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# GLOSOLAN training sessions

## *CATION EXCHANGE CAPACITY AND EXCHANGEABLE BASES DETERMINATION*

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# INTRODUCTION

- Cation exchange capacity (CEC) is the total number of cations that a soil can hold thus a measure of number of negative charge binding sites.
- These adsorb (hold) positively charged ions by electrostatic forces following negative sites created by weathering process e.g. isomorphous substitution in clays or pH dependent charges from hydroxyl groups on clays and oxides or carboxyl groups on SOM.
- Cations are bound in reversible chemical reactions to neutralize the negative charge in the soil created as conceded.
- It can be expressed in terms of milliequivalents/100 g of soil (meq/100 g) or centimoles of positive charge per kg of soil (cmol(+)/kg) or  $\text{cmol}_c/\text{kg}$ , which is numerically equal to meq/100 g (me%).
- Since a soil's CEC comes largely from clay and OM present, CEC of a soil can be estimated from texture and soil colour i.e increases with soil pH due to the greater negative charge development on organic matter and clay minerals such as illite/smectites due to deprotonation of functional groups with increased pH (Sumner and Miller, 1996) See Fig 1. pH versus CEC.

# INTRODUCTION

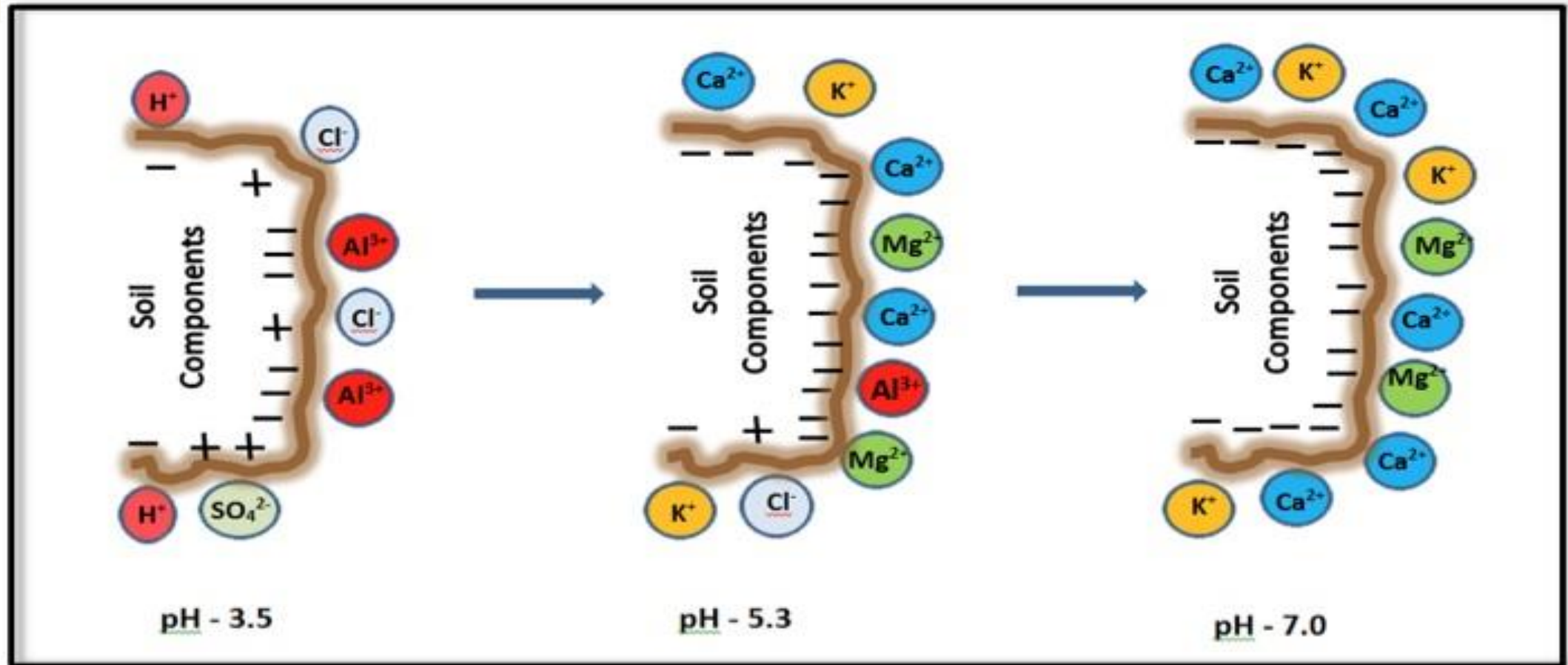


Fig 1. DEFINING Cation Exchange Capacity and Exchangeable Bases of a Soil



# INTRODUCTION

- Clay content, organic matter, and root surfaces all have a direct relationship with soil CEC because they act as seats for negative charge.

Table 1. Cation exchange capacities of some different soil types at pH 7.0

Cation exchange capacities of different textural classes and organic matter at pH 7.0

| Clay Type       | <u>CEC (cmol<sub>c</sub>/kg)</u> | <u>Soil Texture</u> | <u>CEC (cmol<sub>c</sub>/kg)</u> |
|-----------------|----------------------------------|---------------------|----------------------------------|
| Kaolinite       | 3-15                             | Sand                | 1-5                              |
| Illite          | 15-40                            | Fine Sandy Loam     | 5-10                             |
| Montmorillonite | 80-100                           | Loam                | 5-15                             |
|                 |                                  | Clay Loam           | 15-30                            |
|                 |                                  | Clay                | >30                              |
