

Relationship between the cation exchange capacity and physical properties of the Cheliff saline soils (Algeria)

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Abstract

Measurements of the cation exchange capacity (CEC) show significant soil properties, in particular its ability to retain the cations because of their mobility in the soil. Thirteen soil samples rich in electrolytes of the Cheliff plain (Algeria) were analyzed in order to measure their CEC and to draw up the existing relationship between texture, organic matter content and pH. In calcareous soils, the CECe values are always higher than those measured at pH 7. Regression equations using the percentages of organic carbon and clay as independent variables would make it possible to estimate 90% of the variability of the CEC measured in the ammonium acetate buffered at pH 7 and 89% of the variability for that measured at the pH of the soil. The correlations between the salinity indices, the parameters of the saline phase and the physical properties, show that the cobalthexamine method makes it possible to characterize the soil of this plain with more precision than the Metson method. Finally, it is noticed that a sodisation of the adsorbing compound, which consequently generates a reduction in the structural stability and a reduction in the infiltration always leads to the salinity in these soil types.

Key words: CEC, Salinity Index, Salinity, Sodicity, Physical Properties.

1. Introduction

Currently, it is known that the reaction of a saline soil depends upon the amount and the nature of the clay fraction as well as the salinity level and the nature of the common cations and anions in the soil solution [1-6]. The fine clay fraction essentially ensures the regulation of the physicochemical phenomena. This fraction plays an important role not only in the water retention and the soil structure, but also in the retention and the bioavailability of the nutrient elements that are essential to plants. The surface properties of the soil components can be characterized using two types of data, namely the cation exchange capacity (CEC) and the specific surface of the clay fraction (SS). Generally, the total surface is determined using a strongly adsorbed, polar organic molecule such as ethylene glycol monoethylether (EGME) [7]. The cation exchange capacity of a soil measures the surface electric charge of soil components [8,9]. Both CEC and specific surface of the soil were used as a predicting criteria tool to evaluate the properties of the soil components. The water retention to clays is closely related to the cation exchange capacity and specific surface [6,10] showed that the cation exchange capacity was a good estimate of the water properties in the clay horizons of low organic matter content. The CEC measurement has to be done at a specific soil solution pH in order to avoid the variable charges due to the change in soil pH [9]. In the usual methods, the CEC is measured at pH = 7 (Metson method) for the lightly acid or neutral soils and at pH = 8.2 (Bower method) for the alkaline soils. Furthermore, in the presence of differently soluble salts, these methods seem not to be accurate. Under salinity conditions, it is difficult to make a monoionic absorbent on the soil material [8,11].

The objective of the present investigation is to compare the results obtained using two standardized methods of the cation exchange capacity (CEC) and their importance in the calcareous, saline soils of Cheliff plain area, north Algeria, which have clay loam texture. The relationships between the CEC and the salinity, the sodicity and some physical properties of the soils will be also evaluated.

2. Materials and Method

2.1. Study Area

The study was conducted in the Mina area (lat. $36^{\circ}10$ 'N, long. $00^{\circ}30$ ' & $1^{\circ}20$ 'E) of Algerian lower Cheliff Valley (Figure 1). The specific climate is semi-arid where the summer is very hot and the winter is cold. The mean annual rainfall in this area is 350 mm and the mean annual temperature is 18° C with only some major fluctuations through the year. The altitude at this plain is about 70 m above the sea level and the parent material of the soil is alluvium. The studied soils are pedologically young and developed from rich clay calcareous material [12-14]. Soil particles that have a diameter < 2 μ m are mainly illites accompanied with a mixture of clay minerals of smectite, kaolinite and of chlorite [15].

