

Comparison of the base summation method *versus* the direct method to determine the cation exchange capacity of the soil

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Abstract: *The cation exchange capacity (CEC) of soil is an important parameter since it is an indicator of the fertility and physicochemical quality of the soil. There are several methods to find and estimate the CEC of soils. This work aims to compare the direct ammonium distillation method and the exchangeable base summation method based on the analysis of 65 samples taken from 0 to 0.20 m depth of soils in the northern and western areas of Honduras. Initially, the analyses of pH, % organic matter, % clay, and exchangeable bases (Ca, Mg, K, and Na) extracted with ammonium acetate at pH 7.00 were carried out. In addition, they were determined by atomic absorption, exchangeable acidity (H and Al), extracted with IN KCl determined by titration. Subsequently, the CEC was determined by direct method of soil washing and ammonium distillation. The data was subjected to Pearson correlation analysis and linear regression. The % organic matter and clay parameters did not have a significant correlation with both methods; however, the pH presented a positive correlation of $r = 0.73$ with the direct method and $r = 0.81$ with the base summation method. The Ca concentration presented positive correlations of $r = 0.85$ and $r = 0.97$ with the direct and summation method, both methods correlated positively with $r = 0.86$. With the data obtained, it is concluded that both methods are statistically comparable and correlate with each other to estimate the CEC of soils in northern and western Honduras.*

Keywords: *Soil Chemistry, Soil Fertility, Correlation of methods, Cation exchange.*

I. INTRODUCTION

Chemical identification of agricultural soil is necessary to predict the fertility potential of the soil, in addition to preparing a fertilization improvement plan [1], [2]. In this context, the cation exchange capacity (CEC) is an indicator of the soil's ability to absorb and supply nutrients, therefore the CEC is used as an index of soil chemical fertility. Cations found on the soil surface are easily exchangeable in solution, being a reversible process by which solid soil particles absorb cations from the

aqueous phase, releasing at the same time other cations in equivalent quantities, which is expressed in milliequivalents per 100 grams of soil or in centimoles per kilogram of soil, establishing a balance between both phases so that a high CEC makes the soil have a greater capacity to absorb and provide nutrients better than soils with low CEC [3].

The CEC depends on the pH, the amount of organic matter, and the type of clay in the soil. There are soils with variable loads that depend on the pH and there are soils with non-variable loads, and these are the ones that have a CEC defined as 2:1 clay. They are composed of a succession of layers of two tetrahedral sheets sandwiched by an octahedral sheet and separated by an interlayer space. Isomorphic substitutions inside the different sheets drive the evolution of cohesive bonds between successive layers, which can be viewed as long-range interactions. The whole spectrum of the permanent charges is commonly used to classify the 2:1 clay minerals from talc and pyrophyllite to brittle micas [4]. The CEC is determined from the adsorbed amount of an index cation and by saturating a solution containing said cation through a soil sample [5]. On the other hand, the most used methods generally employ NH_4^+ , K^+ , Na^+ , and Ba^{++} as index cations, using buffered solutions, which consist of saturating the soil with a cation that is not normally part of its ions, such as barium. The methods used to estimate CEC are classified as CEC by the sum of exchangeable cations, CEC at soil pH, CEC at buffered pH, and CEC at zero charge point, all of which are based on the saturation of the soil with an index cation [6], [7]. The methods used to estimate the exchange capacity simultaneously determine the positive and negative charges; however, multiple washings and centrifuges involve time, work, and loss of the sample, so an alternative is the use of atomic adsorption spectrometry [6], [8].

The methodologies to determine the CEC are very varied and significant differences have been found between one



Fig. 1 Ubication of Agricultural Chemical Laboratory of the Honduran Foundation for Agricultural Research (FHIA), La Lima, Cortés, Honduras CA

method and another, this is because the methods are different from each other, and the procedures use different materials to estimate the CEC. However, these variations not only impact evaluation costs but also farmers' understanding of the results obtained. In this context, the objective of this research was to apply two methods for the determination of CEC, the methods used included ammonium acetate at pH=7 as an extractive solution, the direct method determined by distillation of ammonium and the method of sum of bases plus exchangeable acidity, both methods were used to analyze 65 samples from the north and west of Honduras.

II. MATERIALS AND METHODS

A. Sample selection

The research was conducted at the Agricultural Chemical Laboratory of the Honduran Foundation for Agricultural Research (FHIA), located in the municipality of La Lima, Department of Cortés, Honduras CA, 65 soil samples were selected from those existing in the laboratory warehouse, coming from producers in the north and west of Honduras. The study was carried out in that region of the country due to the need of farmers in this area to find a more economical and faster method to determine the exchange capacity of the soil.

