

## Cation Exchange Capacity

- Beginnings of soil chemistry.
- 'According to Sestini (1873), as early as 1819, the Italian chemist Gaggeri showed that clay decolourates liquid manure and keeps back its soluble substances which gradually are delivered to the plants.' Wiklander (1946).
- In 1845, a Yorkshire farmer named Harris Stephan Thompson showed that  $\text{NH}_4^+$  added to a soil column would be retained and  $\text{Ca}^{2+}$  released.
- Thompson told Thomas Way, a chemist, and Way conducted a series of experiments showing rapid stoichiometric exchange of common cations for  $\text{Ca}^{2+}$  in a variety of materials, including chalky soil (Way, 1850, 1852).

## Way's experiments

- Added ammonia, potash or magnesia was retained and calcium was released.
- The exchange was rapid and chemically balanced.
- The associated anion did not matter.
- Wrongly observed that *organic matter had nothing to do with it.*
- 'it was evident that the active ingredient in all these cases was clay.'

## Early 1900s

- Simple methods for determining the CEC were developed using neutral salts such as KCl and  $\text{NH}_4\text{Cl}$ .
- Hissink (1920, 1925), working in the Netherlands, developed a methodology using NaCl for exchangeable Ca and Mg, and  $\text{NH}_4\text{Cl}$  for K and Na.
- The 'Hissink' method was used throughout Europe and 'Base Exchange in Soils' was the topic of a Faraday Society meeting in London in 1924.

## Early aluminium concepts

- Although reported in the early 1900's (Veitch, 1904; Paver and Marshall, 1934), Al was not considered an exchangeable cation until the 1950s or 60s.
- Kelley and Brown (1926) observed that acid soils 'may contain trivalent bases in replaceable form' but their experiments led them to conclude that  $\text{Al}^{3+}$  was brought into solution not by exchange but by dissolution as a result of the 'H ions that are displaced from the exchange complex by the neutral salt.'
- From an American Society of Agronomy symposium on the Application of Base Exchange Methods: 'Acid soils do not contain an appreciable amount of exchangeable Fe and Al' (Parker, 1929).

## Exchangeable Al

- Exchangeable Al was rediscovered when it was finally recognized that H-saturated clays transformed into Al-saturated clays through dissolution (Harwood and Coleman, 1954; Low, 1955).
- Coleman et al. (1959) found that 'Al predominated' acid soils of the North Carolina piedmont and 'there were negligible amounts of electrostatically-bonded H in any soil' studied.

## Exchangeable hydrogen

- Repeated neutral salt extractions were found to be acidified by the soil (due to hydrolysis reactions involving Al and OM).
- *However*, the early interpretation of this phenomenon was not that hydrolysis was occurring but that exchangeable H<sup>+</sup> was proving difficult to extract (e.g. Hissink, 1925; Parker, 1929).
- Therefore, new soil extractants buffered at a high pH were introduced to more efficiently remove the H<sup>+</sup>.
- These included pH 7 NH<sub>4</sub>Cl introduced by Schollenberger (1927) in an article in *Science* and pH 8.2 BaCl<sub>2</sub> triethanolamine developed later by Mehlich (1942).

## Variable charge

- The existence of variable charge (both from pH and ionic strength differences) was not widely investigated until the later half of the 20th century
- Mattson (1931) clearly showed the pH dependency of charge in his study 'The laws of soil colloidal behavior: VI. Amphoteric behavior'.
- Mattson (1931a, b) showed variable charge with many types of colloids, including humates, and showed that increasing the proportion of Al in a humate suspension actually lowered its CEC (a finding relevant today).
- In recent decades, variably charged soils have been intensively studied—mostly tropical and volcanic.

## Clay bias

- The concepts of soil chemistry were developed on high-clay soils.
- CEC is strongly correlated with clay content in these soils, especially if they are low in organic matter.
- Most (?) soils of the world contain variably charged oxides and organic matter.
- Forest soils in New England, and many other locales, are low in clay content and high in OM. CEC is correlated with OM.
- Low pH soils (Oa horizons) can be relatively low in Al and high in Ca.