2.2. Soils Samples

Soil samples were collected from the upper layer of the Mina fields, Algerian Cheliff plain. Thirteen samples were taken from the surface horizon (0 - 30 cm) of each cultivated soil and analyzed using the standardized methods. The granulometric analysis was carried out without decalcification after the dispersion with sodium hexametaphosphate. The percentage of organic carbon is given according to the Anne method; the pH of the soil is measured in a 1:2.5 of soil to water suspension. Total calcium carbonate is obtained by a volumetric calcimeter of Bernard. The specific surface was measured using ethylene glycol monoethylether (EGME), according to the protocol developed by [7]. Both cation exchange capacity and the cation exchange extraction were determined in an accredited analysis laboratory of INRA, Arras, France at its usual soil pH and using cobalt hexamine (Cohex) trichloride, [Co(NH3)6]Cl3 as an exchange solution [8] and at pH 7 using ammonium acetate as an exchange solution, which was proposed by [16]. These two methods are standardized [17].



Figure 1. Location of the study area in northern Algeria, showing the lower-Cheliff plain.

2.3. Water Retention

The determination of water retention was related to the fragments size (5 - 10 cm3). The apparent density of the fragments was measured using a petrol method [17,18]. Six water contents were used as metric potential values of -10 kPa (PF = 1), -330 kPa (pF = 2.5), -1000 kPa (pF = 3.0), -3300 kPa (pF = 3.5), -10000 kPa (pF = 4.0), and -15000 kPa (pF = 4.2). Then measurements were carried out using pneumatic devices. This device makes that it is possible to put at balance 30 to 40 bounds on the balance at the same time in only one cell [19]. The water content is measured after 7 days of the setting to the balance at the selected pressure and then, the cell content is oven-dried at 105°C for at least 24 hours.

2.4. Structural Stability

The aggregate stability was measured on a diameter of 3 - 5 mm aggregates according to the method proposed by Le Bissonnais [20]. Its objective is to give a realistic description of the behaviour of soil materials subjected to the action of the rain and to allow a relative classification of materials with respect to this behaviour. In summary, the method is designed to distinguish between the various mechanisms of breakdown: slaking due to fast wetting, microcracking due to slow wetting and mechanical breakdown by stirring of prewetted aggregates.

2. 5. Soil Infiltration Measurement under Simulated Rain

2.5.1. The Rainfall Simulator

The artificial rain was implemented using a sprinkling device. The rain simulator is established according to the model designed by Asseline and Valentin [21]. It consists of a watering system fixed at pyramid tower of 4 meters in height and protected from the wind action by a removable cover. The range of available intensity varies from 20 to 150 mm/h. The protocol of simulation includes several rain tests of an average intensity of 30 mm/h ($\pm 2 \text{ mm} \cdot \text{h}^{-1}$) during one hour and half is 45 mm of precipitation. It corresponds well to that meets in the zone of study for a natural rain event of decennial recurrence. The flux of water through the sample was measured every 5 min., and the ratio between final infiltration and the rainfall (the final infiltration coefficient) was calculated for the experiment. The treatments were replicated three times for each soil.

2.5.2. Preparation of the Samples

The soils samples of approximately 10 cm distance in -between are distributed on a PVC plate measuring 50×50 cm. The soil samples of a volume of 78.5 cm3 resting on a bed of 1 cm of calibrated and washed sand are put in cylinders made of PVC of a diameter of 5 cm and a 5 cm height. They are transparent in order to be able to control the moistening visually. They are perforated at their bases to be used as holes of evacuation for the infiltration measurement. The soils are initially saturated by the base. They are then exposed to a rainfall simulated by using distilled water until the rate of stabilized infiltration is obtained.

3. Results and discussion

3.1. Statistical Characterization of Sample Population

The general statistics of the physical and chemical characteristics of the soils are given in Table 1. They indicate the prevalence of soils that have basic pH and are generally calcareous, with

contents of organic matter ranging between 0.5% and 3% and a clay loam texture. The samples are characterised by averages raised for electrical conductivity and the quantity of total soluble cations translating a strong variability of the results in this area. In the calcareous soils, the value of the CECe measured at the soil pH is always higher than that measured at pH 7.