|                 |                                  | Organic matter      | 200-400                          |

# INTRODUCTION

- CEC is a fundamental property for assessing soil fertility used to predict plant nutrient availability and retention in the soil.
- The term “exchangeable bases” or “total exchangeable bases” refers to the sum of the concentration of the bases (calcium, magnesium, potassium, and sodium) in exchangeable form.
- Under normal management practices, higher CEC soils will show changes in soil pH much more slowly than low CEC soils as cations are lost owing to high buffering capacity will also influence rate of liming etc.

| Cations (+) | symbol           | Anions (-) | symbol  |
|-------------|------------------|------------|---|
| Calcium     | Ca <sup>2+</sup> | Nitrate    | NO <sub>3</sub> <sup>-</sup>  |
| Magnesium   | Mg <sup>2+</sup> | Phosphate  | H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> ;<br>HPO <sub>4</sub> <sup>2-</sup> |
| Potassium   | K <sup>+</sup>   | Sulphate   | SO <sub>4</sub> <sup>-</sup>  |
| Sodium      | Na <sup>+</sup>  | Chloride   | Cl <sup>-</sup>   |
| Hydrogen    | H <sup>+</sup>   |            |   |
| Aluminium   | Al <sup>3+</sup> |            |   |

# Methods for CEC Determination

- The more widely adopted methods of CEC determination are classified as follows:
  - Cation summation
  - Direct displacement
  - Displacement after washing
  - Radioactive tracer
  - Alternate methods use extractants that are either buffered (usually pH 7 e.g. Ammonium acetate or  $\text{BaCl}_2$  (pH 8.2) or unbuffered (field pH).
- The GLOSOLAN SOP is based on the displacement after washing principle

## SCOPE AND FIELD OF APPLICATION- IN VIEW OF INTERFERENCES

- As a number of methods are available for measuring CEC, it is very important to compare CEC and exchangeable bases where the same laboratory method has been used. GLOSOLAN thus have adopted presently the buffered 1N Ammonium Acetate method as one of the most popular methods available to facilitate Proficiency Testing and Regional comparison of data.
- For ideal method of CEC, it is important to know in the first place the intended use of the data. For soil classification a soil's CEC is often measured at standard pH value of which selected method of Ammonium Acetate is recommended.

Often Soil testing laboratories, knowing the importance of CEC but in bid to cut expenses do not provide a direct measure of CEC but use  $CEC_{sum}$  based on summation of quantities of Ca, Mg and K (sodium most often being usually in negligible quantities).