## Organic matter

- The contribution of OM to cation exchange was observed by early researchers (e.g. Hissink, 1925) and clearly documented by Olson and Bray (1938) but the research focus remained on clay minerals.
- Working with agricultural soils acidified in lab experiments, Helling et al. (1964) and McLean and Owen (1969) showed dramatic pH-dependent changes in the CEC derived from OM.
- In one of the first USA studies of forest soils, Wells and Davey (1966) found a linear CEC-pH relationship in pH-adjusted Oe and Oa horizons.
- Kalisz and Stone (1980) presented data from many USA forested sites showing a good correlation between CEC and OM, and large differences between the CEC<sub>e</sub> and the CEC<sub>buf</sub> at pH 7.

## Leftover concepts

- Base saturation (BS): The percent of the CEC (usually measured at pH 7 or 8.2) that is occupied by the base cations.
- Problem: Above a pH of ~5.5, there is no exchangeable Al or H. BS actually measures the "titratable acidity".
- For soil fertility, many practitioners have come to rely on BS and the saturation of Ca, Mg, and K.
- In reality, the cations are not bases and they usually comprise 100% of the CEC.

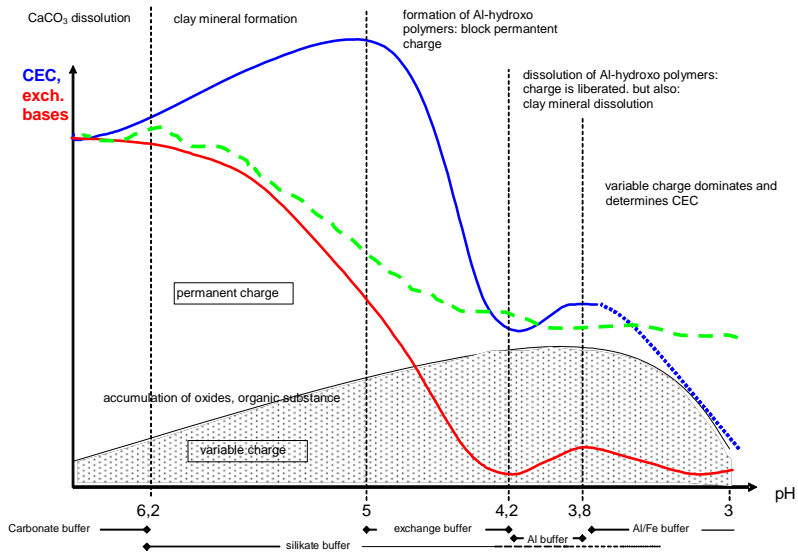
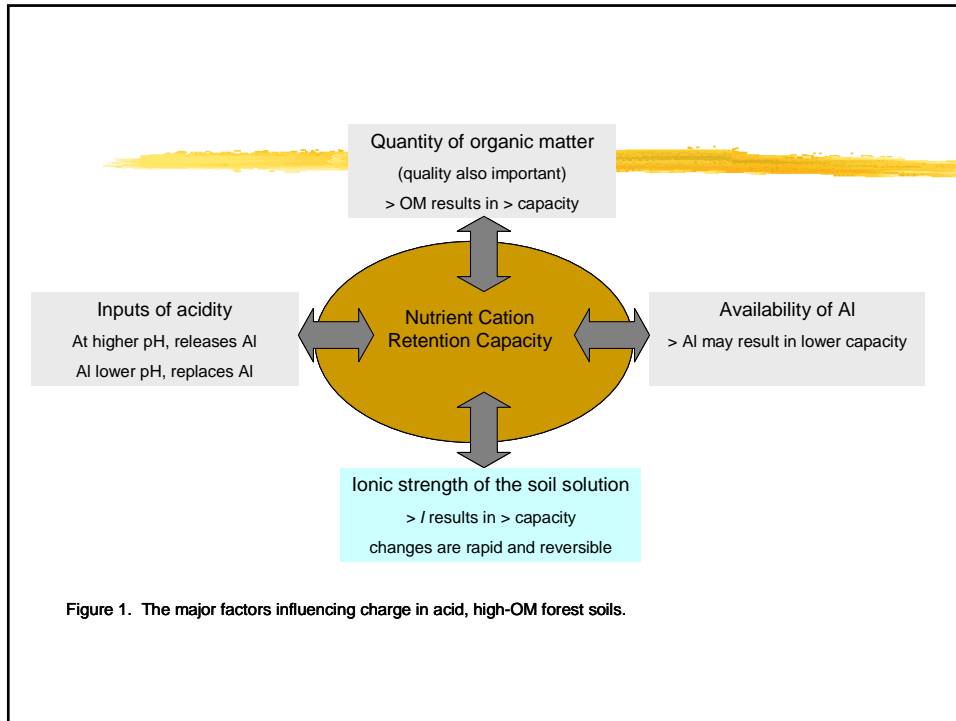
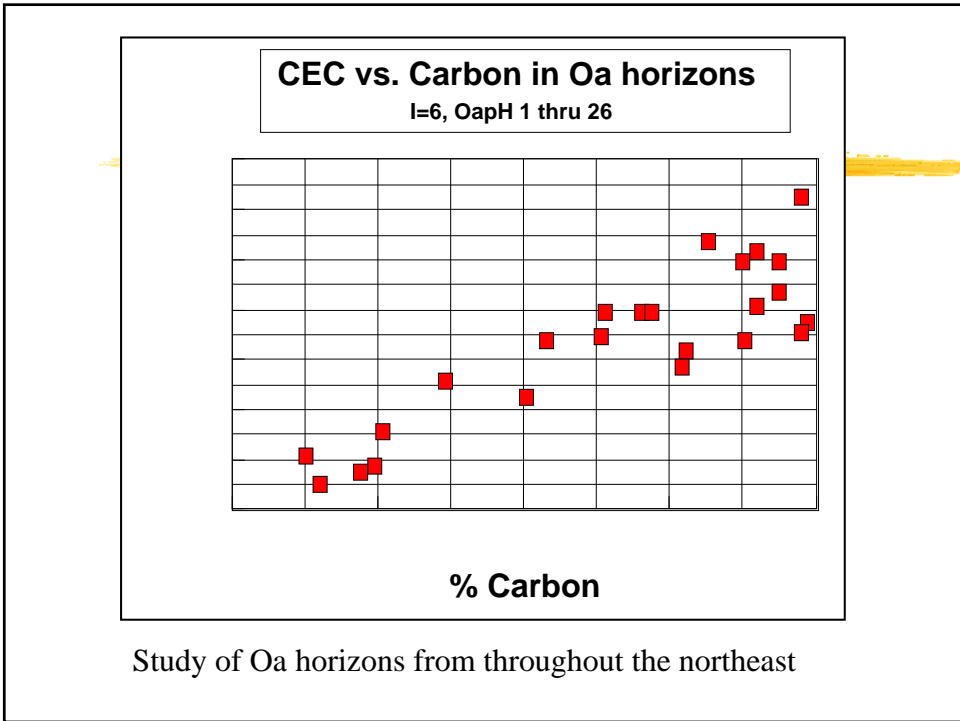
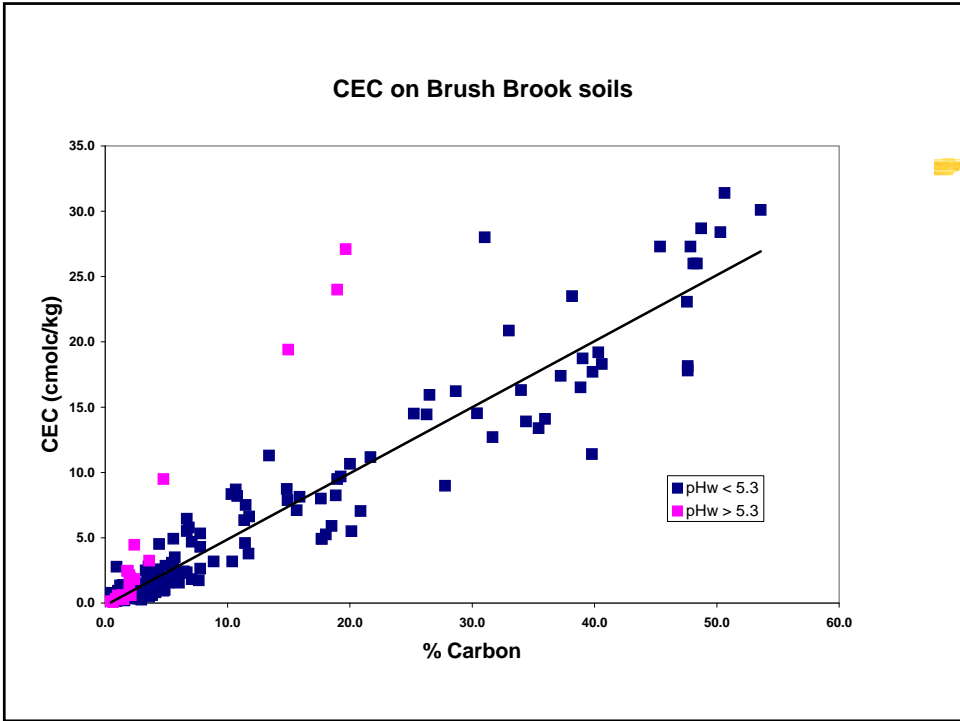
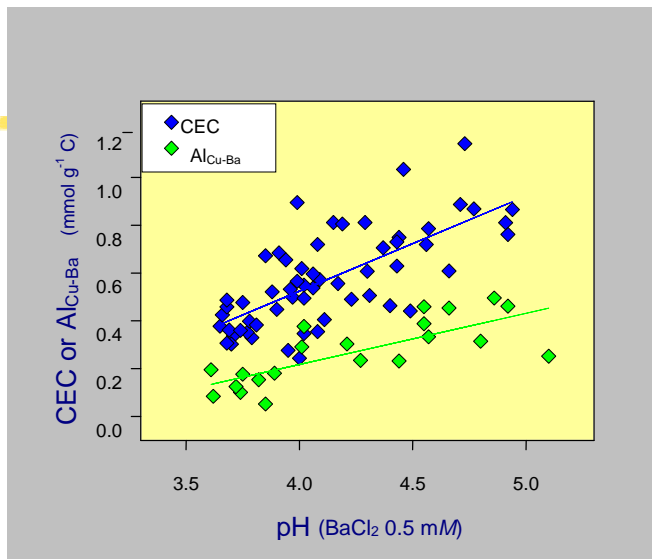
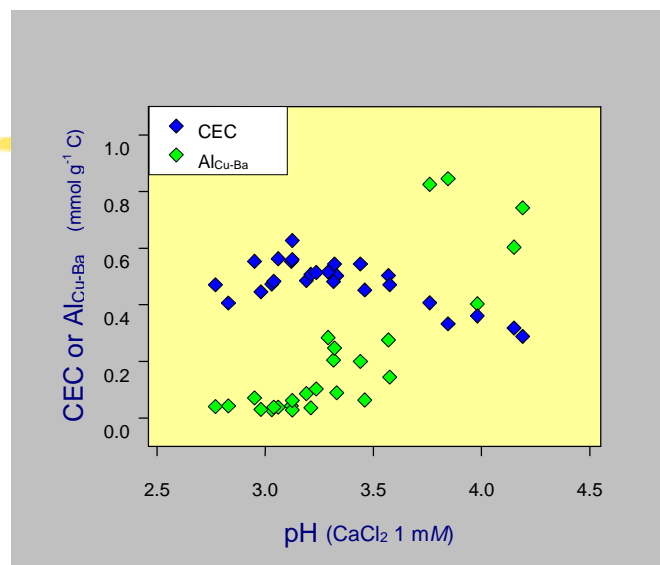


