Soil Colloids and Cation Exchange Capacity

Chapter 8
p. 316-362

What should you know?

• Soil colloids - what they are, their properties
• Differences between soil clay minerals
• Properties of humic substances (active organic matter)
• Cation exchange and CEC

Colloids

• Very small, chemically surface reactive particles
• Usually < 1 µm diameter
• Very high surface area per unit mass (specific surface area)
• Common examples of colloidal suspensions
  – Jello
  – Milk

Characteristics of Soil Colloids

• High surface area
  – Smectites & vermiculites: 1 g = 800 m²
  – Range: 10 - 800 m² g⁻¹
• Electrically charged surface
  – Usually net negative surface charge
  – In low pH soils dominated by sesquioxides, allophane, imogolite, surfaces may be net positive

Types of Soil Colloids

• Silicate clays
  – Aluminosilicate minerals
  – Crystalline and poorly crystalline types
• Humic substances
• Al and Fe oxides, hydroxides, and oxyhydroxides
  – Sesquioxides
  – Amorphous (gel-like), poorly crystalline

What is Clay?

• Soil particle-size
  – < 0.002 mm (< 2 µm)
• Soil textural class
• A class of silicate minerals
  – The clay minerals: phyllosilicates or layer silicates or sheet silicates
Origin of the Clay Minerals
- Secondary minerals formed by the:
  - Alteration of primary phyllosilicates (structure is inherited)
  - Modification of other complex silicates (e.g., feldspars, amphiboles, pyroxenes) by neoformation
- They may form
  - In place: authigenic (pedogenic)
  - Deposited prior to soil formation: detrital

Layer Silicate Clay Minerals
- Aluminosilicate minerals
- Crystalline structure
- Structural units
  - Silicon (Si⁴⁺) tetrahedral units
  - Aluminum (Al³⁺), magnesium (Mg²⁺), and iron (Fe²⁺/Fe³⁺) octahedral units
- Individual units linked into SHEETS
- Sheets are combined in LAYERS
- Many layers = crystal structure or CLAY MICELLE

The Si Tetrahedron (4 sides)
Si⁴⁺ coordinated with 4 O²⁻: a net charge of –4

The Al & Mg Octahedron (8 sides)
Al³⁺ (or Mg²⁺) coordinated with 6 OH⁻: a net charge of –3 (or –4)

Si and Al Sheets
Individual tetrahedral and octahedral units are linked to form sheets

Al & Si sheets are Linked to Form Layers
Example: 2:1
Layers are Linked to Form 2:1 Minerals
Muscovite Mica

Sources of Charge on Clay Minerals
pH dependent charge (charge is a function of solution chemistry)
• Dissociable –OH groups (weak acids)
• As pH increases, deprotonation increases
• Occurs at crystal edges
  – $\equiv$SiOH$^0 \rightarrow \equiv$SiO$^- + H^+$
  – $\equiv$AlOH$^0 \rightarrow \equiv$AlO$^- + H^+$
  – $\equiv$AlOH$^0 + H^+ \rightarrow \equiv$AlOH$_2^+$
• Surfaces that develop pH-dependent charge are called **amphoteric** if they can be either + or – depending on pH

Classes of Silicate Clay Minerals
• Many different types; differentiation generally based on tetra:octa layer ratio and extent of isomorphic substitution (layer charge)
• 1:1 clays (no layer charge)
  – Kaolinites
• 2:1 non-expanding clays (high layer charge)
  – Micas (muscovite and biotite)
  – Illite
  – Chlorites
• 2:1 expanding clays
  – Intermediate layer charge: vermiculites
  – Low layer charge: smectites

Layers are Linked to Form 1:1 Minerals
Kaolinite

Source of Charge on Clay Minerals
• Permanent (structural) charge: from **isomorphic substitution**
• Occurs in 2:1 minerals **when they form**
• One element substitutes for another of similar size
  – Al$^{3+}$ substitutes for Si$^{4+}$ in the tetrahedral layer
  – Fe$^{2+}$ or Mg$^{2+}$ substitutes for Al$^{3+}$ in the octahedral layer
• Because the substituting ion has lesser charge than the true charge-neutralizing ion, there is charge imbalance