3.2. Importance of CEC in the Context of the Saline Phase

Two methods were tested in this study. The first one is based on the determination of the CEC at the natural pH of the soil (CECe). The value of the CEC then depends upon the geochemical environment, in particular the pH. The second method determines the CEC at pH 7 which makes to compare materials on the standard bases (CECMetson). The results of Table 1 show that the CEC values vary from 17 to 25 cmol kg^{-1} when it is measured at the natural pH of the soil and from 12 to 20 cmol kg^{-1} when it is measured at the pH 7. The difference between the cobalthexamine method of [11] and the Metson method [16] takes account of the pH reached during the initial saturation of samples [9]. In the first method, it is the usual pH, that the soil approaches, but in the second one, the soil pH equals to 7. Comparing the values of the two methods in Figure 2, it is realized that the CEC values with cobalthexamine (CECe) are higher compared to those of the Metson method (CEC7). However, the exchangeable bases of the Metson method are higher compared to those of the cobalthexamine method (Table 1). According to [22], this difference resides in the fact that during measurement with pH equal to 7, a part of the carbonates is dissolved. The result is that the cations extracted come in particular from the setting in calcium solution. On the other hand, the CEC with the cobalthexamine measured at the pH of the soil (CECe). This makes that it is possible to extract the exchangeable cations and those that are present in the solution from the soil without the effect of carbonate dissolution. Moreover, the CEC values of the soil depend, at the same time, upon the mineralogical nature of clays and the electric surface charges developed by the organic matter. The multiple linear regressions (Table 2) show that the CEC of the clays and the organic matter are regarded as additives [23,24]. An average value of CECe of 41.26 cmol·kg⁻¹ is obtained for clays of Cheliff plain. Clay content explains 65% of the CEC variability of the soil measured with the cobalthexamine. On the other hand, when one uses the Metson method, the average CEC value of clay is 39.94 cmol \cdot kg⁻¹ and clay content explains only 60% of the variability

The organic matter explains a large part of variability for Metson method than cobalthexamine method. Differences between the CEC values of the organic matter are obtained. These last differences (on the basis of 58% of carbon) are evaluated, with 1710 mmol(+)·kg⁻¹ for the Metson method and 1630 mmol(+)·kg⁻¹ for that with the cobalthexamine. However, as the organic matter content is weak, its weight is not as significant as that of clay. This explains 0.4% and 15% of the variability of the cobalthexamine CECe and the CEC Metson, respectively. It appears that the value of the CEC results from the cumulated properties of the clay and the organic matter.

The fact that there is a measurement difference between both methods according to their implementation (pH of the soil, CECe; and pH 7, CEC7), makes the possibility to coarsely characterize the state of reactive surfaces and their contribution to the pH of the sample. In this direction, for the Metson method, the used (pH) corresponds to the difference between the pH of the soil and the pH of the extraction solution.

Minimum	Maximum	Mean	Standard Deviation
8.00	8.33	8.17	0.009
0.8	6.27	2.09	1.64
1.93	41.33	12.48	12.73
17.53	22.1	19.77	1.42
0.53	3.38	2.37	0.68
40.80	55.37	46.14	4.35
35.49	52.15	42.21	4.02
4.01	18.6	11.65	5.08
3.24	52.16	14.03	14.36
1.32	1.79	1.66	0.12
3.51	7.02	4.39	1.01
0.26	0.72	0.41	0.15
17.1	24.6	19.58	1.89
12.5	19.7	15.13	1.93
19.1 53.6 310.08	107.69 227.85 359.79	38.7 85.29 327.8	28.61 55.86 15.46
	Minimum 8.00 0.8 1.93 17.53 0.53 40.80 35.49 4.01 3.24 1.32 3.51 0.26 17.1 12.5 19.1 53.6 310.08	MinimumMaximum 8.00 8.33 0.8 6.27 1.93 41.33 17.53 22.1 0.53 3.38 40.80 55.37 35.49 52.15 4.01 18.6 3.24 52.16 1.32 1.79 3.51 7.02 0.26 0.72 17.1 24.6 12.5 19.7 19.1 107.69 53.6 227.85 310.08 359.79	MinimumMaximumMean 8.00 8.33 8.17 0.8 6.27 2.09 1.93 41.33 12.48 17.53 22.1 19.77 0.53 3.38 2.37 40.80 55.37 46.14 35.49 52.15 42.21 4.01 18.6 11.65 3.24 52.16 14.03 1.32 1.79 1.66 3.51 7.02 4.39 0.26 0.72 0.41 17.1 24.6 19.58 12.5 19.7 15.13 19.1 107.69 38.7 53.6 227.85 85.29 310.08 359.79 327.8