Samples were selected and taken from 0 to 0.2 m depth, dried at room temperature and under shade, macerated, and passed through a 2 mm sieve to obtain a homogeneous sample.

B. Analytical processes

Granulometric analyses were carried out on the 65 soil samples to determine the percentage of clay following the Bouyoucos methodology where the size of the suspended solids is estimated from the density of the solution measured with a hydrometer (densimeter), at different times [5], the pH in water with a ratio of 1:2.5 [6], and the percentage of organic matter by acid digestion with dichromate potassium [7].

1) Cation Exchange Capacity Direct Method

To determine the cation exchange capacity, the direct method, Chapman's methodology was followed [8], for which, 10 g of dry and sieved soil was weighed, and 50 mL of 1N $\text{CH}_3\text{COONH}_4$ pH=7 extractant solution was added, the sample was shaken for 30 minutes at 120 rpm and filtered through Whatman # 1 paper. Soil samples were washed five times with 10 mL of 1N $\text{CH}_3\text{COONH}_4$ pH = 7, allowing each portion to drain completely before adding the next. The extract was transferred to a 50 mL capillary to then read K^+ , Na^+ , Ca^{2+} , and Mg^{2+} in the atomic absorption spectrophotometer.

The ammonium-saturated soil was washed with methyl alcohol, distilled water, and four 25 mL portions of 8% NaCl solution. To 25 mL of the wash was added 5 mL of 50% NaOH solution and then distilled for eight minutes in the micro Kjeldahl collecting the distilled ammonium in an Erlenmeyer of 125 mL containing 20 mL of boric acid with mixed indicator. Total NH₄ was determined by titration with 0.1 N sulfuric acid.

To calculate the CEC, the following formula (equation 1) was used:

$$CEC_{cmol^+kg^{-1}} = \frac{(G)(N)(100)(4)}{w} \quad (1)$$

Where:

CEC= Cation exchange capacity by direct method

G= Sulfuric acid used in titration (mL)

N= Normality of the acid.

w= Sample weight (kg)

100 = Volume of ammonium acetate used for extraction

4 = Conversion factor of the sodium chloride aliquot

2) Determination of interchangeable bases

The methodology of Thomas [9] was followed for which the ammonium acetate extract resulting from the first filtrate in the cation exchange capacity methodology was taken. In 20 mL capillaries, 1 mL of the original extract was deposited, and 9 mL of distilled water was added, from this dilution 1 mL was taken and deposited in 10 mL capillaries and 9 mL of 1% strontium chloride solution was added. Sodium and potassium were analyzed from the original extract. From the one-in-nine dilution with strontium chloride, calcium, and magnesium were analyzed. The equipment readings are multiplied by the corresponding dilution factors and converted from mgkg⁻¹ to cmol⁺kg⁻¹.

To determine the exchangeable acidity H⁺ and Al³⁺, 10 g of dry soil was weighed, 50 mL of 1 N KCl solution was added and stirred for 30 minutes. The sample was filtered and washed with 50 mL of 1 N KCl solution. Three drops of methyl orange were added to the filtrate, and it was titrated with 0.049 N NaOH solution. After the color change, three drops of phenolphthalein were added and titrated with 0.049 N NaOH, and the ml spent were recorded. To obtain the result of the exchangeable acidity that corresponds to H⁺ and Al³⁺, the following formulas were used (Equation 1 and Equation 2):

$$H^+_{cmol^+kg^{-1}} = \frac{(mL_1)(N)(100)}{w} \quad (2)$$

$$Al^+_{cmol^+kg^{-1}} = \frac{(mL_2)(N)(100)}{w} \quad (3)$$

Where:

H⁺= Amount of Hydrogen ions present in the soil.

Al³⁺= Amount of Aluminum ions present in the soil.

mL₁= Milliliters of sodium hydroxide spent in the titration with methyl orange.

mL₂= Milliliters of sodium hydroxide spent in the titration with phenolphthalein.

N= Normality of sodium hydroxide.

100 = Volume of potassium chloride used for extraction

The cationic exchange capacity was determined by the base summation method, adding the exchangeable bases and acidity. Using the following formula (Equation 4):

$$ECEC = Ca^{2+} + Mg^{2+} + K^+ + Na^+ + H^+ + Al^{3+} \quad (4)$$

Where:

ECEC= Cation exchange capacity by summation of bases

Ca²⁺= Amount of Calcium ions present in the soil (cmol⁺kg⁻¹)

Mg²⁺=Amount of Hydrogen ions present in the soil (cmol⁺kg⁻¹)

K⁺= Amount of Potassium ions present in the soil (cmol⁺kg⁻¹)

Na⁺= Amount of Sodium ions present in the soil (cmol⁺kg⁻¹)

H⁺= Amount of Hydrogen ions present in the soil (cmol⁺kg⁻¹)

Al³⁺=Amount of Aluminum ions present in the soil (cmol⁺kg⁻¹)

C. Statistical analysis

The data was analyzed using Pearson correlation and linear regression, a significance of 95% was used to determine the tabulated correlation coefficient.