1:1 Phyllosilicates (Secondary)
• Ratio of Si to Al sheets is 1:1
• 1:1 layer attached to adjacent 1:1 layers by H-bonds (non-expansive)
  – No H$_2$O in the interlayer: kaolinite, Al$_2$Si$_2$O$_5$(OH)$_4$
  – H$_2$O in the interlayer: halloysite, Al$_2$Si$_2$O$_5$(OH)$_4$·2H$_2$O

$$d$-spacing = 0.71 – 0.73 \text{ nm}$

$$\text{CEC} = 1 – 10 \text{ cmol}_e \text{ kg}^{-1}$$

$$\text{SA} = 10 – 20 \text{ m}^2 \text{ g}^{-1} \text{ (all external)}$$
1:1 Characteristics

• Low surface area: 10 to 20 m² g⁻¹
• Low water holding capacity
• Pedogenic and common to moist, warm, weathered soils (kaolinite is present in almost all soils; halloysite present in volcanic soils)
• Low negative charge
  – Mostly pH dependent
  – Very little isomorphic substitution
  – < 10 cmolc kg⁻¹

2:1 Non-Expanding (Primary)

• Organization
  – Ratio of Si to Al sheets is 2:1
  – 2:1 layer attached to adjacent 2:1 layers by electrostatic forces (bridging cations)
  – K⁺ ions in the interlayer: mica minerals (& illite): muscovite, K₆(Al₃Si₃)O₁₀(OH)₂; biotite, K(Mg,Fe²⁺)₃(Al₂Si₃O₁₀)(OH)₂
  – Mineral sheets in the interlayer: chlorite minerals, (LiAl₂)(OH)₆•Al₂(Si₃Al)O₁₀(OH)₂

2:1 Non-Expanding (Primary)

• Characteristics
  – Micas are primary minerals; illite is secondary; chlorites may be primary or secondary
  – Moderate surface area, 70 to 150 m² g⁻¹
  – Low water holding capacity, non-swelling
  – Extensive isomorphic substitution, but minerals are non-expansive (no access)
  – Surface charge from isomorphic substitution of Al³⁺ for Si⁴⁺ in Si-sheets and pH-dependent edge sites: 10 to 40 cmolc kg⁻¹

Mica Structure

- 1.0 nm d-spacing: All mica minerals are non-expanding
- SA = 70 – 120 m² g⁻¹ (all external)
- CEC = 10 – 40 cmolc kg⁻¹

Chlorite Structure

- d-spacing = 1.44 nm
- Continuous metal hydroxide sheet holds 2:1 layers together by electrostatic interactions
- SA = 70 – 150 m² g⁻¹ (all external)
- CEC = 10 – 40 cmolc kg⁻¹

2:1 Expanding: Vermiculites

• Organization
  – Ratio of Si to Al sheets is 2:1
  – 2:1 layer attached to adjacent 2:1 layers by electrostatic forces (bridging exchangeable hydrated cations)
  – Moderate layer charge from isomorphic substitution of Al³⁺ for Si⁴⁺ in Si-sheets (0.6 to 0.9 per formula)
  – Structure inherited from mica minerals
  – K₀.₉(Al, Mg, Fe)₉(Si₂₂Al₂₃O₄₀)(OH)₂
  – Most species are high in Mg & Fe
2:1 Expanding: Vermiculites

• Characteristics
  – Vermiculites are secondary minerals
  – Extensive surface area, 600 to 800 m² g⁻¹
  – Intermediate water holding, intermediate swelling
  – Extensive surface charge 100 to 200 cmolc kg⁻¹

Vermiculite Structure

Variable d-spacing:
  - Ca²⁺-sat: 1.44 nm
  - K⁺-sat: 1.0 nm
Interlayer is occupied by hydrated cations and water molecules; the ions are exchangeable