Table 1. General statistics of various physical and chemical characteristics of the soil Cheliff saline soils.

(*) Chlorure de Cobaltihexammine Method; (**) Metson Method; a: Sodium Absorptio Ratio SAR = Na+/((Ca2+ + Mg2+)/2), []: meq/l-1; b: Electric Conductivity of Saturated Paste Extract (CE); c: Organic Matter (OM); d: Exchange Sodium Percent ESP = $Na+ \times 100/CEC$, [Na+]: Sodium adsorbed en cmolc/kg, CEC: Cation Exchange Capacity (cmolc/kg); e: Final Infiltration Rate; f: Mean Weight Diameter; g: Cation Exchange Capacity (cmolc/kg).

Table 2. Linear regression between the CEC of the soil and their physical and chemical characteristics.

pН	Linear regression	r2	Estimate	Standard							
-			standard error	Error on r							
	CEC cobaltihexammine										
$\mathbf{p}\mathbf{H} = (\mathbf{p}\mathbf{H}_{sol} - \mathbf{g})$	ECsol = $41.26 \times 10^{-2} \text{ A} + 281.24 \times 10^{-2} \text{ C} - 1942.23 \times 10^{-2} \text{ pH}$	0.89	0.9591	0.1430							
pH = (pHsol - 8)	Avec r2 = 0.89 (dont A = 0.65 ; C = 0.004 et pH = 0.23)										
	CEC Metson										
	CEC7 = $39.94 \times 10^{-2} \text{ A} + 295.46 \times 10^{-2} \text{ C} - 628.88 \times 10^{-2} \text{ pH}$	0.90	0.9335	0.1390							
pH = (pHsol - 7)	Avec r2 = 0.90 (dont A = 0.60; C = 0.15 et pH = 0.15).										

A = clay %; C = organic carbon % and pH of soil



Figure 2. Relationship between the cation exchange capacity measured with the cobalthexamine trichloride method and with the Metson method.

With regard to the cobalthexamine method, the used pH corresponds to the difference between the real pH and the minimum pH found in the studied soils. The regression equations indeed use a differentiation factor of the (pH) as independent variable to justify 23% and 15% of the CECe and CEC7 variability, respectively. This CEC variation due to (pH) is attributed to the action of protonation/ deprotonation. Shortly, to evaluate the CEC by these two methods, one can realize that the independent variables explain 89% and 90% of the CEC variability. The CECe that carried out with the pH close to the soil is less influenced by the organic matter, since its contribution is, in this type of soil, often unimportant. It is justified only by 0.4% of variability due to organic matter and would be dependent on the clay which presents variable loads of edge according to the pH. The CEC at the standard pH 7 (Metson method), is justified by 15% of variability due to the dissociation of the phenol groupings of the organic components at pH 7. According to regression equations, these various ratios are useful because they make it possible to estimate the CEC of the soil at any pH only starting from the organic matter and of texture. These values agree with the bibliographical data [23].

3.3. Salinity Index Determination

According to the various CEC results obtained and the exchangeable cations, which were extracted using ammonium acetate and the cobalthexamine (Cohex) trichloride, two salinity indices could be defined. These indices will be applied to both methods used in the determination of CEC and exchangeable cations.