To correlate the data, we compared both methods against the percentage of clay, the pH, and the percentage of organic matter, and a correlation between both methods. The Infostat Statistical program was used.

III. RESULTS AND DISCUSSION

A. Organic matter and clay content

Pearson's correlation analysis for the organic matter and clay data showed no significance, these correlations being weak and positive (Table 1), indicating that these two parameters have little influence in estimating the cation exchange capacity for both methods and for these soil types.

In the study by Thomas [10] it is mentioned that organic matter influences the exchange capacity but at greater depths and in undisturbed soil. However, in disturbed soil, it has no significant effects. Gruba et al. [11] reported similar results indicating that organic matter does not affect the fertility of the first centimeters of forest soils; on the contrary, its effect would be seen in the deeper layers of the soil.

The clayey material of the soil has a minimal effect on the cation exchange capacity of the soil because other factors of the soil itself and its vegetation are more significant [12]. Clay becomes significant when the amount exceeds the other fractions and if the type of clay is 2:1 [13].

TABLE I

PEARSON CORRELATION MATRIX BETWEEN CATION EXCHANGE CAPACITY DIRECT METHOD, CATION EXCHANGE CAPACITY SUMMATION METHOD, SOIL pH, ORGANIC MATTER PERCENTAGE, CLAY PERCENTAGE, AND CALCIUM CONCENTRATION OF SOILS FROM THE NORTHERN AND WESTERN REGION OF HONDURAS.

	CEC	ECEC	pH	MO	Clay	Ca
CEC	1.00					
ECEC	0.86	1.00				
pH	0.73	0.81	1.00			
MO	0.40	0.33	0.23	1.00		
Clay	0.50	0.44	0.17	-0.07	1.00	
Ca	0.85	0.97	0.81	0.36	0.39	1.00

CEC = Cation Exchange Capacity direct method, ECEC = Cation Exchange Capacity base summation method, MO = Organic Matter, Ca = Calcium

B. Influence of pH and Calcium on the cation exchange capacity of the soil

In Table I we observe the Pearson correlation matrix between all the data analyzed, the soil pH presents significant correlations with both methods, $r = 0.73$ (direct method) and $r = 0.81$ (base summation method) which indicates that the pH

has a strong influence to estimate the exchange capacity. In the regression analysis (Fig. 2) a positive trend is observed, showing that as the pH of the soil increases, the cation exchange capacity of the soil tends to increase, for both methods.

The pH is the parameter that modifies the availability of nutrients and depending on the type of soil, it influences the cation exchange capacity, usually different [14]. With increasing pH and Calcium concentration, an increase in cation exchange capacity is observed [15], on the other hand, in organic and acid forest soils, cation exchange between aluminum and hydrogen ions is an important pH buffering process [16].

In our results, Calcium is the cation that had the most influence in estimating the exchange capacity by the summation method and by the direct method (Table I).

In Fig. 3, it was observed that, as the concentration of Calcium in the soil increases, the trend of the cation exchange capacity increases in both methods.

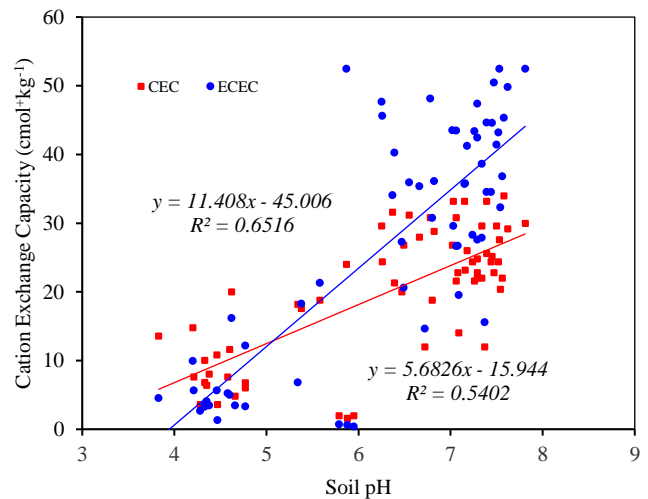


Fig.2 Scatter plot and linear regression between soil pH versus Cation Exchange Capacity direct method and Cation Exchange Capacity base summation method, of soils from the northern and western regions of Honduras.

