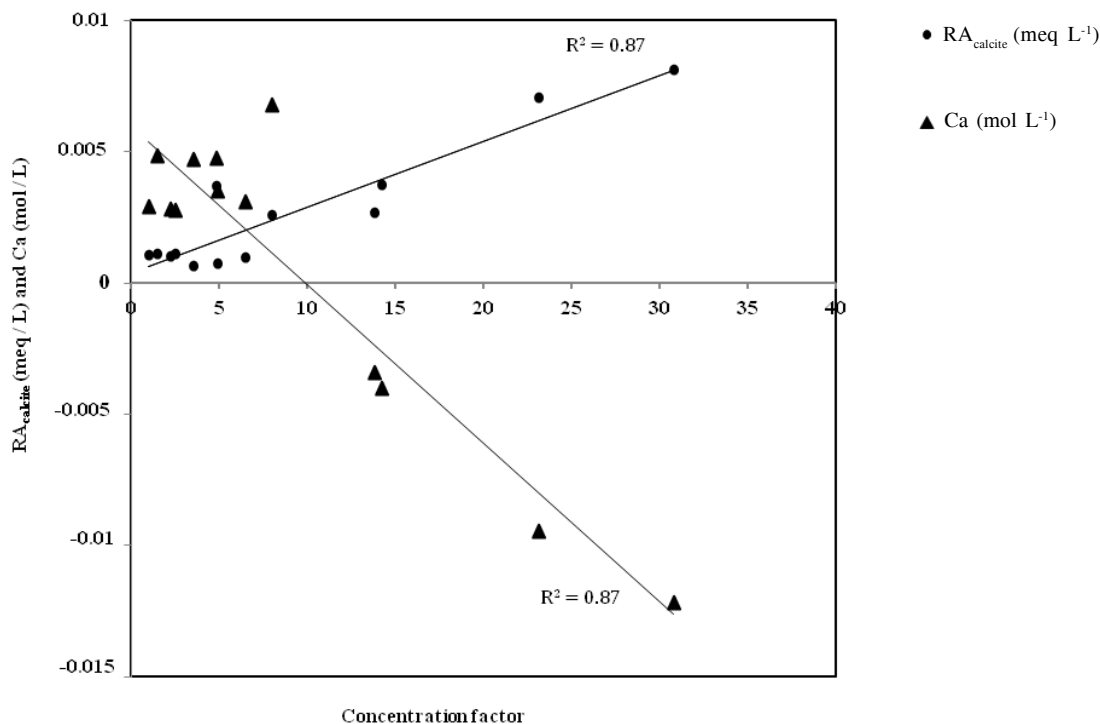
Fig. 8: The evolution of residual alkalinity calcite and calcium in terms of the
concentration factor of waters.

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