Salinity index 1 (SI1) =
$$\Sigma$$
 cations/CEC (1)

Salinity index 2 (cmolc·kg⁻¹) (SI2) =
$$\Sigma$$
 cations – CEC (2)

SI1 and SI2 are related to the method with the cobalthexamine, whereas for the Metson method SI3 and SI4 are used.

Figure 3 indicates the relation between the salinity index 2, which represents the quantity of cations in soil solution, and the total soluble cations of the extract of saturated soil paste. The equation of the straight regression line shows that the slope value is lower than 1, which explains why the sum of total soluble salts extracted from saturated soil paste is higher than those extracted with the cobalthexamine. To characterize the saline soils of Cheliff plain, the CEC effective and the exchangeable cations extracted at the pH of the soil used as a criterion of

evaluation must be adapted well compared to those extracted with standard pH 7.

3.4. Influences of Salinity Index on Soil Physical Properties

3.4.1. Water Retention

Measurements of water retention were taken on the natural water samples of various salinity levels. The results had a range of potentials from 10 kPa (pF = 1.0) to 15000 kPa (pF = 4.2), i.e. that represented a range of moisture content going from the field capacity to the point of permanent witting of the plants. With water potential bottoms (pF = 4.2), the water retention appears to be very strongly correlated to the cation exchange capacity when it is measured at the standard pH 7 (CEC7) and to the specific surface (SS) area (Table 3).



Sum of soluble cations in the saturated paste extract (cmolc·kg⁻¹) **Figure 3.** Relationship between the salinity index 2 estimated by the cobalt hexamine trichloride method and the total soluble cations from the saturated paste extract.

On the other hand, the relationship obtained with CEC effective measured using cobalthexamine method is not close to the coefficient of correlation (r = 0.68). It also appears that the standard CEC (Metson method) and specific surface area (SS) could be used as a suitable criterion for the soil water retention. These results agree with those of [6] and [24]. For high water potentials in the vicinity of the field capacity (pF between 1 and 3), the correlation coefficients obtained between the CEC and the water content are weak. On the other hand, the best relations are obtained with the inverse of the bulk density (1/Da). The bulk density of the soil is also an indicator of the water retention for the field capacity because the variation of water content is primarily related to the evolution of structural porosity and thus to the structure of the soil. These results are in accordance with these of [26], which showed that the soil water retention at pF 2.5 was well correlated to the inverse of the bulk density (1/Da).

3.4.2. The Structural Stability and the Hydrodynamic Behaviour of the Soils

As it is shown in Table 4, the salinity index calculated using the results of cobalthexamine measurement is well correlated to the inverse of the mean weight diameter (1/MWD) and to the final infiltration coefficient (FIC).

	pF1	pF2.5	pF3	pF3.5	pF4	pF4.2	1/Da	CECe	CECm	SS
pF1	1.00									
pF2.5	0.85	1.00								
pF3	0.79	0.95	1.00							
pF3.5	0.65	0.83	0.93	1.00						
pF4	0.71	0.84	0.93	0.97	1.00					
pF4.2	0.34	0.44	0.55	0.50	0.53	1.00				
1/Da	0.80	0.98	0.90	0.76	0.76	0.38	1.00			
CECco	0.15	0.20	0.40	0.58	0.53	0.68	0.09	1.00		
CECm	0.38	0.44	0.59	0.70	0.68	0.80	0.33	0.97	1.00	
SS	0.52	0.69	0.69	0.56	0.59	0.86	0.66	0.43	0.65	1.00
IS1	0.15	0.31	0.23	0.15	0.00	-0.29	0.33	-0.11	-0.08	-0.07
IS2	0.17	0.33	0.25	0.17	0.03	-0.29	0.34	-0.09	-0.06	-0.07
IS3	0.31	0.54	0.42	0.24	0.13	-0.03	0.59	-0.16	-0.05	0.23
IS4	0.39	0.62	0.51	0.32	0.22	0.10	0.67	-0.09	0.04	0.35

Table 3. Matrix of linear correlation between the salinity indexes and the water retention properties (the significant correlations at p = 0.005 are underlined).