SA = 600 – 800 m² g⁻¹
  (all external)
CEC = 100 – 200 cmolc kg⁻¹

2:1 Expanding: Smectites

• Organization
  – Ratio of Si to Al sheets is 2:1
  – 2:1 layer attached to adjacent 2:1 layers by electrostatic forces (bridging exchangeable hydrated cations)
  – Low layer charge from isomorphic substitution of Mg²⁺ for Al³⁺ in Al-sheets (0.2 to 0.6 per formula)
  – Structure inherited from illite or vermiculite, or formed pedogenically by neoformation processes

Smectite Structure

Variable d-spacing:
  - large organic cations & Na⁺ (wet) → ~∞ nm
  - Ca²⁺-sat: 1.44 nm
  - K⁺- or Na⁺-sat (dry): 1.2 nm
Interlayer is occupied by hydrated cations and water molecules; the ions are exchangeable

SA = 600 – 800 m² g⁻¹
  (all external)
CEC = 80 – 150 cmolc kg⁻¹

2:1 Expanding: Smectites

• Characteristics
  – Smectites are secondary minerals
  – Smectites are a chemically and structurally complex group of minerals → numerous species
  – Common species: montmorillonite
    Ca₀.₂(Al₁.₆Mg₀.₄)Si₄O₁₀(OH)₂
  – Extensive surface area, 600 to 800 m² g⁻¹
  – Large water holding, extensive swelling
  – Moderate surface charge 80 to 150 cmolc kg⁻¹

Montmorillonite Structure

Variable d-spacing:
  - large organic cations & Na⁺ (wet) → ~∞ nm
  - Ca²⁺-sat: 1.44 nm
  - K⁺-or Na⁺-sat (dry): 1.2 nm
Interlayer is occupied by hydrated cations and water molecules; the ions are exchangeable

SA = 600 – 800 m² g⁻¹
  (all external)
CEC = 80 – 150 cmolc kg⁻¹

Allophane and Imogolite

• Mixtures of silica and alumina that are poorly-crystalline to microcrystalline
• Allophane: Al₂O₃·(SiO₄)₁–₂·2.5–3H₂O
• Imogolite: Al₂SiO₃(OH)₄
• Common in young volcanic (andic) materials
  – Insufficient weathering
  – High soluble silica concentrations
• pH dependent charge
• Exchange capacity
  – CEC: 10 to 40 cmolc kg⁻¹ at pH 7
  – AEC: 5 to 30 cmolc kg⁻¹ at pH 4
Sesquioxides - Al and Fe Oxides

- As weathering continues:
  - Base cations and $H_2SiO_4$ are leached
  - Soils become acidic, further enhancing weathering processes
- After extensive weathering
  - Low solubility (stable minerals) sesquioxides
  - Resistant primary oxides and silicates

Sesquioxides - Al and Fe Oxides

- Sesquioxides
  - Gibbsite $[Al(OH)_3]$: ubiquitous in soils, particularly those that are highly weathered (Oxisols & Ultisols) and in Al-rich soils (Andisols)
  - Goethite $[FeOOH]$: the most common hydrous Fe oxide (found in all soils), particularly in cool, moist climates
  - Hematite $[Fe_2O_3]$: found in almost all soils, favored in warm, dry climates and in the tropics and subtropics

Recalcitrant (Remnant) Minerals

- Found in all soils; concentrated in highly weathered soils
  - Titanium oxides
    - Rutile $[TiO_2]$
    - Anatase $[TiO_2]$
    - Ilmenite $[FeTiO_3]$
  - Corundum $[Al_2O_3]$
  - Zircon $[ZrSiO_4]$

Charge on Sesquioxides

- pH dependent
- In acid soils, may have positive charge
- Surface charge depends on crystallinity
  - Well-crystalline: CEC ~ 1 cmol c kg$^{-1}$, AEC ~ 3 cmolc kg$^{-1}$
  - Poorly-crystalline: CEC ~ 10 - 100 cmol kg$^{-1}$, AEC ~ 30 - 300 cmolc kg$^{-1}$