# APPLICABILITY, ADVANTAGES / DISADVANTAGES

- Ideal when soil pH is  $>7.3$  and the soil has not been limed in the last 6 months or have not been fertilized by Ca, K or Mg fertilizers,  $CEC_{sum}$  can be a reasonable estimate of  $CEC_e$
- On the other hand above pH 7.5 significant quantities of free salts or unreacted lime may have been just dissolved in the extracting solution used for leaching

## ADVANTAGES OF pH 7 buffered AMMONIUM ACETATE

- It is rapid and cost effective hence can be easily implemented by many laboratories
- May underestimate CEC of tropical peats.

## DISADVANTAGES OF AMMONIUM ACETATE CEC buffered method

The major problem with this method is that it buffers soil pH at 7.0 . So will only approximate a soil's  $CEC_e$  if a soil's pH is 7.0 otherwise the results obtained can be a large overestimation of  $CEC_e$  Of many acid soils (common in Africa). If soil pH is  $< 5.5$  then  $Al^{3+}$  which might be present might not be measured accurately by the exctractants hence need to use alternative e.g. KCl.



# The harmonized GLOSOLAN SOP



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## Standard operating procedure for cation exchange capacity and exchangeable bases

1N ammonium acetate, pH 7.0 method

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# SCOPE AND FIELD OF APPLICATION - OVERVIEW

- This procedure outlines the process for the determination of cation exchange capacity (CEC) and exchangeable bases (calcium, magnesium, potassium and sodium) in soil using 1N ammonium acetate buffered at pH 7.
  - The method gives an estimation of plant-available exchangeable bases.
  - It should be noted though that when a soil is extracted at higher pH, this induces weakly acidic components to dissolve and liberate  $H^+$  which are measured as exchangeable acidity.
- 
- ❖ This method overestimates the CEC of acidic soils as additional negative charge is developed on colloidal exchange sites after the addition of ammonium acetate solution having pH 7 (i.e at pre-determined pH).
  - ❖ The method underestimates the CEC of soils containing carbonates or gypsum because the release of calcium carbonates or sulfates from the soil into the ammonium acetate solution limits the saturation of exchange sites by ammonium ions.

# SCOPE AND FIELD OF APPLICATION

- The unbuffered method (just in passing) allow exchange at soil pH often referred to as ECEC and the pH will be at a lower value than buffered extractant salt solutions as it does not include latent acidity.
- Caution should be exercised in using this method for soils dominated by vermiculite and mica clays because ammonium ions are fixed between the layers of these clays. This methods thus causes the layers to collapse and the fixed ions can no longer be exchanged by sodium ions.
- In relation to the exchangeable bases, for soils in the presence of gypsum (calcium sulfate), extraction with ammonium acetate only allows the quantification of exchangeable magnesium, sodium and potassium, since the calcium content is affected by the excess calcium in the gypsum

# SCOPE AND FIELD OF APPLICATION

- Likewise, in soils containing calcium and magnesium carbonates, extraction with ammonium acetate only allows the quantification of exchangeable sodium and potassium, since the content of calcium and magnesium is affected by the excess of ions from the carbonate
- Similarly when lime has recently been applied, carbonate will liberate calcium which will bind to new site and this will result in an increase in ECEC. So direct soils CEC for the just amended fertilizer/lime should be taken with caution and better avoided.
- Another problem arises in soils affected by salts, because the soluble cations (from the salts) are extracted together with the exchangeable bases
- Hence EC is a crucial guide in soils suspected to be salt affected

# PRINCIPLE AMMONIUM ACETATE (buffered at pH 7.0) SOP

- This SOP describes the most widely used method for agricultural soils.
- The soil is treated with 1 normal ammonium acetate solution buffered at pH 7.0 to remove exchangeable cations from the exchange sites of the soil colloids as conceded in introduction of CEC and to saturate them with  $\text{NH}_4^+$  ions.