ESP_{eq}: ESP estimated by the equation of USSL Staff (1954); 1/Da: The inverse of the bulk soil density.

 Table (6): Matrix linear correlation between the salinity indices, the parameters of salinity and sodicity and the physical properties (n=13 samples)

	IS1	IS2	IS3	IS4	EC	SSC	SEC	ESP	SAR	ESPeq	1/MWD	FIC
IS1	1.00											
IS2	099	1.00										
IS3	0.87	0.86	1.00									
IS4	0.80	0.79	0.99	1.00								
CE	0.93	0.93	0.93	0.89	1.00							
SSC	0.87	0.87	0.99	0.97	0.94	1.00						
SEC	0.98	0.98	0.90	0.84	0.98	0.91	1.00					
ESP	0.93	0.92	0.84	0.76	0.94	0.85	0.96	1.00				
SAR	0.92	0.92	0.78	0.69	0.92	0.81	0.94	0.98	1.00			
ESPeq	0.92	0.92	0.78	0.69	0.92	0.80	0.95	0.98	1.00	1.00		
1/MWD	0.72	0.72	0.53	0.45	0.61	0.52	0.68	0.70	0.67	0.67	1.00	
FIC	-0.58	-0.59	-0.51	-0.47	-0.62	-0.48	-0.62	-0.67	-0.64	-0.65	-0.77	1.00

ESPeq: ESP estimated by the equation of USSL Staff (1954). SSC: Sum of soluble cations SEC: Sum of exchangable cations

The structural stability and the water infiltration of the soils remain the most adapted means to evaluate the sensitivity of the soils to the mechanisms of disintegration. The linear correlation coefficients estimated between these tests (1/MWD and FIC) and the parameters of the saline phase (Table 4) indicate rather strong relations between the electrical conductivity of saturated paste extract (ECe), the sum of the exchangeable cations (SEC), the exchangeable sodium

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percentage (ESP) and the sodium absorption ratio (SAR). The sum of the soluble cations (SSC) is not significantly dependent on any of the physical parameters. So, the effect of the soil solution concentration is less apparent. Both the inverse of the mean weight diameter (1/MWD) and the final infiltration coefficient of (FIC) have correlation coefficients slightly higher with sodicity than with salinity. It is noticed that the variables of sodicity (ESP, SAR and ESPeq) are better than the variables of salinity (ECe and SI). This means that the exchangeable sodium content controls the physicochemical mechanism of dispersion during disintegration, which involves the production of fine particles. This influence is explained by the role of sodium in the dispersion of soil particles [4,27] and the reduction of water infiltration. These two effects strongly contribute to closing the surface when the samples are subjected to the simulated rains of 30 mm/h [28,29].

4. Conclusion

The present study shows that it is possible to estimate the cation exchange capacity of the Cheliff soils from the clay content, the organic matter content and the pH of the soil. It also reveals that measurements of the CEC and the total cations carried out at the pH of the soil with the cobalthexamine cation make that it is possible to approach the chemical properties of the soils, such as sodicity. On the other hand, the measurement of the CEC at pH 7 presents the disadvantage of dissolving a part of carbonates and thus it is not adapted to measure the exchangeable cations and CEC in calcareous soils. However, the measurement of the CEC carried out at the standard pH 7 seems an indicator of the hydraulic soil properties at water potential bottoms, in relation to specific surface area. The inverse of the apparent density and the specific surface seems good indicators to estimate the properties of water retention at the field capacity and the permanent witting point, respectively. The influence of salinity is relatively less significant than the sodicity and the cation concentration of soil solution is not synonymous with bad stability. In general, it is clear that the relation of the saline phase and the physical properties results is not on the agenda. A detailed study is necessary. So, in this direction, we started a study on the effects of exchangeable sodium and cation concentration of the solution on the physical properties of clay materials of the Cheliff plain. We can say shortly that our study is a contribution to evaluate the quality of the estimate and the development of the pedotransfer functions to predict the behaviours of the Cheliff saline soils

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