$\begin{align*}
\text{Acidic} & : & \text{Al} – OH^+ & \leftrightarrow & \text{Al} – OH_2^+ & \leftrightarrow & \text{Al} – O^- & \leftrightarrow & \text{Al} – OH^0 & \leftrightarrow & \text{Al} – OH^+ & \leftrightarrow & \text{Al} – O^- \\
\text{Neutral} & : & \text{Al} – OH^+ & \leftrightarrow & \text{Al} – OH_2^+ & \leftrightarrow & \text{Al} – O^- & \leftrightarrow & \text{Al} – OH^0 & \leftrightarrow & \text{Al} – OH^+ & \leftrightarrow & \text{Al} – O^- \\
\text{Alkaline} & : & \text{Al} – OH^+ & \leftrightarrow & \text{Al} – OH_2^+ & \leftrightarrow & \text{Al} – O^- & \leftrightarrow & \text{Al} – OH^0 & \leftrightarrow & \text{Al} – OH^+ & \leftrightarrow & \text{Al} – O^- 
\end{align*}$

Weathering and Clays

- Arid to subhumid - 2:1 expanding are common (intermediate weathering stage)
- Weathering of micas forms 2:1 non-expanding illite or expanding vermiculite
- Poor drainage favors smectite formation
- Continued weathering strips out silica & bases
- High precipitation & good drainage favors decomposition of 2:1 clays and formation of 1:1 clays
- Very warm with high precipitation favors continued dissolution and formation of simple Fe and Al sesquioxides

Organic Colloids – Humic Substances

- Stable organic matter left after decomposition of plant and animal detritus
- Dark brown to black, solubility in water is variable (fulvates are soluble; humins and humates not so much)
- Very high reactivity, mostly negative charge
  - pH dependent
  - CEC = 60 to 300 cmol kg$^{-1}$ SOM at pH 7; may account for 25% to 90% of the CEC of mineral soils
- High water holding capacity
- Very important relative to clays (can mask properties of clays)
Charge on Humic Substances

- Negative charge from carboxylic acid and phenolic groups; positive from amino groups

\[
\begin{align*}
\text{Humic macro-molecule} & \quad \text{OH} \\
\text{Humic macro-molecule} & \quad \text{NH}_3^+ + H^+ \\
\text{Acidic Soil} & \quad \text{Neutral to Alkaline Soil}
\end{align*}
\]

Cation Exchange

- Soil colloids have negative charge
  - pH dependent = variable charge
  - Isomorphic substitution = permanent charge
- Cations from the soil solution must satisfy this charge so that mineral and organic surfaces appear to be charge neutral

Basic Concepts

- **Cations** (→ metals)
  - Positively charged ions
  - $\text{Al}^{3+}$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{K}^+$, $\text{Na}^+$, $\text{NH}_4^+$, $\text{H}^+$, etc.
- **Anions** (→ ligands)
  - Negatively charged ions
  - $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{H}_2\text{PO}_4^-$, $\text{HPO}_4^{2-}$, $\text{Cl}^-$, $\text{OH}^-$, etc.
- Cation exchange sites
  - Negatively charged sites on clay and humic colloids
  - Cations are retained at these sites by electrostatic forces

Basic Cation Exchange Concepts

- Adsorbed cations can be replaced by other, competing cations
- Law of Mass Action and Le Châtelier’s principle are obeyed (large quantity of one cation can displace different cations from sites)
- Exchange reactions are reversible, rapid, and stoichiometric with respect to charge
  \[2(\text{K}^+ - \text{Soil}) + \text{Ca}^{2+} \rightarrow 2\text{K}^+ + \text{Ca}^{2+} - (\text{Soil})_2\]
- Ease of cation displacement is a function of cation size and charge