# PRINCIPLE (continued)

- Then the exchangeable cations in the leachate are then quantified using different instrumental methodologies that are available (Atomic Absorption/Emission spectrometry, flame emission or Inductively Coupled Plasma or MP-AES) etc.
- In the sediment, the excess of ammonium ions in the soil samples are removed by washing with ethanol. Then the adsorbed ammonium ions on soil sample are extracted using acidified sodium chloride and measured by distillation and titration.
- In saline soils, one of the options is to pre-wash samples with 70% alcohol to eliminate the salts (soluble bases)

# APPARATUS -1

1. Reciprocal shaker
2. Precision balance
3. Centrifuge
4. Volumetric dispensers
5. Filter funnels and qualitative fine porous filter paper
6. 100 ml volumetric flasks
7. pH meter and buffer solutions

# APPARATUS -2

8. 50 ml Plastic tubes/centrifuge tubes with screw on caps
9. Graduated or automatic burette
10. Steam distillation unit
11. 250 Kjeldhal distillation tubes
12. Erlenmeyer flasks 250 and 100 ml
13. Stirrer and magnetic bar
14. Flame or Plasma spectrophotometer
15. Atomic absorption

# MATERIALS

- 1) Deionised/distilled water
- 2) Concentrated Ammonium hydroxide ( $\text{NH}_4\text{OH}$ , AR)
- 3) Glacial acetic acid ( $\text{CH}_3\text{COOH}$  99.5%, AR)
- 4) Ammonium acetate ( $\text{NH}_4\text{CH}_3\text{COO}$ , AR)
- 5) Methyl orange
- 6) Sodium chloride ( $\text{NaCl}$ , AR)
- 7) Concentrated hydrochloric acid ( $\text{HCl}$ , 32-36%)
8. Sodium chloride ( $\text{NaCl}$ ) solution 10%(m/v), pH 2.5
9. Sodium hydroxide ( $\text{NaOH}$ ) solution 10 mol/l
10. 1N Hydrochloric acid/Sulphuric acid, AR
11. Boric acid ( $\text{H}_3\text{BO}_3$ ) AR
12. Boric acid ( $\text{H}_3\text{BO}_3$ ) solution 4% m/v (4g/100ml)
13. Ethanol (95 – 96%)
14. Gases (as determined by instruments)

# HEALTH AND SAFETY

- Personnel safety
  - Metal salts used in this procedure are extremely corrosive and may be fatal if ingested
  - Use protective clothing: lab coats, aprons, gloves and eye protection face shield, goggles or safety glasses
- Chemical hazards
  - concentrated HCl, NaOH and  $H_2SO_4$  to be used under a fume hood
  - Neutralize spilled acids with dilute solution of sodium bicarbonate or cover with sand
  - Alcohol is flammable
  - Ammonium acetate is corrosive
  - Refer to MSDS



# PROCEDURE - 1

1. Weigh 5g of <2mm sieved soil in a 50 mL container/extraction tubes;  
NOTE: Include a blank and reference sample in every batch
2. Add 33ml of 1N ammonium acetate pH 7.0
3. Shake 15 min in a reciprocal shaker
4. Centrifuge and filter the supernatant in a clean 100 mL volumetric flask with qualitative fine porous filter paper. Repeat steps 2 to 3 two more times to obtain a total of approximately 100 mL at the end. Fill up to the 100 mL mark with ammonium acetate and mix well.

**N.B. For CEC determination** Keep the soil sample in the 50 mL extraction/centrifuge tubes for Procedure 3 step 6.

# PROCEDURE- 2

5. Analyze the leachate for Ca, Mg, Na and K by Atomic Absorption flame or plasma spectrophotometry. Following the manufacturer's guide for the elements required: Some of the suitable spectral lines for Atomic Absorption Spectrophotometer are:

Ca = 422.7 nm;

Mg = 285.2 nm;

Na = 589.0 nm;

K = 766.5 nm.

Ca<sup>2+</sup> and Mg<sup>2+</sup> are measured on dilute extracts, whereas, extracts of Na<sup>+</sup> and K<sup>+</sup> analysis are only diluted if over range. For plasma, suitable wavelengths are: Ca = 430.25 nm; Mg = 285.2 nm; Na = 588.96 nm; and K = 766.49 nm. While It is suggested to use AAs/flame photometer if available an ICP-OES can also be used.

The range of standards presented in table 1 is recommended.