Figure 3. Conceptual scheme of changes in CEC and nutrient cations over a broad range of soil pH.

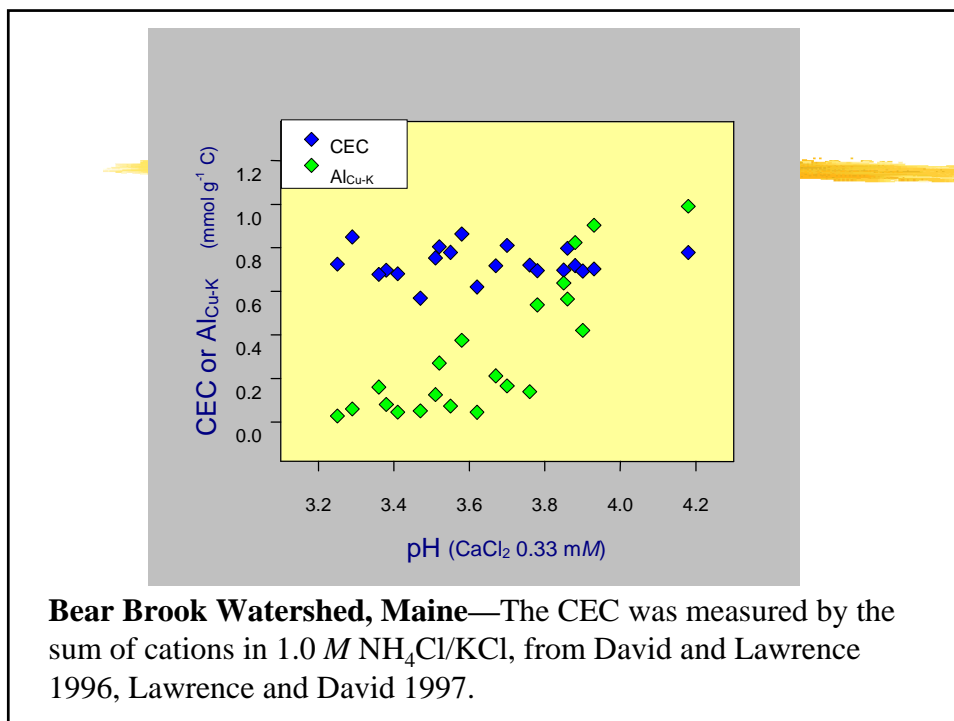




**European Beech soils from southern Sweden**—The CECE by the sum of cations in 0.05 M  $\text{NH}_4\text{Cl}$ . from Matschonat and Falkengren-Grerup 1997



**Northeastern US sites**—The CEC was measured by the  $\text{BaCl}_2$  compulsive exchange method, from Ross and Bartlett 1995.



## Cation exchange equations

- The earth's crust has approximately the same content of Ca, Mg, K and Na.
- The CEC of soils contains much higher concentrations of Ca than Na.
- The oceans contain much higher concentration of Na than Ca.
- Cation selectivity explains this—the valency and the strength of hydration explain differences.
- The simplest model is charge density—higher valency and lower hydrated radius = higher charge density.

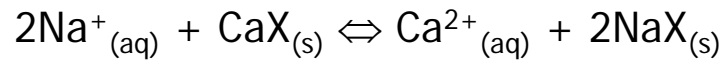
## Lyotropic series

- $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$
- $\text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ = \text{NH}_4^+ > \text{Na}^+$
- $\text{Ba}^{2+} > \text{Pb}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$   
 $> \text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+} > \text{Ag}^+ >$   
 $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Li}^+$

## Selectivity Coefficients

- This term is used because they are not true equilibrium equations.
- The selectivity coefficients are often "conditional" in that they change with the type of charged surface and with the proportion of the cations sorbed.
- The main problem arises from the difficulty of measuring the activity of the exchange complex.
- Ca-Mg, Ca-K, and Ca-Na exchange all behave fairly similarly with different exchangers and differing concentrations, and selectivity coefficients work.

## Selectivity Coefficients (Kerr)



$$\text{Kerr (1928)} \quad K_k = \frac{[\text{Ca}]\{\text{NaX}\}^2}{[\text{Na}]^2\{\text{CaX}\}}$$

[ ] concentration in solution phase in mol L<sup>-1</sup>

{ } concentration in solid phase in mol kg<sup>-1</sup>

Simple “equilibrium” equation but uses concentrations not activities

## Selectivity Coefficients (Vanselow)

$$\text{Vanselow (1932)} \quad K_v = \frac{N_{\text{Ca}} (\text{Na})^2}{(N_{\text{Na}})^2 (\text{Ca})}$$