Chemistry concepts

- 1 mole = $6.022 \times 10^{23}$ entities (e.g., atoms)
- 1 cmol = mol ÷ 100
- Molecular weight (MW) = mass (g) of a substance in 1 mol
  - $\text{Ca} \approx 40$ g mol$^{-1}$, $\text{K} \approx 39$ g mol$^{-1}$
  - $\text{Al} \approx 27$ g mol$^{-1}$, $\text{Mg} \approx 24$ g mol$^{-1}$
  - $\text{Na} \approx 23$ g mol$^{-1}$, $\text{H} \approx 1$ g mol$^{-1}$
- So, 1 mol Ca = 40 g; 1 cmol Ca = 0.4 g

What is cmol$_c$?

- Units of CEC are cmol$_c$ kg$^{-1}$: centimoles of charge per kilogram of soil
- 1 cmol K$^+$ = 1 cmol$_c$
- 1 cmol Ca$^{2+}$ = 2 cmol$_c$
- 1 cmol Al$^{3+}$ = 3 cmol$_c$
- A soil with a CEC of 10 cmol$_c$ kg$^{-1}$ would require:
  - 10 cmol kg$^{-1}$ of K$^+$, or 5 cmol kg$^{-1}$ of Ca$^{2+}$, or 3.3 cmol kg$^{-1}$ of Al$^{3+}$
to neutralize the soil exchange complex
Factors Affecting Cation Adsorption

- Soil solution composition
  - The exchange complex reflects soil solution composition: Ca²⁺ dominates in soil solutions, also dominates exchange complex
- Soil pH
  - Acid soils: higher Al³⁺ and H⁺ in solution and on exchange complex
  - Al is actually present as Al(OH)₂⁺
  - Neutral to alkaline (pH > 6.5): low Al³⁺ and H⁺, high Ca²⁺, Mg²⁺, K⁺, & Na⁺

Factors Affecting Cation Adsorption

- Strength of adsorption increases as:
  - Cation valence (z_C) increases
  - Hydrated size (R_hyd) decreases
  - Strength of negative charge on colloid (z_soil) increases

- Force of attraction of a cation to the soil exchange complex obeys Coulomb's Law:

\[ F = \frac{z_C z_{soil}}{\varepsilon R_{hyd}^2} \]

Factors Affecting Cation Adsorption

- The relative replaceability of exchangeable cations (ease of removal) is described by a lyotropic series
  - For monovalent cations: Li⁺ ≈ Na⁺ > K⁺ ≈ NH₄⁺ > Rb⁺ > Cs⁺
  - For divalent cations: Mg²⁺ > Ca²⁺ > Sr²⁺ ≈ Ba²⁺
  - Monovalent cations are not necessarily easier to displace then divalent cations

Exchange Complex Composition

<table>
<thead>
<tr>
<th>Ion</th>
<th>pH &lt; 6</th>
<th>pH &gt; 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>3.80</td>
<td>25.18</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1.65</td>
<td>10.06</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.25</td>
<td>1.21</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.23</td>
<td>0.74</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>8.76</td>
<td>0</td>
</tr>
</tbody>
</table>

Importance?

- Storage of plant nutrients
  - Major source of K, Mg, Ca
- Buffering Capacity
  - Moderates change in solution pH and nutrient concentrations (high CEC requires high limestone to increase pH of acid soils)
- Adsorption of trace metals
  - Cd²⁺, Pb²⁺, Ni²⁺, Cu²⁺, Zn²⁺, others
- Adsorption of cationic pesticides, other organic compounds

Cation Exchange Capacity – CEC

- Definition: moles of exchangeable cation charge adsorbed per unit mass of soil
- Units: centimoles of positive charge from cations per kilogram of soil: cmol_c kg⁻¹
- Recall that ½ cmol Ca²⁺, ½ cmol Al³⁺, or 1 cmol K⁺ or Na⁺ will neutralize 1 cmol_c of soil charge
CEC and Soil Orders