On the other hand, in soils with a high calcium carbonate content, they overestimate the cation exchange capacity when adding the bases, because the Calcium cation is found in solution in high quantities and not necessarily in the exchange complex of the soil [17]. The addition of calcareous products high in Calcium to the soil increases the pH and, as a secondary effect, increases the base saturation, which increases the

effective cation exchange capacity by adding the exchangeable bases [18], [19].

The positive and strong correlation between pH and Calcium (Table I) explains why both parameters and the cation exchange capacity are related to each other. Calcium, being the cation with the greatest influence in these soils, significantly modifies the pH and the capacity of exchange. Thus, according to some authors, it is possible to predict the exchange capacity of soil knowing the concentration of Calcium and the pH of the soil due to the correlation that exists between these two parameters [20].

C. Base summation method vs direct method

The Pearson correlation analysis (Table I) indicates that the direct method correlates 86% with the base summation method, presenting a positive and significant trend (Fig. 4). Therefore, we can use both methods to calculate the cation exchange capacity of these soils.

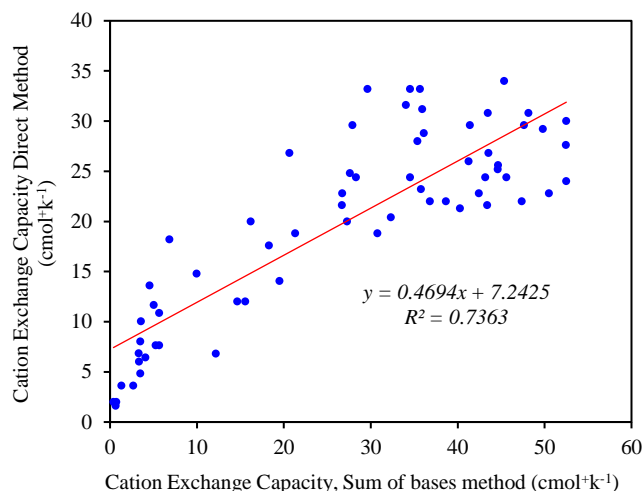


Fig. 4 Scatter plot and linear regression between the Cation Exchange Capacity direct method and Cation Exchange Capacity base summation method, of soils from the northern and western regions of Honduras.

The cation exchange capacity of the soil determined by the summation method increases and overestimates when an excess of calcium carbonates and sulfates is found because the Ca cation in solution is found in quantities that exceed the exchange spaces of the soil [21]. On the other hand, it is possible to estimate the exchange capacity of soil by any method if the amount of bases in a solution that are not part of the exchange complex is known [22], moreover, if all the factors involved in estimating the cation exchange capacity of the soil are taken into account, it is feasible to correlate methods to save time and money [23], [24].

IV. CONCLUSION

The direct and summation of base methods for estimating the cation exchange capacity of soils in northern and western Honduras have a strong and positive correlation, so both methods have the same effectiveness and precision for determining the cation exchange capacity of soils.

The percentages of clay and organic matter do not influence the exchange capacity of the soils under study, while pH and calcium concentration are strongly related to the cation exchange capacity of the soils of northern and western Honduras.

The strong correlation between pH and both methods can be an easy and economical method to predict the

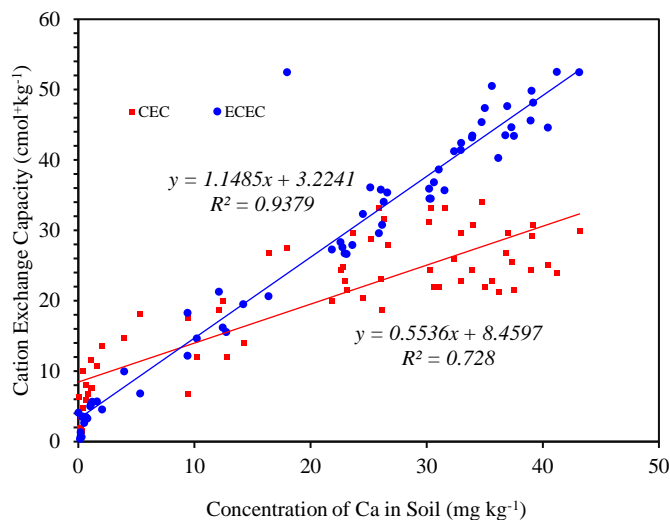


Fig. 3 Dispersion graph and trend between soil Calcium concentration versus the Cation Exchange Capacity direct method and Cation Exchange Capacity base summation method, in soils from the northern and western regions of Honduras.

exchange capacity of the soils of northern and eastern Honduras.

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