## TABLE 2 - Recommended standard guide range

| 100 ml flask | Ca              |                  | Mg              |                  | Na              |                  | K               |                  |
|--------------|-----------------|------------------|-----------------|------------------|-----------------|------------------|-----------------|------------------|
|              | Vol. of 100mg/l | Final conc. mg/l | Vol. of 100mg/l | Final conc. mg/l | Vol. of 100mg/l | Final conc. mg/l | Vol. of 100mg/l | Final conc. mg/l |
| Flask 1      | 0               | 0                | 0               | 0                | 0               | 0                | 0               | 0                |
| Flask 2      | 2               | 2                | 1               | 1                | 5               | 5                | 5               | 5                |
| Flask 3      | 4               | 4                | 2               | 2                | 10              | 10               | 10              | 10               |
| Flask 4      | 6               | 6                | 3               | 3                | 15              | 15               | 15              | 15               |
| Flask 5      | 8               | 8                | 4               | 4                | 20              | 20               | 20              | 20               |
| Flask 6      | 10              | 10               | 5               | 5                | 25              | 25               | 25              | 25               |

## PROCEDURE – 3: CEC ANALYSIS ON AFTER LEACHATE SEDIMENT

6. To displace the adsorbed ammonium ions ; Place the sediment into the leaching apparatus and add 50 mL of 95-96 % Ethanol and leach wash.
7. Decant and repeat the process of leach washing with ethanol with another fresh 50 ml portion and decant thereafter.
8. Add 33 mL of a 10% NaCl solution to the sample, stopper and shake for 15 minutes.
9. Centrifuge and filter into a clean 100 mL volumetric flask.
10. Repeat step 8 two more times to obtain a total of approximately 100 mL of NaCl solution at the end. Fill up to 100 mL with NaCl and mix well.

# PROCEDURE – 4 DISTILLATION AND TITRATION

10. Transfer 50 mL of aliquot NaCl extract into the distillation tube and connect to the distillation unit.
11. Add 10 mL sodium hydroxide and distilled water cautiously after set up of boric acid receiver have been set up with 25 ml in an Erlenmeyer flask in place if instrument does not have automatic addition of reagents in place.
12. Titrate the distillate with 0.01N H<sub>2</sub>SO<sub>4</sub> or HCl to the indicator end point.



# CALCULATIONS – for CEC

## 1. Calculations for CEC in $\text{cmole}_c/\text{kg}$ soil

Sample weight = 5 g

Extract = 100 mL

Aliquot = 50 mL

HCl concentration = 0.01 N

CEC  $\text{cmole}_c/\text{kg}$  or  $\text{meq}/100\text{g}$  soil = (HCl used for sample - HCl used for blank) \* HCl concentration \* 100/5 \* 100/50

# CALCULATIONS – FOR EXCHANGEABLE BASES

Ca cmol(+)/kg soil = (Sample concentration in mg/l - blank concentration in mg/l) x 100/1000 x 1000/5 x 2/40.08 x 1/10 x dilution factor

Mg cmol(+)/kg soil = (Sample concentration in mg/l - blank concentration in mg/l) x 100/1000 x 1000/5 x 2/24.31 x 1/10 x dilution factor

Na cmol(+)/kg soil = (Sample concentration in mg/l - blank concentration in mg/l) x 100/1000 x 1/10 x 1/22.99 x 1000/5 x dilution factor

K cmol(+)/kg soil = (Sample concentration in mg/l - blank concentration in mg/l) x 100/1000 x 1/10 x 1/39.098 x 1000/5 x dilution factor

% Exchangeable base saturation

Is given by  $100 (\text{Ex Ca} + \text{Ex Mg} + \text{Ex K} + \text{Ex Na})/\text{CEC}$

*100/1000 conversion to L*

*1/10 conversion to centimol*

*1000/5 conversion to Kg*

# QUALITY ASSURANCE/QUALITY CONTROL

## a) Precision Test

- Perform replicate analysis on one sample at every 10 (or 20) samples in batch tests in a single run on a single day
- Calculate the Percent Relative Standard Deviation (%RSD) to determine if the replicate analysis is out of the control.

## b) Accuracy Test

- Participate in Inter-laboratory Proficiency Test (either national or international)
- Analyse CRM or QRM

# QUALITY ASSURANCE/QUALITY CONTROL

## c) Quality Control Chart

- Analyse at least a duplicate of the check sample (Internal Quality Control sample, IQC) or Internal Reference Material (IRM) in every batch.
- Plot the results in a control chart.

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THANK YOU!!!