( ) activity

defined exchanger phase activity in terms of mole fraction

$N$  = fraction of the CEC occupied by the cation

Uses activity of solution phase but not of solid phase (difficult to estimate). The mole fraction is the proportion of the CEC occupied by the cation in question. If the CEC is 8.4 cmol<sub>c</sub> kg<sup>-1</sup> and there are 6.3 cmol<sub>c</sub> kg<sup>-1</sup> of Ca<sup>2+</sup>, the mole fraction ( $N_{\text{Ca}}$ ) is 6.3/8.4 or 0.75

## Selectivity Coefficients (Gapon)



$$\text{Gapon (1933)} \quad K_G = \frac{\{\text{K-soil}\}[\text{Ca}^{2+}]^{1/2}}{\{\text{Ca}_{1/2}\text{-soil}\}[\text{K}^+]}$$

[ ] concentration in solution phase in mmol L<sup>-1</sup>

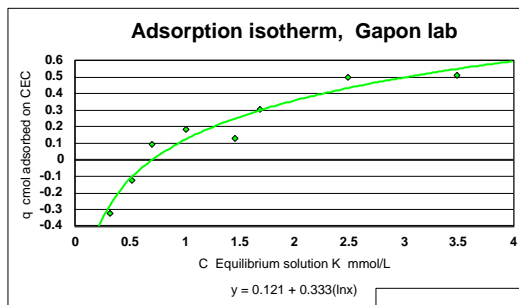
{ } concentration in solid phase in cmol kg<sup>-1</sup>

## Gapon

- ESR or EPR: exchangeable sodium (or potassium) ratio
  - $[\text{NaX}] / [(\text{Ca}^{2+} + \text{Mg}^{2+})_{1/2}\text{X}]$
  - Or if no other cations:  $[\text{NaX}] / [\text{CEC-NaX}]$
- SAR or PAR: sodium or potassium adsorption ratio
  - $[\text{Na}^+] / [\text{Ca}^{2+} + \text{Mg}^{2+}]^{1/2}$

# Gapon

- For Na, the Gapon coefficient is between 0.010 and 0.015
  - $K_G = \text{ESR} / \text{SAR}$
  - Or the fraction of Na on the exchange complex  $\sim = 0.010 \times$  the ratio of solution Na to the square root of solution Ca + Mg.
- For K, the Gapon coefficient is about an order of magnitude higher.

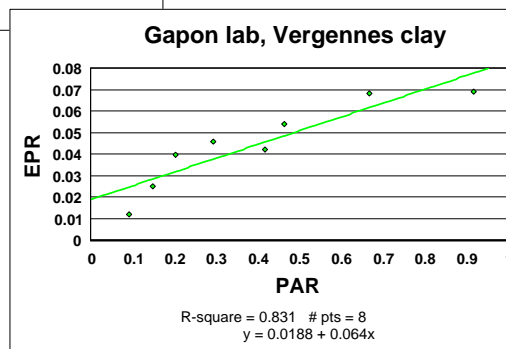


exchangeable potassium ratio (EPR)  
potassium adsorption ratio (PAR).

$$\text{EPR} = K / \text{CEC} - K \text{ cmol}_c \text{ kg}^{-1}$$

$$\text{PAR} = K / (\text{Ca} + \text{Mg})^{1/2}$$

$$\text{EPR} = 0.036 + 0.1051 * \text{PAR}$$



## Examples of Gapon calculations using data from Table 8.1

CEC 36.5 cmolc/kg  
 exch Ca 25.2  
 exch Mg 10.1  
 exch Na 1.2

$$\text{ESR} = \frac{1.2}{(36.5 - 1.2)} = 0.034$$

$$\text{SAR} = \frac{\text{ESR}}{0.01} = 3.40$$

If solution Ca + Mg = 10 mmol/L  
 $3.40 = [\text{Na}] / [10]^{1/2}$

solution [Na] = 10.8 mmol/L

CEC 36.5 cmolc/kg  
 exch Ca 25.2  
 exch Mg 10.1  
 exch K 1.2

$$\text{EPR} = \frac{1.2}{(36.5 - 1.2)} = 0.034$$

$$\text{PAR} = \frac{\text{EPR}}{0.10} = 0.34$$

If solution Ca + Mg = 10 mmol/L  
 $0.34 = [\text{K}] / [10]^{1/2}$

solution [K] = 1.1 mmol/L