<table>
<thead>
<tr>
<th>Order</th>
<th>cmolc kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfisols</td>
<td>15.4</td>
</tr>
<tr>
<td>Andisols</td>
<td>30.9</td>
</tr>
<tr>
<td>Aridisols</td>
<td>17.8</td>
</tr>
<tr>
<td>Entisols</td>
<td>19.9</td>
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<tr>
<td>Inceptisols</td>
<td>21.1</td>
</tr>
<tr>
<td>Mollisols</td>
<td>24.0</td>
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<tr>
<td>Oxisols</td>
<td>7.6</td>
</tr>
<tr>
<td>Spodosols</td>
<td>26.7</td>
</tr>
<tr>
<td>Ultisols</td>
<td>8.9</td>
</tr>
<tr>
<td>Vertisols</td>
<td>50.1</td>
</tr>
</tbody>
</table>

Measuring CEC

- Soil is rinsed of soluble cations
- Soil exchange complex is saturated with an index cation, such as Na⁺
  - Na⁺ replaces native cations, which are rinsed away
- The Na⁺-saturated soil is treated with a second index cation, such as NH₄⁺
  - NH₄⁺ replaces the Na⁺
- The displaced Na⁺ is measured
- The cmol of displaced Na⁺ per kg of soil is the CEC

Effect of Texture on CEC

- Sands: 1 to 5 cmolc kg⁻¹
- Sandy loams: 5 to 10 cmolc kg⁻¹
- Loams and silt loams: 5 to 15 cmolc kg⁻¹
- Clay loams: 15 to 30 cmolc kg⁻¹
- Clays: > 30 cmolc kg⁻¹
- Why differences?
- What does this mean for soil properties?

Estimating CEC

- Measure or estimate % clay and % SOM
- Assign each component an average CEC
  - Montmorillonite = 100 cmolc kg⁻¹
- Convert CEC of component from cmolc kg⁻¹ to cmolc %⁻¹
  - 1 kg mont. clay = 100 cmolc
  - 100 % mont. clay = 100 cmolc
  - 1 % mont. clay = 1 cmolc, or 1 cmolc %⁻¹ mont.
- Multiply mineral CEC/% by the actual % in soil
- Add all components

Example

- Soil has 2 % SOM, 20 % montmorillonite, 10 % illite
- SOM = 200 cmolc/kg = 2 cmolc/%
- mont. = 100 cmolc/kg = 1 cmolc/%
- illite = 40 cmolc/kg = 0.4 cmolc/%
- CEC = (2% × 2 cmolc/%) + (20% × 1 cmolc/%) + (10% × 0.4 cmolc/%)
- CEC = 28 cmolc/kg soil
CEC Calculations

- Assume soil with CEC = 20 cmolc/kg
  - Ca-saturation = 45%
  - Mg-saturation = 20%
  - K-saturation = 10%
  - Al-saturation = 25%
- How many kg of Ca per hectare-15 cm of soil?

\[
\text{cmol}_c / \text{kg as Ca}^{2+} = 20 \text{ cmol}_c / \text{kg} \times 0.45 = 9 \text{ cmol}_c
\]
\[
9 \text{ cmol}_c (\text{Ca}^{2+})/\text{kg} \times 0.2 \text{ g Ca/cmol}_c = 1.8 \text{ g Ca}
\]
- 1 hectare (ha)-15 cm = 2 x 10^6 kg soil

<table>
<thead>
<tr>
<th>kg Ca</th>
<th>cmol Ca</th>
<th>0.2 g Ca</th>
<th>2 x 10^6 kg</th>
<th>kg Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>ha - 15 cm</td>
<td>kg soil</td>
<td>cmol Ca</td>
<td>ha - 15 cm</td>
<td>1000 g Ca</td>
</tr>
<tr>
<td>ha - 15 cm</td>
<td>3600 kg Ca (exchangeable Ca^{2+} only)</td>
<td></td>
<td></td>
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</tbody>
</table>